DOE/ER/60134--4

DE88 016258

STUDIES OF TRANSPORT PATHWAYS OF TH, U, RARE EARTHS, Ra-228, AND Ra-226 FROM SOIL TO PLANTS AND FARM ANIMALS

Final Report

for Period 1983 - 1988

Principal Investigator: Paul Linsalata, Ph.D.

Report No. DOE/ER60134-4

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

STUDIES OF TRANSPORT PATHWAYS OF Th, U, RARE EARTHS, Ra-228, AND Ra-226 FROM SOIL TO PLANTS AND FARM ANIMALS

Final Progress Report

Principal Investigator: Paul Linsalata, Ph.D.
New York University Medical Center
Institute of Environmental Medicine

Co-Investigator: Eduardo Penna Franca, Ph.D.
Federal University of Rio de Janeiro
Institute of Biophysics

July, 1988

Prepared for the
U.S. Department of Energy
Offices of Health and Environmental Research, and
Civilian Radioactive Waste Management
Agreement No. DE-AC02-83ER60134

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed or represents that its use would not infringe privately-owned rights.

TABLE OF CONTENTS

Page

Publications Resulting from the Morro do Ferro Project..... iv

Acknowledgements..... 1

PART I Studies of the Transport Pathways of Th, Ra and Light Rare Earth Elements from Soils to Edible Vegetables

Abstract to Part I..... 2

I. Introduction..... 3

A. Research Objectives and Rationale..... 5
B. The Analogies..... 7

II. Methods..... 9

A. Field Sampling and Sample Preparation..... 9
B. Analytical..... 10
C. Quality Assurance and Control, Statistics and Reporting Results..... 13

III. Results..... 15

A. Soils of the Pocos de Caldas Plateau..... 15
B. Vegetable/Soil Concentration Ratios..... 16

IV. Discussion..... 19

References..... 26
Tables..... 32
Figures..... 39

PART II Studies of the Transport Pathways of Th, U, Ra and Light Rare Earth Elements from Soil to Farm Animals

Abstract to Part II..... 1

I. Introduction..... 3

A. Research Objectives and Rationale..... 5

II. Methods..... 8

A. Field Sampling and Sample Preparation..... 8
B. Analytical..... 10

III. Results and Discussion..... 11

A. Soils..... 11
B. Cattle Feeds..... 12
C. Apportionment of Intakes for Beef Cattle..... 14
D. Concentrations, Tissue Distributions, and (tissue/soil) CR's in U.S. Beef Cattle..... 16
E. Concentrations and (tissue/soil) CR's for Animals Raised in Pocos de Caldas..... 20

IV. Additional Discussion and Conclusions..... 25

References..... 27
Tables..... 31
Figures..... 56
Appendix 1 to Part II..... 60

PART III Physicochemical Studies of the Thorium, Rare Earth Element Ore Body at Morro do Ferro

Abstract to Part III..... 1

I. Introduction..... 2

A. Background..... 2

II. Distribution of Th, REE's, Ra and U in MF Ore and Water..... 5

A. Concentrations in Water and Mobilization Rate Estimates..... 7

III. Natural Series Disequilibrium Measurements in Cores and Water..... 8

A. Cores..... 8
B. Ground and Surface Water..... 11

IV. Speciation of Th and REE's in MF Ore..... 12

References..... 16
Tables..... 20
Figures..... 29
Appendix 1 to Part III: The Importance of Organic Compounds on the Mobilization of Th in the Morro do Ferro..... 42

Publications Resulting from the Morro do Ferro Project

DE-AC02-83-ER60134

April 1983 - April 1988

Eisenbud, M., K. Krauskopf, E. Penna Franca, W. Lei, R. Ballad, P. Linsalata and K. Fujimori. Natural analogues for the transuranic actinide elements: An investigation in Minas Gerais, Brazil. Environ. Geol. Water Sci. 6 (1): 1-9 (1984).

Linsalata, P., M. Eisenbud and E. Penna Franca. Thorium and the light rare earth elements in soils, crops and domestic animals from abnormally high and typical radiation background areas. In: Proc. of the Eighteenth Midyear Topical Symposium of the Health Physics Society - Environmental Radiation '85 (Colorado Springs, CO; January 6-10, 1985), pp. 535-542 (1985).

Miekeley, N., R.M. Dotto, I.L. Kuchler and P. Linsalata. The importance of organic compounds on the mobilization and bioassimilation of thorium in the Morro do Ferro Environment. In: Scientific Basis for Nuclear Waste Management VIII, Materials Research Society Symposia Proceedings, Vol. 44 (Materials Research Society: Pittsburgh), pp. 591-597 (1985).

Eisenbud, M., P. Linsalata and E. Penna Franca. High level wastes in the terrestrial environment: What can we learn from nature? Health Phys. 49 (1): 136, Abstract MPM-C6 (1985).

Linsalata, P., E. Penna Franca and M. Eisenbud. Determination of the human intake of thorium and the light rare earth elements from high and typical natural radiation environments. In: Trace Substances in Environmental Health-XIX, Delbert D. Hemphill, Ed. (University of Missouri: Columbia), pp. 257-263 (1985).

Linsalata, P., E. Penna Franca and M. Eisenbud. Ingestion estimates of thorium and the light rare earth elements based on measurements of human feces. Health Phys. 50 (1): 163-167 (1986).

Lei, W., P. Linsalata, E. Penna Franca and M. Eisenbud. Distribution and mobilization of cerium, lanthanum, and neodymium in the Morro do Ferro Basin, Brazil. Chem. Geol. 55: 313-322 (1986).

Eisenbud, M., P. Linsalata and E. Penna Franca. Use of natural analogues to predict the behavior of transuranic actinide elements in the environment. In: Radioactive Waste, Proceedings of the Twenty-First Annual Meeting of the National Council on Radiation Protection and Measurements, Proceedings No. 7, (NCRP: Bethesda), pp. 133-148 (1986).

Linsalata, P., R. Morse and H. Ford. Sequential determination of environmental levels of isotopic thorium, uranium and the light rare earth elements within the terrestrial food chain by induced coupled

plasma and alpha spectrometry. In: Proceedings of the Thirty-Second Annual Conference on Bioassay, Analytical and Environmental Radiochemistry (Gaithersburg, MD; October 21-23, 1986), Paper # 7-3 (1986).

Campos, M.J., E. Penna Franca, N. Labao, H. Trindade and I. Sachett. Migration of radium from the thorium ore deposit of Morro do Ferro, Poços de Caldas, Brazil. J. Environ. Rad. 3: 145-161 (1986).

Linsalata, P., E. Penna Franca, I. Sachett, M.B. Castro, N. Lobão, R. Ballad, W. Lei, H. Ford, R.S. Morse and M. Eisenbud. Radium, thorium and the light rare earth elements in soils and vegetables grown in an area of high natural radioactivity. In: Environmental Research for Actinide Elements, CONF 841142 (NTIS: Springfield) (in press, 1987).

Linsalata, P. Biogeochemical studies of the Ra, U, Th and REE deposit at Morro do Ferro: A qualitative application to improve confidence in radionuclide immobilization processes. Presented at Natural Analogues in Radioactive Waste Disposal, a conference sponsored by the Commission of the European Communities (Brussels, Belgium; April 28-May 1, 1987).

Linsalata, P., M. Eisenbud and E. Penna Franca. Soil-to-edible vegetable and soil-to-farm animal tissue concentration ratios for Ra, Th, U and rare earth elements. Health Phys. 54, Supplement 1, p. S51, Abstract THAM-F1 (1988).

Linsalata, P., R.S. Morse, H. Ford, M. Eisenbud, E. Penna Franca, M.B. de Castro, N. Lobão, I. Sachett and M. Carlos. An assessment of soil-to-plant concentration ratios for some natural analogues of the transuranic elements. Health Phys. (accepted for publication, July 1988).

Dissertations and Theses Resulting from the Morro do Ferro Project

Pivetta, F.R., Study of the Chemical Composition of Water from Morro do Ferro: Transport of Thorium and Trace Elements in Solution, M.S. Thesis, Catholic University of Rio de Janeiro, RJ, Brazil (1983).

Lei, W., Thorium Mobilization in a Terrestrial Environment, Ph.D. Dissertation, New York University, Graduate School of Arts and Science, New York, NY (February 1984).

Vasconcellos, L.M.H., The Uptake of Ra-226 and Pb-210 in Foodstuffs of the Poços de Caldas Plateau, M.S. Thesis, Federal University of Rio de Janeiro, RJ, Brazil (1984).

Campos, M.J., Migration of Radium from the Thorium Deposit of Morro do Ferro During Base Flow Regimes, M.S. Thesis, Federal University of Rio de Janeiro, RJ, Brazil (1984).

Dotto, R.M., Studies of the Assimilation of Thorium in Plants from Morro do Ferro, M.S. Thesis, Catholic University of Rio de Janeiro, RJ, Brazil (1985).

Annual Reports Resulting from the Morro do Ferro Project

New York University Medical Center, Institute of Environmental Medicine, and Federal University of Rio de Janeiro, Institute of Biophysics, Studies of Transport Pathways of Th, U, REE's, Ra-228, and Ra-226 from Soil to Farm Animals, Progress Report to the U.S. Department of Energy, Office of Health and Environmental Research, for the Period April 1, 1983 - December 31, 1983 (January, 1984).

New York University Medical Center, Institute of Environmental Medicine, and Federal University of Rio de Janeiro, Institute of Biophysics, Studies of Transport Pathways of Th, U, REE's, Ra-228 and Ra-226 from Soil to Farm Animals, Progress Report to the U.S. Department of Energy, Office of Health and Environmental Research and Office of Geologic Repository, for the Period April 1, 1983 - January 31, 1985 (February, 1985).

New York University Medical Center, Institute of Environmental Medicine, and Federal University of Rio de Janeiro, Institute of Biophysics, Studies of Transport Pathways of Th, U, Rare Earths, Ra-228, and Ra-226 from Soil to Plants and Farm Animals, Progress Report to the U.S. Department of Energy, Office of Health and Environmental Research and Office of Civilian Radioactive Waste Management, for the Period April 1, 1985 - February 28, 1986 (February, 1986).

Acknowledgments

The research reported here was supported, in part, by contract No. DE-AC02-83ER60134 with the U. S. Department of Energy Offices of Health and Environmental Research and Civilian Radioactive Waste Management, by grants obtained from the Swedish Nuclear Fuel and Waste Management Company (SKB), the Swiss Nationale Genossenschaft fur die Lagerung Radioaktiver Abfalle (NAGRA), and by the Comissao Nacional de Energia Nuclear (CNEN) of Brazil. Additional support was provided by core grant Nos. ES 00260 of the National Institute of Environmental Health Sciences and CA 13343 of the National Cancer Institute.

The principle investigators are indebted to Dr. Merril Eisenbud who proposed the study and directed it over the first two years. We also acknowledge the technical assistance of Mr. Robert Morse and Ms. Helen Ford (NYUMC), Mr. Ruy Frayha of Pocos de Caldas, Brazil, and Ms. Marcia Carlos, Ms. Miriam de Castro, Mr. Nazio Labao, and Mr. Ivanor Sachett (Federal University of Rio de Janeiro, Brazil). The technical contributions of both Drs. Joao Alfredo Medeiros and Norbert Miekeley (Catholic University of Rio de Janeiro, Brazil) are greatly appreciated.

PART I

Studies of the Transport Pathways of Th, Ra and Light Rare Earth Elements from Soils to Edible Vegetables

Part I: Studies of the Transport Pathways of Th, Ra and Light Rare Earth Elements from Soils to Edible Vegetables

Abstract: Part I

A field study was conducted in an area of enhanced, natural radioactivity to assess the soil to edible vegetable concentration ratios (CR = concentration in dry vegetable/concentration in dry soil) of Th-232, Th-230, Ra-226, Ra-228, and the light rare earth elements (REE's), La, Ce and Nd. Twenty eight soil, and approximately 42 vegetable samples consisting of relatively equal numbers of seven varieties, were obtained from 11 farms on the Pocos de Caldas Plateau in the state of Minas Gerais, Brazil. This region is the site of a major natural analogue study to assess the mobilization and retardation processes affecting thorium and the REE's at the Morro do Ferro ore body, and uranium series radionuclides at the Osamu Utsumi open pit uranium mine. Thorium (IV) serves as a chemical analogue for quadrivalent plutonium, the light REE's (III) as chemical analogues for trivalent americium and curium, and uranium (VI) as an analogue for transuranics with stable oxidation states above IV, eg., Pu (VI).

The geometric mean CR's (all times 10^{-4}) decreased as Ra-228 (148) > Ra-226 (76) > La (5.4) > Nd (3.0) = Ce (2.6) > Th-232 (0.6), or simply as M (II) > M (III) > M (IV). These differences may reflect the relative availibility of these metals in soils to plant roots. Significant differences were found in the CR's (for any given analyte) among many of the vegetables sampled. The CR's for the different analytes were also highly correlated. The reasons for the correlations in CR's seen among elements with such diverse chemistries as Ra-REE or Ra-Th, are not clear but are apparently related to the essential mineral requirements or mineral status of the different vegetables sampled. This conclusion is based on the significant correlations obtained between the Ca content of the dryed vegetables and the CR's for all of the elements studied.

I.Introduction: Part I

This is a final report summarizing the major findings concerning the study of "Transport Pathways of Thorium, Uranium, Rare Earth Elements, Radium-228 and Radium-226 from Soil to Plants and Farm Animals". Part one of this report summarizes the results of the plant/soil program and part two that of the animal tissue/soil program.

A field study was conducted about 300 km north of Sao Paulo, Brazil, in the state of Minas Gerais, to assess in a natural setting, the soil to edible vegetable, and soil to farm animal (steers, pigs and chickens) concentration ratios (CR's) of the naturally occurring radionuclides Ra-226, Ra-228, Th-232, Th-230, and Th-228, as well as of the light rare earth elements (REE's) La, Ce and Nd. Uranium isotopic data (U-238, 235 and 234) have been obtained in the animal program but were omitted from the vegetable work. For comparative purposes, a second, smaller-scale field program was conducted in Orange County, New York. This study was focused on the analyses of these radionuclides and REE's in the tissues of cattle (Black Angus), and in soils, grasses and feeds. A limited number of (vegetable/soil) analyses were also obtained.

The CR is defined as the quotient of the (plant or animal tissue/substrate) elemental concentrations, where the concentrations of both numerator and denominator are expressed on a dry weight basis usually to reduce the variability associated with varying moisture content. In the case of animal tissues however, fresh weight concentrations are determined mainly as the result of the difficulty in obtaining dry weights for fatty tissues. As recently discussed by Sheppard and Sheppard (1985), the CR approach for predicting uptake into the biota assumes that a linear relationship (with zero intercept) exists between plant (or animal) and substrate concentrations and that the system is in equilibrium with respect to uptake and loss of the element by the plant (or animal).

primarily because of the naturally enhanced (5 to 20 times higher than U. S. soils) concentrations of these elements in the soils (NYUMC, 1984, NYUMC, 1985, NYUMC, 1986, and Linsalata et al., 1985) and secondarily because of their proximity to a well characterized Th-REE ore body known as the Morro do Ferro (MF). The Morro do Ferro (Mountain of Iron) is a small (140 m height) and deeply weathered hill at the center of the plateau containing within 50 meters of its surface, about 30,000 mtons of Th (and associated radioactive daughters) and about 100,000 mtons of REE's, predominantly Ce, La and Nd (Wedow, 1961, Wedow, 1967, Frayha, 1962, Lei, 1984, and Lei et al., 1986).

Initially, our work was centered on the farms within the MF watershed (Farms 1, 2 and 3, Fig. 1), particularly Farm 1, which utilizes seepage and overland runoff waters from the MF for both drinking and irrigation purposes (NYUMC, 1984). Estimates of the annual ingestion of thorium isotopes and the light REE's by local farm residents were previously reported based on the analyses of fecal samples (Linsalata et al., 1986). Using median fecal concentrations and a standard fecal elimination rate, we estimated intakes (in mg y^{-1}) to range between 24-42, 10-15, 3-5 and 0.6-1.0 for Ce, La, Th and Sm, respectively. This order reflects the relative concentrations observed in soils as well as in edible vegetables. Between five to nine percent of the intakes for Th and La could be attributed to drinking stream water. A similar type of analysis for residents of New York State resulted in ingestion estimates of 2.9, 1.0, 0.2 and 0.1 mg y^{-1} for Ce, La, Th and Sm, respectively. The differences between the New York and Pocos de Caldas ingestion estimates were shown to be more or less directly proportional to the relative differences in the local soil concentrations. These findings were important because they indicated: no obvious enhancement in intake resulting from the proximity of these residents to the MF ore body (1.5-3.0 km); that a general similarity exists with respect to the transfer of Th and the light REE's to man; and that fecal analysis can provide a reasonable and quick estimate of intake for elements which are highly discriminated against at the level of the gastrointestinal (G.I.) tract [earlier estimates of Th ingestion by man in the U. S. are about 0.3 mg y-1 (NCRP, 1975 and Bondietti et al., 1979)].

Recent research efforts at the MF have concluded that the current mobilization rates of Th-232 (Lei, 1984 and Eisenbud et al., 1984), the REE's (Lei et al., 1986) and Ra-228 (Campos et al., 1986) resulting from groundwater solubilization and stream transport are extremely slow (i.e., 10^{-9} to 10^{-7} per year). These very slow removal rates, which correspond to residence times on the order of 10^{7} to 10^{9} years, have been attributed to solubility limitations resulting in part, from very dilute concentrations of inorganic complexing agents and sorption onto the surfaces of the abundant clay minerals present (Lei, 1984, Eisenbud et al., 1984, Lei et al., 1986, Barretto and Fujimori, 1986 and Campos et al., 1986). Naturally occurring, high molecular weight (> 10,000 equivalent molecular weight units) colloidal humic acids have been shown to be of much greater consequence in solubilizing Th and probably the REE's from this deposit (Miekeley et al., 1985 and Miekeley and Kuchler, 1987).

There is no easily discernable soil stratigraphy within the plateau. The soil is composed of a fine grained argillaceous silty clay that can form concretions of gravel size and larger. Topsoil is generally no more than several centimeters thick and supports a thin layer of grasses. In some areas, annual field burning is employed to encourage the growth of perennial grasses. The soil is classified as a dystrophic cambisol and red-yellow dystrophic latosol (Embrapa, 1981). Nonfertilized soil of the plateau is quite poor for agricultural purposes and displays characteristics which are consistant with the intense laterization that has occurred (Wedow, 1962). Rainfall averages 170 cm per year with 80% occurring over a four month period (Nov.- Feb.) during the Brazilian summer. The region is used primarily for growing vegetables and raising cattle although mining activities (uranium, zirconium and bauxite) contribute substantially to the regions economic base.

A. Research Objectives and Rationale

Relatively few published data exist concerning the transfer from soil of naturally occurring REE, Th-series and U-series radionuclides (except Ra-226) to the edible portions of plants (Laul et al., 1977, Trabalka and Garten, 1983, Bondietti et al., 1979, and Tracy et al., 1983). Even less data exist regarding the concentrations (hence CR's) of these elements in farm animal tissues and feeds . An understanding of the

transfer of these natural radionuclides to the biota is important in itself for accurate dose assessment and predictive modeling along terrestrial food chains. The elements studied bear additional significance as a result of their chemical similarity to several manmade transuranic elements, most notably plutonium, americium and curium. Although certain isotopes of these transuranic elements exist in measurable quantities in surface soils as a result of global fallout following thermonuclear test detonations in the atmosphere during the 1950's and early 1960's, their measurement within the terrestrial biosphere, eg., edible plant and animal tissues, is quite difficult. This results from relatively low concentrations in soils coupled with high (soil/pore water) partition coefficients which effectively limits their availability to plant roots culminating in very low uptake within edible plant portions (Wildung and Garland, 1980 and Watters et al., 1980). Additional discrimination of ingested transuranic elements by all mammals at the level of the G.I. tract is by now a well documented occurrence.

We have focused our attention on these chemical analogues to the transuranic elements in the natural environment with a view towards providing relevant data on biological uptake for these elements and those long-lived, chemically analogous, anthropogenic radionuclides considered important in nuclear waste isolation. Since one can safely assume that the elements studied are in equilibrium with respect to geochemical and mineralogical phases of the soil (a situation not encountered in earlier studies based on fallout contamination, freshly contaminated environments, and, or tracer experiments), the results obtained should be more relevant to aged contaminant scenarios. That is at times much beyond those required to insure equilibrium between the soil substrate and the relevant long-lived radionuclides or daughter products requiring long geologic containment times (eg., Pu-239,240,241, 242, Th-229,230, Am-241,243, Cm-245,246, Ra-226, and U-234,235,238).

Our specific research objectives are: to provide new values for, and to assess the variability of, the (edible vegetable/soil) CR for members of the U and Th-series as well as for the light REE's; to examine the usefulness of the (animal tissue/soil) CR for predicting tissue concentrations in steady-state models currently used in dose assessment; to examine the comparative behavior within terrestrial food chains of

elements with stable oxidation states of II (Ra), III (REE), IV (Th) and VI (U); and by the chemical analogies associated with the (REE-Am, Cm) and (Th-Pu) pairs, provide data useful for assessing the potential long-term behavior of the tri- and quadrivalent transuranics within terrestrial food chains. This last aspect is particularly important since aside from those few environments studied which received a substantial, and in some cases, aged insult of the long-lived transuranic elements, reliable measurements of plant/soil and most certainly, animal/soil CR values within edible species are generally lacking. For the data to be useful in environments other than that studied, they must be shown not to be totally unique with respect to climatic conditions, soil characteristics and agricultural practices.

B . The Analogies

The basis for the Th-Pu and light REE-Am,Cm analogies has been investigated both on theoretical (thermodynamic) and experimental grounds (Watters et al., 1980, Weimer et al., 1980, Wahlgren and Orlandini, 1982, Trabalka and Garten, 1983, Lei, 1984, Eisenbud et al., 1984, and Krauskopf, 1986). It is not our intention to review here the findings of these studies and the intracacies of under which prevailing conditions the analogies hold up and where they fail for many examples could be stated in both instances. This is especially true regarding the Th-Pu pair and mainly attributable to the multiplicity of oxidation states that Pu can exist in simultaneously (i.e., III, IV, V and VI) verses a single, stable oxidation state of Th (IV). As the analogies affect the plant/soil, animal/plant and animal/soil systems under consideration here, the available data suggest that regardless of initial oxidation state or chemical form, plutonium added to soils will ultimately exist in the quadrivalent state, where, in a manner similar to that of Th, its' chemistry will be governed by hydrolytic-precipitation reactions, the stability of both the organic and inorganic complexes formed, and its' sorption characteristics (Watters et al., 1980 and Bondietti and Tamura, 1980). Even when oxidized plutonium is assimalated by plant roots, it appears to be radiply reduced to Pu (IV) within the plant (Delaney and Francis, 1978). Once in the quadrivalent state, the similarities between the values of stability constants and solubility products of complexes and compounds of Pu and Th are such that the

physicochemical analogy sould be robust over a broad range of soil and pore water chemistries (Krauskopf, 1986).

In support of the expected chemical similarities are the comparative field studies of the uptake of initially soluble forms of Pu and Th in both indigenous and cultivated plants and in the carcasses of small mammals done in a previously contaminated (1944) Tennessee floodplain. These studies have shown that the CR's for the pair were very similar in the native animals studied (cotton rats) and across a wide range of plant types examined (Bondietti et al., 1979, Garten, 1981 and Garten et al., 1981). The authors suggested from these and earlier findings related to the similar geochemical associations of Pu and Th in soil that Pu was probably present in the quadrivalent state. Unfortunately, comparative data from other environments are not available.

Comparative studies of the light REE-Am,Cm pair in the terrestrial biosphere are also few. Weimer et al. (1980) have shown in laboratory experiments, that both (soil/water) partition coefficients and (plant/soil) CR's were nearly identical for Nd, Am and Cm. As a result of their nearly identical ionic radii and identical stable oxidation states (III), the light REE's (including Nd and Pr and possibly La, Ce and Sm) should probably perform better as analogues to Am and Cm under more varying conditions than Th does for Pu (Krauskopf, 1986). Using very sensitive measurement techniques (neutron activation analysis), Laul et al. (1977) have shown that the uptake patterns of the chondrite-normalized REE concentrations in vegetables behave, with some exceptions, as a smooth function of their ionic radii.

Relative to the environmental data, a much more extensive and precise data base exists with respect to the uptake and metabolism of the transuranic elements and radium in experimental animals as well as in man (see for example, Maletskos et al., 1969, ICRP, 1977, ICRP, 1979, Hodge et al., 1973 and Rundo et al., 1983). The data are less abundant for Th and the light REE's (Durbin et al., 1956, Durbin, 1962, ICRP, 1979, Singh et al., 1983). As a very generalized statement, many of the above references indicate that the G.I. absorption factors in mammals of Th (IV), Pu (IV), Am,Cm (III) and the REE's (III) are all very low and quite similar, i.e, on the order of 10^{-4}.

Very recent data on the differential G.I. absorption of Pu (IV) and Pu (VI) in both fed and fasted animals (rats, mice, dogs and baboons) have indicated that there are no differences in systemic absorption between these different oxidation states of plutonium (Bhattacharyya et al., 1985). Alteration within the G.I. tract to a common oxidation state prior to systemic absorption was suggested by the authors. Fed animals generally displayed about a ten fold lower G.I. absorption (~2 x 10^{-4} for Pu VI) than fasted animals (~2 x 10^{-3} for Pu VI). Although prior dietary regimes are obviously important in determining G.I. absorption factors (Sullivan et al., 1983), the fact remains that if oxidized species of Pu are reduced within the gut to the most stable, quadrivalent state, than the subsequent formation of Th and Pu complexes with the ligands present should not result in any radical divergences in absorption.

Durbin (1962) has presented the most detailed picture of comparative metabolism (in the rat) for systemic rare earths and actinide elements. These data reveal that among the major organs of deposition in the rat (and other mammals as well), i.e., the liver and skeleton, the fractional retentions (% of injected dose) of Am and Cm were nearly identical to those of the light REE's, particularly Ce. As was observed by Laul et al in plants, the relative deposition in liver and skeleton of the REE's and trivalent actinides as well, occurred as a function of ionic radii. The data for Th and Pu were considerably more divergent as Th tended to deposit more in bone (66% verses 55% for Pu) and less in liver + feces (10% verses 30% for Pu). Human autopsy data from environmentally exposed individuals also suggests that Th and Pu are metabolised differently (Singh et al, 1983). The human organ burden data for liver and skeleton tends to confirm the observations made in rats. Additional discussion is provided in Part 2 of this report.

II. Methods

A. Field Sampling and Sample Preparation

A total of 29 composited soil samples (at least 10 aliquots per sample) were collected from 11 farms on the P.C. plateau to depths of 15-20 cm using a hand auger. Three additional samples were collected from a farm off of the P.C. plateau in neighboring Sao Paulo State. The farms were selected according to the vegetables

they produced in order to obtain a variety of species. Soils were air dryed and coarse screened to remove rocks and debris greater than 2 mm. The soils were mechanically blended and aliquots taken for different analyses.

The vegetables that were collected represent the main agricultural crops produced or consumed in the region. We have reported here the results of about 40 samples representing approximately six independent analyses of seven different vegetables. The cash crops sampled include: potato (Solanum tuberosum), brown beans (Visna sinensis), corn (Zea mays), and carrots (Daurcus carota). The staple foods largely consumed by the local population and grown in several small gardens include: manioc or tapioca (Manihot atilissima), couve or collard green (Brassica oleracea acephale), and a squash variety (Carrabita pepo). Between 2-10 kg fresh weight of each of the 40 samples were obtained. The vegetables were thoroughly washed and processed as for human consumption. Corn was shucked, washed and the kernels removed; potatoes, carrots and manioc (a true root) were washed, peeled and washed again; beans were removed from pods and washed; squash was not peeled but thoroughly scrubbed, and the leafy green vegetable couve, was scrubbed and washed leaf by leaf. All samples were weighed fresh and oven dried (110° C) until constant weight was obtained. Samples were next dry ashed at 450° C, the ashes homogenized, and two aliquots taken: from 10-20% for radium isotopic analysis and generally the remainder for the sequential analysis of Th isotopes and the REE's.

B. Analytical

All reagents used were of analytical grade. All water used was distilled and deionized. All analyses (except basic soil characterization) were performed on the same samples either at the Institute of Biophysics (Federal University of Rio de Janeiro) or at the Institute of Environmental Medicine (New York University Medical Center). Soil samples were characterized pedologically, i.e., for particle size distribution, nutrients, pH, organic carbon, exchangable cations, etc., at the Institute of Pedology (Embrapa) in Rio de Janeiro. For soils, total Th, i.e., Th-232, and the REE's were determined by an isotope induced, X-ray fluorescence procedure (Laurer et al., 1982). (Uranium was generally present at concentrations below XRF sensitivities.)

Radium-228 and Ra-226 were determined by gamma analysis (GeLi) of the Ac-228 and Pb-214 (respective) daughter photopeaks following the necessary ingrowth period in sealed, aluminum containers. On occasion, Th and U isotopes as well as the light REE's were determined sequentially in the same soil samples by alpha spectrometry and ICPOES following complete sample dissolution and radiochemical seperations discussed below (Linsalata et al., 1987 and NYUMC, 1986).

Only a brief outline of the radiochemical procedures and quality assurance programs used can be given here. Detailed methodologies have been given both in the progress reports cited earlier and in some of the references cited in this section.

For both the Ra and Th-U-REE procedures, the plant ashes are thoroughly solubilized using concentrated mineral acids including HF when silicious matter is present. The radiochemical tracers which are added during acid decomposition include Ba-133 for the radium isotopes, a self-cleaning (Sill, 1974) U-232 tracer (to continually remove the ingrown Th-228 daughter) for the uranium isotopes, either Th-229 or Th-234 for the Th isotopes, and Ce-144 for the light REE's which include La-Sm. We have previously shown Ce-144 to be an adequate tracer for the light REE's as a group (NYUMC, 1985).

The Ra procedure is adapted from that reported by Kamath et al. (1964) and McCurdy and Mellor (1981) and is based on Ra purification by repeated coprecipitation with $BaSO_4$, followed by redissolution in alkaline EDTA. After a final precipitation, the $Ba(Ra)SO_4$ is filtered and counted twice; first for yield (Ba-133), and after a 48 hr ingrowth period, for Ac-228 using a beta-gamma coincidence technique. An aliquot of the EDTA solution is used for Ra-226 determination by an emanation technique (Lucas, 1964).

The sequential procedure developed for Th, U, and the light REE's involves an initial collection of Th and the REE's by coprecipitation with calcium oxalate at pH 3. Uranium does not precipitate under these conditions and can thus be treated seperately. Prior to the first precipitation, 1% of the initial sample solution volume is removed for the determination of the stable elements Ca, P and Fe by induced coupled

plasma optical emission spectroscopy (ICPOES). (These elements were analyzed initially to optimize our radiochemical procedures and unexpectedly provided some valuble information which will become apparent in the discussion.) The oxalate is filtered, decomposed with HNO_3, and a second precipitation done to further purify the Th-REE fraction, especially in regard to the elimination of phosphate ion which would otherwise complex Th. The filtration and decomposition of the oxalate is repeated, the solution evaporated, and the remaining salts dissolved in 30 ml of M HNO_3.

The M HNO_3 solution is loaded onto a preequilibrated cation exchange column (BioRad^R AG-50W-X8) which retains Th and the REE's (Crock and Lichte, 1982). Following two successive washings with M and 2M HNO_3 to remove Ca (discard), the REE's are eluted with successive additions of 6M and then 8M HNO_3 (100 ml ea.). These eluates are combined, evaporated, and the residue dissolved in exactly 10 ml of M HNO_3 prior to yield assay (Ce-144 by GeLi spectroscopy). This solution is aspirated into an Instrument Laboratories^R (IL-200) ICP for sequential determination of the REE's.

Thorium is next eluted with 250 ml of 3M H_2SO_4. Fifty µg of purified Ce carrier (to remove traces of U and Th-series radionuclides) are added, the solution evaporated, and Th isotopes coprecipitated with CeF_3 after the procedure of Sill and Williams (1981). This ultra-fine suspension is vacuum filtered onto a 25 mm diameter (0.1 µm pore size) Gelman Tuffryn^R filter prepared in advance with a CeF_3 substrate which serves to plug pore spaces thus avoiding unnecessary degradation in the alpha spectrum. Alpha particle counting was done using 300 mm^2 silicon surface barrier detectors. Typical resolution with this technique is 55-80 keV FWHM for one to five kg vegetable samples.

Although uranium data are not available for vegetables, the method developed for animal tissues (Part II) is appropriate for plants. The uranium-containing solutions obtained after filtering the two calcium oxalate precipitates are combined, wet ashed to

destroy excess oxalic acid and evaporated. The iron-bearing salts remaining are dissolved in 100 ml of 6M HCl, 2 g of Ca carrier are added and the uranium solution extracted into 50 ml of 30% Alamine-336 (General Mills) in toluene (v/v) after Fisenne et al., (1980). The extraction is repeated with fresh Alamine-336 and the inorganic phase discarded. The two organic phases are combined and washed four times with 6M HCl (discard washings). Uranium is stripped with three, consecutive 100 ml portions of M HNO_3 which are combined and evaporated in the presence of 2 ml of H_2SO_4. Both HNO_3 and HCl are added (several ml) to oxidize organics and increase the solubility of iron which is coextracted with the U. We have generally found it useful at this point to further purify the uranium fraction by dissolving the evaporite in 50 ml of HCl and retaining the U on a small (1.5 x 20 cm) anion exchange column (Dowex AG 1 x 4, 100-200 mesh, preequilibrated with 100 ml of HCl). The column is washed with 100 ml of HCl (discard) and U eluted with 100 ml of 0.5 M HCl. This solution is evaporated and the U-containing evaporite dissolved in 6-10 ml of M HCl (with 100 µg of Ce carrier added for coprecipitation with CeF_3) and transfered to a plastic C-tube. Uranium is reduced to the IV state by the addition of 10-20 drops of freshly prepared 20% $TiCl_3$. Twenty five drops of HF are then added to the C-tube and the solution cooled in an ice bath for 30 minutes to complete the coprecipitation. Preperation of the sample for alpha spectrometry from this point proceeds as for Th. A summary of the methodologies used for the different analytes and the associated detection limits is provided in Table 1.

C. Quality Assurance and Control, Statistics and Reporting Results

Nearly 40 complete reagent blanks were obtained for Th isotopes and the REE's. Ten reagent blanks were processed for uranium isotopes. All analyte concentrations were corrected for detector efficiency, tracer yield, counter background and reagent blank activity or mass. All counting errors were propagated to include the uncertainties associated with each of these variables. The sample masses analyzed and the chemical yields, were sufficiently large (Table 2), and blanks consistantly low, such that

net sample activity or mass for all of the analytes almost always exceeded the detection limits reported in Table 1 by a substantial margin. Minor exceptions are Nd and Th-230. The Nd blank was shown to be quite varible relative to the other REE's (NYUMC, 1986) and as a result possess the highest detection limit among the REE's analyzed (about 2.5 μg/kg or ppb for a 2.0 kg fresh weight sample). Difficulty in measuring Th-230 by alpha spectrometry occurred in those samples containing very high levels of Ra-228 (eg., bone, manioc and couve) as a result of subsequent ingrowth of the Th-228 granddaughter during the plant (or animal) maturation period in the field, and the sometimes long delay time between sample collection in Brazil and analysis in New York. Depending on peak resolution and the magnitude of the Th-228 alpha peak (which is of higher energy than either Th-230 or Th-232), a tailing effect from the Th-228 peak into the neighboring Th-230, and to a lesser extent the Th-232 peak energy regions, resulted in spectral degradation causing added uncertainty in deducing net concentrations. Because of this, we have not reported CR's for Th-230 or for Th-228. The Th-228 concentrations in themselves are meaningless as they are a direct consequence of ingrowth from the Ra-228 grandparent and can not be used for CR determinations.

The occasional tailing into the Th-232 region is of much greater significance since this is the major isotope of concern. For those samples in which a potential problem existed, the actual sample filters were analyzed for Th-232 by a fission track etch technique, capable of detecting Th at levels 10^{-3} that obtainable by alpha spectrometry (courtesy of J. A. Medeiros, Catholic University of Rio de Janeiro). The intercomparison results were in excellent agreement providing assurance that Th-232 concentrations were correctly calculated in these samples (NYUMC, 1986).

The overall accuracy of our procedures was continually monitored by routinely analyzing standardized matricies containing certified concentrations of the analytes. These matricies included U.S.G.S.-supplied minerals (andesite, granite and granodiorite) for elements analyzed by XRF; I.A.E.A.-supplied soils (Soil-5) for isotopic Th, isotopic U and the REE's; N.B.S.-supplied organic matricies (SRM-1573, tomato and SRM-1571, orchard leaves) for Th (i. e., total Th which is essentially Th-232), U,

the REE's, Ca, P and Fe; N.B.S.-supplied human lung (SRM-4351) for Th; and for radium isotopes, E.P.A.-supplied solutions. Our results have been shown to be in excellent agreement with certified values (NYUMC, 1984, 1985 and 1986).

From eight measurements of the I.A.E.A. Soil-5 standard, the overall precision (expressed as a coefficient of variation or % CV) of our methods is about 8% for Th, REE's and U. For actual field samples of cattle feeds (unwashed ground corn cobs and corn silage) which were blended and analyzed four times each, the CV ranges from 11-16% for Th, and from 6-19% for REE's.

Individual soil and plant sample concentrations (±SD) and CR's for all analytes have been given in previous progress reports and are not repeated here. For any individual analyte, the propagated analytical uncertainties associated with individual sample (plant type/soil) CR's are always much smaller (eg., ±10-30% at 1 SD) than the uncertainties obtained in the CR's for a given analyte among plant samples of a particular species (eg., ± 50-120% at 1 SD about the mean). It is principally for this reason that results are not given for individual samples but rather for groups of samples according to analyte and plant species.

III. Results

A. Soils of the Pocos de Caldas Plateau

As mentioned in the introduction and shown in Table 3, for small plots and commercial farms, plateau soils are characteristically very high in clay minerals (72%), acidity (pH of 5.1), Al_2O_3 (32%) and Fe_2O_3 (8%), and contain low amounts of SiO_2 (22%) and essential exchangeable cations such as Ca (3-7 meq 100 g^{-1}) and Mg (0.8-1.5 meq 100 g^{-1}). These soil characteristics are reflective of the intense laterization that has occurred throughout the region. Aside from displaying higher pH and a higher base saturation % (resulting primarily from less exchangeable H^+ and greater exch. Ca^{+2} and Mg^{+2} due to liming), there are not many differences between farm soils which are professionally tended and those maintained by individuals.

The distributions of radium isotopes (N=29), Th and the light REE's (N=24) in the farm soils appear to be normally distributed albiet with considerable positive skewness

as is typical of lognormally distributed data (Table 4). As would be expected based on their similar chemistries, La and Nd are highly correlated in soils (r=0.95), although Ce was more closely correlated with Th (r=0.51, $p < 0.02$) than with La (r=0.41, $0.02 < p < 0.05$). This has also been observed in soils and ore from the MF (Lei et al., 1986) and previously attributed to the possibility that Ce exists in this environment in the quadrivalent oxidation state, perhaps in part, as the mineral cerianite (CeO_2). The mean concentrations of these elements within farm soils located in the MF watershed (farms 1, 2 and 3, Fig. 1) are not significantly different than elsewhere on the plateau.

Mean soil concentrations (in $\mu g\ g^{-1}$ except for radium isotopes which are in Bq g^{-1}) for Ra-228, Ra-226, Th, La, Ce and Nd are 0.32, 0.20, 90, 278, 838 and 116, respectively (Table 4). Uranium abundances determined by XRF analyses (essentially U-238) are generally < 20 μg g-1 and range from 7-14 $\mu g\ g^{-1}$ in three farm soils analyzed radiochemically. Uranium is thus present at about five times the worldwide average concentration of 2 $\mu g\ g^{-1}$ (UNSCEAR, 1982). Using the specific activity of Th-232 (4.03 mBq μg^{-1}), the mean activity concentration of 0.36 Bq $g^{-1}$is about 14 times the worldwide average in soils (UNSCEAR, 1982). The ratio of the mean activity concentrations of Ra-228/Th-232 (= 0.89), is not significantly different from unity indicating secular equilibrium.

From earlier analyses of 12 farm soils collected across the U.S. (Linsalata et al., 1985), and seven soils collected from farms in New York (NYUMC, 1986), Ce, La and Nd are enriched by factors of 14, 7 and 3 respectively, in the P.C. soils. The relative abundances of Ce and La (relative to the entire lanthanide series) have been shown to be markedly enriched when the comparison is made to the relative abundances of these two elements in chondritic meteorites or North American shales (Lei et al., 1986). The rare earth concentrations are considerably more variable in these soils than either Th or isotopic radium concentrations (Table 4).

B. Vegetable/Soil Concentration Ratios

The median, dry weight CR's for all analytes and associated ranges are shown in Figure 2 for the seven vegetable species sampled. The minimum and maximum CR's

are reported here as an indication of variability because the number of analyses obtained were in some cases quite limited (eg., N=4 for squash and 4-5 for brown beans). For any particular vegetable specie, the range of CR's was generally well within an order of magnitude for Th and radium isotopes, and very often a factor of 10 or 20 for the light REE's.

There are several points requiring discussion from Figure 2. The first is the obvious differences in CR's between elements with stable oxidation states of II (Ra), III (REE's) and IV (Th). These differences are seen more easily in Table 5, in which the CR data for each analyte are combined across all the samples analyzed. Shown in Table 5 are a variety of discriptive statistics including arithmetic mean values (±SE), the geometric mean (GM) and its 95% confidence interval, and the probabilities that the CR variable when viewed for "vegetables" as a composite group is a normally (p) or lognormally [p(ln)] distributed variable. Based on the p values obtained for the CR and ln-transformed CR values, it is clear that when treating the data in composite form, i.e., treating "vegetables" as a group (as is often done in dose assessment models), the CR is better represented as a lognormally distributed variable. This is also obvious from the differences in arithmetic and geometric means (the geometric means are smaller by factors of two to six).

We cannot test the differences in the GM's shown in Table 5 statistically, because the data are not evenly matched. However, based on the 95% confidence intervals, it is clear that the CR's decrease in the order Ra (~0.01) > REE (~3.5×10^{-4}) > Th (0.6×10^{-4}). Using the Wilcoxon Rank Sign Test (a nonparametric counterpart to the paired T-Test) for paired observations, we can conclude that the CR's for these elements are significantly different ($p < 0.001$). Further comparisons testing the differences in paired CR data between the radium isotopes and between all combinations of the three REE's were all significant (p less than or equal to 0.001) with the exception of the Nd-Ce comparison ($p = 0.25$).

Treating the data collectively has the advantage of simplicity in arriving at "a number" for the CR, but carries the disadvantage of loosing information about species differences relative to uptake. It appears from Figure 2 that, for a given analyte, there

are differences in the CR variable among the vegetables sampled. The question asked is whether or not the variability in CR's (for a given analyte) between vegetable species is greater than the variability within species. The answer to this question is yes ($p < 0.001$ for all analytes) based on either analysis of variance (oneway ANOVA using ln-transformed data) or a nonparametric counterpart (Kruskal-Wallis test). While these tests indicate there are significant differences in the mean CR's (for all analytes) among the different vegetables sampled, they don't indicate where the differences occur.

The significance of the differences in CR's (for a given analyte) among the vegetables sampled was analyzed using the Tukey multiple comparison procedure (Zar, 1984). The results of the tests which were performed on ln-transformed data are given in Figure 3 for Ra-228, La and Th as representative examples. For illustration, we will consider the results for Ra-228. For this nuclide, differences in the geometric mean CR's are significant ($p < 0.05$) for five distinct subsets or combinations of the seven vegetable species sampled. Corn kernels and potatoes comprise two of the subsets and as such they're CR's are significantly different from each other and from every other specie sampled. No differences were found among the CR's for manioc, beans and squash (subset 3), or among beans, squash and carrots (subset 4). No difference exists between carrots and couve (subset 5). The CR for manioc is however different from that of carrots and from that of the leafy vegetable couve. The CR for beans is different from that of couve as is the CR for squash.

Based on the many similarities in the vegetable subsets formed between Ra-228, La and Th (Fig. 3) and the similar trends observed in CR's for all the analytes (Fig. 2), it is apparent that the CR's are correlated. Because of their identical (radium isotopes) or nearly identical chemistries (light REE's) we expected and found CR's to be highly correlated within each group ($R = 0.95$ for radium isotpes and ranged from 0.78 to 0.89 for various REE combinations). Because of their different environmental chemistries, we did not necessarily expect significant correlations between the CR's for radium isotopes and REE's (for example, $R = 0.64$ for Ra-226 and La, $p < 0.001$), for radium isotopes and Th ($R = 0.57$ for Ra-226 and Th, $p < 0.001$), or less unexpectedly,

between Th and REE's (for example, $R = 0.69$ for Th and La, $p < 0.001$).

IV. Discussion

As pointed out by several investigators, CR's determined from field studies are usually greater and more variable than those derived under laboratory conditions mainly as a result of the resuspension of particulate matter onto plant surfaces (Trabalka and Garten, 1983, Pimpl and Schuttelkopf, 1981). If the foreign matter is not removed prior to analysis, results will be biased high and exhibit unpredictable variability. Even when sample preparation is conducted very carefully, the CR's determined in field studies cannot unequivocally be attributed to root uptake and subsequent translocation because of the possibilities of some residual surficial contamination and, or actual solubilization and uptake from the site of surficial deposition (Nishita et al., 1978). Offhand, one might postulate that the correlations observed in CR's between the different elements is simply an artifact of soil contamination. If we assume however, that the geometric mean CR's (Table 5) reflect true root uptake, than the presence of a given amount of soil would affect the CR's for the different elements quite differently. For example if 100 mg of Pocos de Caldas soil remained unwashable from our average analytical plant sample mass of 0.65 kg-dry, the relative contributions from the contamination to the concentrations in the sample would be on the order of 1%, 22% and 72% for Ra-228, La and Th, respectively. Considering the variable nature of surficial deposition and removal of soil, it is difficult to reconcile how the correlations between Ra and REE's or between Ra and Th would be obtained under a contamination scenario. Perhaps more compelling, is the fact that the CR's for Th and any REE, or among the REE's (except Nd and Ce) are significantly different. If soil contamination was the overriding mechanism responsible for the measured concentrations in edible vegetables, then there is no way that these CR's should differ significantly.

Why should we observe correlations in the CR's between elements with such diverse chemical properties as Ra, Th and the REE's? The answer may be related to the mineral requirements, status and, or mineral metabolism of the particular species,

or the tissues of those species sampled. It is commonly observed both among nutrient elements (Bollard, 1960 and Menzel, 1965) and nonessential elements (eg. Pu in roots and shoots of barley, Wildung and Garland, 1974; and Ra in roots and shoots of beans, D'Souza and Mistry, 1971) that different parts of the same plant show marked differences in concentrations which probably change with time. For example, an early work cited by Menzel (Latshaw and Miller, 1924) indicated Ca (an essential element) to be ten times more concentrated in corn leaves than in grain with eight additional elements also more concentrated in leaves than in grain, cobs or stems. According to Menzel, this would be expected for most elements since carbohydrates constitute more of the dry weight in grains, cobs and stems than they do in leaves. In nearly all of the literature cited in this discussion, the actinide elements (and Ra) have, in general, been reported to decrease within various plants as: roots > stems and leaves > seeds and fruit. To some degree, the similar trends in CR's observed between edible portions of different plants (Fig. 2) reflect the order of uptake established within different parts of the same plant. For example the CR's for Ra-228, La and Th are all significantly greater in the leaves of couve than in the seeding portion (kernel) of corn or the fruiting portion of squash (Fig. 3). However, CR's for any of the analytes were never seen to be greater in manioc (a true root) or carrot (a pseudo-root) than in leaves of couve (Figs. 2 and 3).

An observation we have made which is apparently related to both the differences in CR's (at least among some plant species, Fig. 3) for a given analyte and the correlations among the different analytes (Fig. 2), is that the CR's for all of the analytes are highly correlated with the dry weight calcium concentrations of the vegetables analyzed. Shown in Figure 4 as examples, are the arithmetic mean (±1 S.D.) CR's for Ra-226, La and Th plotted against the mean % Ca in the various vegetables. A log-log scale is used soley to encompass the large range of mean values obtained in both the ordinate and the abcissa and is not meant to imply that a power function describes the relationships best (correlation coefficients were in fact slightly higher assuming linear relationships). The standard deviations about the Ca means (Table 2) are only shown with the Ra-226 CR data (for clarity) since they would plot the same for La and Th (i.e., all analyses were done on the same samples). Linear correlation coefficients (R) are

0.96, 0.98 and 0.93 for Ra-226, La and Th, respectively. Using the individual data pairs i.e., (% Ca, CR) to encompass the true range of values obtained for the approximately 42 samples analyzed, the R values of course decrease ($R = 0.76$, 0.67 and 0.75 for Ra-226, La and Th, respectively) but remain highly significant ($p << 0.001$). As for the other essential minerals which were analyzed in vegetables (Table 2), weaker correlations were obtained between the individual CR's and the iron concentrations ($R = 0.38$, $p = 0.008$ for Ra-226, $R = 0.27$, $p = 0.044$ for La, and $R = 0.48$, $p < 0.001$ for Th). No significant correlations were obtained between the CR's and the phosphorous concentrations. Concentration ratios within vegetable species were also examined as functions of the plants Ca concentrations and were found not to be correlated. Thus the variability in CR's observed <u>within</u> samples of a particular specie could not be accounted for by the sample to sample variability observed in the plants Ca content. In general, the plant tissues which are expected to have relatively high carbohydrate concentrations (eg., corn and potato) contain relatively low Ca and correspondingly low CR's (and vice-versa).

While others have stated (D'Souza and Mistry, 1971) that the distribution pattern of Ra is similar to that of Ca within different tissues of the same plant (as would be expected since both are divalent alkaline earths), similar trends have not, to our knowledge, been reported between different tissues of different plants. This is certainly true of the unexpected correlations observed between Ca concentrations and the CR's for the trivalent REE's and quadrivalent Th. According to Bollard (1960), Ca is regarded as the most immobile of the essential elements in plants, exhibiting little translocation once delivered to a particular organ. D'Souza and Mistry have also indicated this to be true of Ra. Yttrium, which exhibits chemical properties similar to the REE's was also reported to behave like Ca in plants (Rediske and Selders, 1954). Since the transport of Ra to aerial tissues in bean plants grown in nutrient solutions has been shown to be mediated by metabolic processes (D'Souza and Mistry), the question arises as to whether similar processes control the fate of REE's, Th and their chemical analogues in plant tissues. Since the slopes of the linear fits for (mean % Ca vs. mean CR) for Ra-226, La or Th, were significantly different (0.054 ± 0.007, 0.0055 ± 0.00049, and

0.00016 ± 0.00003, ± SE, respectively), the processes themselves are probably different and undoubtedly complex. Clearly, further investigations of the robustness of the Ca-CR trends (eg, in different plants from other environments and in different tissues of the same plant), are needed before we can consider the use of Ca in plants for predictive purposes.

Virtually all of the soil parameters given in Table 3 were tested for linear correlation with the CR data for each of the analytes studied (individual pairwise testing, eg, % clay vs. La CR, etc.). At the 1% level of significance, no correlations were evident. This "non-finding" does not diminish the importance of soil type, the organic matter content and the soil pH parameters, which have been shown to be significant variables for predicting plant uptake of several radionuclides (Sheppard, 1985 and Frissel and Koster, 1987). The lack of any significant findings between CR's and soil parameters in Pocos de Caldas is probably a function of the relatively greater variability in the CR's than in the values of the soil parameters.

Exchangeable Ca and Mg cations in these soils are not inversly correlated with either the isotopic Ra CR's or the Ra concentrations in the vegetables, as might otherwise have been expected if competition between these essential elements and Ra at the soil-root interface was a key factor for predicting Ra uptake. Although the data for comparisons are limited, no differences were found in the CR's for any given analyte among similar vegetables grown in soils from the larger, commercial farms (which generally are better fertilized, Table 3) and those grown in smaller, individual plots which generally exhibit poorer soil characteristics. With the possible exception of Ra-228 in brown beans, concentrations of all other elements and nuclides in vegetables grown on Farm 1, which is irrigated with stream water originating at the base of the MF, were not different than those in like vegetables grown elsewhere on the plateau. This is consistant with earlier findings that human ingestion of Th and REE's is not related to proximity to the MF (Linsalata et al., 1986).

For 38 vegetable samples in which concentrations for both Th-232 and Th-230 were obtained, the Th-232/Th-230 ratios ranged between 0.3 and 3.0 and averaged 1.48 ± 0.62 (± 1SD). For five soil samples which were analyzed isotopically, the ratios

ranged from 1.18 to 2.93 and averaged 1.94 ± 0.83. From these limited data, we cannot conclude that Th-230 (U-238 series) is taken up by plants any differently than Th-232. The observation that the CR's for the radium isotopes are significantly different (the Ra-228 CR exceeded that of Ra-226 in all but two samples) is perplexing and cannot be resolved without investigating the relative availiblity of these isotopes in the soil substrate. The same can be said for the significant differences found among CR's for some of the light REE's analyzed.

Are the findings obtained in Pocos de Caldas for the elements and vegetables studied relevant to other environments, or are the data unique to this environment? If the data are unique then clearly, the usefulness of the CR's in dose assessment models, and their usefulness relative to the Th-Pu and REE-Am, Cm analogies would be limited to this or perhaps very similar environments. One aspect of the data which required further investigation was the Ca content of vegetables. Because exchangeable Ca is relatively low in the Pocos soils (Table 3) and a weak, but significant correlation ($R = 0.36$, $p = 0.008$) was obtained between exchangeable Ca in soils and total Ca in plant tissue, we questioned whether or not the vegetable Ca concentrations were atypical. Based on available information (EML, 1983) the Ca content in both corn kernels and potatoes from Pocos may be low by a factor of 4-5 although comparisons with the other vegetables sampled resulted in reasonablly similar values. Using Ca data obtained from potato and corn sampled in Orange County, New York (NYUMC, 1986) the Pocos vegetables are still lower, but only by factors of two and 30%, respectively. Thus the vegetable Ca data do not appear to be unique. Although only a limited number (15) of samples were obtained in New York (see footnote h, Table 6), significant correlations were obtained between the Ca concentrations and the CR's for Th ($R = 0.60$, $p = 0.0096$), La ($R = 0.65$, $p = 0.006$) and Ce ($R = 0.80$, $p < 0.001$) indicating that the relationships observed between these variables in the Pocos samples are probably not unique.

The data reported in Table 6 summarizes the few comparative results we have obtained either from the literature or by analysis. Our own analytical data are for the CR's for Ra-226, Th, La and Ce obtained in soils and vegetables grown in New York

State (NYUMC, 1986). These soils are markedly different than those of Pocos de Caldas. They are silty-clay loams (about 50% silt, 25% clay) with typical pH values around 6.0, organic C contents not unlike those of Pocos, much lower Fe and Al and more Si oxides than the Pocos soils, and exhibit much greater exchangeable Ca and saturated base percentages. Where comparisons could be made between the P.C. and the N.Y. data sets, i.e., for the same types of vegetables, the CR values appear to be in reasonable agreement (considering the differences in soil composition) with the exceptions of Ce in corn, and Ra and Th in squash. Comparisons with the Laul et al. (1977) data for La and Ce (INAA analyses) are not as favorable as are the comparisons based on in-house analyses, with only one value (La CR in potato) falling within the 95% confidence intervals given for the P.C. vegetables. The Laul et al. data also indicate that the CR's for Th exceed those for La and Ce, an occurrence which we have almost never observed. Other data sets concur with our observations that the CR's for M (III) elements are almost always greater than those for M (IV) elements (Bondietti et al., 1979, Schreckhise and Cline, 1980 and Garten, 1981). These differences have been attributed by these same authors, to relatively higher solubilities (resulting in lower K_d's hence greater availibility to plant roots) of the M (III) elements.

Although comparisons between differing varieties of edible vegetables are of limited use, the summary datum given by McDowell-Boyer et al. (1980) for the Ra-226 CR in vegetables falls well within our 95% C. I. for this nuclide. The median Th CR (2×10^{-4}) determined by Bondietti et al. (1979) for a variety of vegetables does lie above the 95% C. I. given in Table 6 but is still only a factor of three greater than the geometric mean CR of 0.6×10^{-4} determined for the Pocos samples.

Considering the sometimes tremendous variabilities (eg., five to seven orders of magnitude) that have been reported for plant/soil CR's (Pimpl and Schuttelkopf, 1981), especially among those elements that have relatively large soil/water partition coefficients (K_d's) like Pu, Th, Am, Cm and the REE's, the CR data obtained in this field study appear to be notably less variable, both within samples of a given variety, and among different varieties of vegetables. The real differences that have been observed

in CR's among the edible portions of vegetables sampled are apparently related to the plants (or the particular portion of the plants) mineral requirements or status, as illustrated by the correlations between CR's and Ca or Fe contents.

REFERENCES

Barretto, P.M.C. and Fujimori, K. 1986. Natural analogue studies: Geology and mineralogy of Morro do Ferro, Brazil. Chem. Geol. 55(No. 3/4): 297-312.

Bhattacharyya, M.H., Larsen, R.P., Oldham, D., Moretti, E.S., and Spaletto, M.I. 1985. Gastrointestinal absorption of plutonium in mice, rats and dogs: Application to establishing values of F_1 for soluble plutonium. NUREG/CR-4208. U.S. Nuclear Regulatory Commission, Washington, DC. 84 pp.

Bollard, E.G. 1960. Transport in the xylem. Ann. Rev. Plant Physiol. 11: 141-166.

Bondietti, E.A., Trabalka, J.R., Garten, C.T., and Killough, G.G. 1979. Biogeochemistry of actinides: A nuclear fuel cycle perspective. In: Radioactive Waste in Geological Storage (S. Fried, ed.). American Chemical Society Symp. Series 100. pp. 241-265.

Bondietti, E.A. and Tamura, T. 1980. Physicochemical associations of plutonium and other actinides in soils. In: Transuranic Elements in the Environment (W.C. Hanson, ed.). DOE/TIC-22800, NTIS, Springfield, VA. pp. 145-164.

Campos, M.J., Penna-Franca, E., Lobão, N., Trindade, H., and Sachett, I. 1986. Migration of radium from the thorium ore deposit of Morro do Ferro, Poços de Caldas, Brazil. J. Environ. Radioactivity 3: 145-161.

Crock, J.G. and Lichte, F.E. 1982. Determination of rare earth elements in geologic materials by inductively coupled argon plasma/atomic emission spectrometry. Anal. Chem. 54: 1329-1332.

Delaney, M.S. and Francis, C.W. 1978. The relative uptake of Pu-237(IV) and Pu(VI) oxidation states from water by bush beans. Health Phys. 34: 492-494.

D'Souza, T.J. and Mistry, K.B. 1971. Studies on the uptake, distribution and metabolic fate of radium in plants. In: International Symposium on Use of Isotopes and Radiation in Agriculture and Animal Husbandry Research. New Delhi, India. pp. 428-438.

Durbin, P.W., Williams, M.H., Gee, M., Newman, R.H., and Hamilton, J.G. 1956. Metabolism of the lanthanons in the rat. In: Proc. Soc. Exper. Biol. Med. 91: 78-85.

Durbin, P.W. 1962. Distribution of the transuranic elements in mammals. Health Phys. 8: 665-671.

Eisenbud, M., Krauskopf, K., Penna Franca, E., Lei, W., Ballad, R., Linsalata, P., and Fujimori, K. 1984. Natural analogues for the transuranic actinide elements. Environ. Geol. Water Sci. 6 (1): 1-9.

Empresa Brasileira da Pesquisa Agropecuaria (EMBRAPA). 1981. Manual of Methods for Soil Analysis. Rio de Janeiro Servico Nacional de Levantamento e Conservaçao (SNLCS).

Environmental Measurements Laboratory. 1983. EML Procedures Manual, 26th Edition (H.L. Volchok and G. de Planque, eds.). HASL-300, U.S. Department of Energy, New York, NY.

Fisenne, I.M., Perry, P.M., and Welford, G.A. 1980. Determination of uranium isotopes in human bone ash. Anal. Chem. 52: 777-779.

Frayha, R. 1962. Uranio e torio no planalta de Poços de Caldas, Nat. Dept. of Mineral Production. Bull. 116. 75 pp.

Frissel, M.J. and Kester, J. 1984. Soil to plant transfer factors of radionuclides: Expected values and uncertainties, a summary of available data. Manuscript prepared for the International Union of Radioecologists Soil to Plant Working Group. Available through RIUM, P.O. Box 1, 3720 BA Bilthoven, The Netherlands.

Garten, C.T., Jr. 1981. Comparative uptake of actinides by plants and rats from the shoreline of a radioactive pond. J. Environ. Qual. 10: 487-491.

Garten, C.T., Jr., Bondietti, E.A., and Walker, R.L. 1981. Comparative uptake of uranium, thorium and plutonium by biota inhabiting a contaminated Tennessee foodplain. J. Environ. Qual. 10: 207-210.

Hodge, H.C., Stannard, J.N., and Hursh, J.B. (eds.). 1973. Uranium, Plutonium and Transplutonic Elements. Handbook of Experimental Pharmacology XXXVI. Springer-Verlag, New York, NY.

ICRP, International Commission on Radiological Protection. 1977. Recommendations of the ICRP Publ. 26. Pergamon Press, New York, NY.

ICRP, International Commission on Radiological Protection. 1979. Limits for Intakes of Radionuclides by Workers. ICRP Publ. 30, Part 1. Pergamon Press, New York, NY.

Kamath, P.R., Bhat, I.S., Rudran, K., Iyengar, M.A.R., Koshy, E., Waingankar, U.S., and Khanolkar, U.S. 1964. Recent radiochemical procedures for bio-assay studies at Trombay. In: Assessment of Radioactivity in Man. IAEA STI/PUB/84. International Atomic Energy Agency, Vienna, Austria. pp. 195-216.

Krauskopf, K.B. 1986. Thorium and rare earth metals as analogs for actinide elements. Chem. Geol. 55(No. 3/4): 323-335.

Latshaw, W.L. and Miller, E.C. 1924. J. Agr. Res. 27: 845.

Laul, J.C., Weimer, W.C., and Rancitelli, L.A. 1977. Biogeochemical distribution of rare earths and other trace elements in plants and soils. BNWL-SA-6078, Battelle Pacific Northwest Laboratories,

Richland, WA. 14 pp.

Laurer, G.L., Furfaro, J., Carlos, M., Lei, W., Ballad, R., and Kneip, T.J. 1982. Energy dispersive analysis of actinides, lanthanides, and other elements in soil and sediment samples, In: Advances in X-ray Analysis, Vol. 25. (J.C. Russ, C.S. Barrett, P.K. Predecki and D.E. Leyden, eds.). Plenum Publishing, New York, NY. pp. 201-208.

Lei, W. 1984. Thorium Mobilization in a Terrestrial Environment. Ph.D. Dissertation, New York University, New York, NY. 414 pp.

Lei, W., Linsalata, P., Penna Franca, E., and Eisenbud, M. 1986. Distribution and mobilization of cerium, lanthanum and neodymium in the Morro do Ferro Basin, Brazil. Chem. Geol. 55(No. 3/4): 313-322.

Linsalata, P., Eisenbud, M., and Penna Franca, E. 1985. Thorium and the light rare earth elements in soils, crops and domestic animals from abnormally high and typical radiation background areas. In: Proc. of the Eighteenth Midyear Topical Symposium of the Health Physics Society - Environmental Radiation '85 (Colorado Springs, CO; January 6-10, 1985). pp. 535-542.

Linsalata, P., Penna Franca, E., and Eisenbud, M. 1986. Ingestion estimates of thorium and the light rare earth elements based on measurements of human feces. Health Phys. 50 (1): 163-167.

Linsalata, P., Penna Franca, E., Sachett, I., Castro, M.B., Lobão, N., Ballad, R., Lei, W., Ford, H., Morse, R.S., and Eisenbud, M. 1987. Radium, thorium and the light rare earth elements in soils and vegetables grown in an area of high natural radioactivity. In: Environmental Research for Actinide Elements, CONF 841142. NTIS, Springfield, VA. pp. 131-146.

Lucas, H.F. 1964. A fast and accurate survey technique for both radon-222 and radium-226. In: The Natural Radiation Environment (J.A.S. Adams and W.M. Lowder, eds.). University of Chicago Press, Chicago, IL. pp. 315-329.

Maletskos, C.J., Keane, A.T., Telles, N.C., and Evans, R.D. 1969. Retention and absorption of ^{224}Ra and ^{234}Th and some dosimetric considerations of ^{224}Ra in human beings. In: Delayed Effects of Bone-Seeking Radionuclides (C.W. Mays, W.S. Jee, R.D. Lloyd, B.J. Stover, J.H. Dougherty, and G.N. Taylor, eds.). University of Utah Press, Salt Lake City, UT. pp. 29-49.

McCurdy, D.E. and Mellor, R.A. 1981. Determination of radium 224, 226 and 228 by coincidence spectrometry. Anal. Chem. 53: 2212-2216.

McDowell-Boyer, L.M., Watson, A.P., and Travis, C.C. 1980. A review of parameters describing terrestrial food-chain transport of Lead-210 and Radium-226. Nucl. Safety 21: 486-495.

Menzel, R.A. 1965. Soil-plant relationships of radioactive elements. Health Phys. 11: 1325-1332.

Miekeley, N., Dotto, R.M., Kuchler, I.L., and Linsalata, P. 1985. The importance of organic compounds on the mobilization and bioassimilation of thorium in the Morro do Ferro Environment. In: Scientific Basis for Nuclear Waste Management VIII, Materials Research Society Symposia Proceedings, Vol. 44. Materials Research Society, Pittsburgh, PA. pp. 591-597.

Miekeley, N. and Kuchler, I.L. 1987. Interactions between thorium and humic compounds in surface waters. Inorg. Chim. Acta (submitted for publication).

NCRP, National Council on Radiation Protection and Measurements. 1975. Natural Background Radiation in the United States. NCRP Report No. 45. NCRP, Washington, DC.

New York University Medical Center. 1984. Studies of Transport Pathways of Th, U REE's and Radium Isotopes from Soil to Farm Animals. Annual Progress Report to DOE/OHER, Jan., 1974. 71 pp.

New York University Medical Center. 1985. Studies of Transport Pathways of Th, U, REE's and Radium Isotopes from Soil to Farm Animals. Annual Progress Report to DOE/OHER, Jan., 1985. 200 pp.

New York University Medical Center. 1986. Studies of Transport Pathways of Th, U, Rare Earths, Ra-228 and Ra-226 from Soil to Plants and Farm Animals. Annual Progress Report to DOE/OHER, Feb., 1986. 120 pp.

Ng, Y.C., Colsher, C.S., and Thompson, S.E. 1982. Soil-to-plant concentration factors for radiological assessments. Lawrence Livermore National Laboratory, NUREG/CR-2975. UCID-19463. 133 pp.

Nishita, H., Wallace, A., and Romney, E.M. 1978. radionuclide uptake by plants. NUREG/CR-0336. U.S. Nuclear Regulatory Commission, Washington, DC. 87 pp.

Pimpl, M. and Schuttelkopf, H. 1981. Transport of plutonium, americium and curium from soils into plants by root uptake. Nucl. Safety 22: 214-225.

Rediske, J.H. and Selders, A.A. 1954. Am. J. Botany 41: 238-242.

Rundo, J., Failla, P., and Schlenker, R.A. (eds.). 1983. Radiobiology of Radium and the Actinides in Man. Health Phys. 44 (Supplement No. 1). Pergamon Press, New York, NY.

Sartor, J.D., Lane, W.B., and Allen, J.J. 1966. Uptake of radionuclides by plants. AD-649009, Stanford Research Institute, Menlo Park, CA.

Schreckhise, R.G. and Cline, J.F. 1980. Comparative uptake and distri-

bution of plutonium, americium, curium, and neptunium in four plant species. In: Transuranic Elements in the Environment (W.C. Hanson, ed.). DOE/TIC-22800, NTIS, Springfield, VA. pp. 361-370.

Sill, C.W. 1974. Purification of radioactive tracers for use in high sensitivity alpha spectrometry. Anal. Chem. 46: 1426-1431.

Sill, C.W. and Williams, R.L. 1981. Preparation of actinides for α spectrometry without electrodeposition. Anal. Chem. 53: 412-415.

Sheppard, M.I. 1985. Radionuclide partitioning coefficients in soils and plants and their correlation. Health Phys. 49 (1): 106-111.

Sheppard, M.I. and Sheppard, S.C. 1985. The plant concentration ratio concept as applied to natural U. Health Phys. 48: 494-500.

Singh, N.P., Wrenn, M.E., and Ibrahim, S.A. 1983. Plutonium concentrations in human tissues: comparison to thorium Health Phys. 44 (Supplement No. 1): 469-476.

Sullivan, M.F., Miller, B.M., and Gorham, L.S. 1983. Nutritional influences on plutonium absorption from the gastrointestinal tract of the rat. Radiat. Res. 96: 580-591.

Trabalka, J.R. and Garten, C.T., Jr. 1983. Behavior of the long-lived synthetic elements and their natural analogs in food chains. Advances in Radiation Biology 10. Academic Press, Inc., New York, NY. pp. 39-104.

Tracy, B.L., Prantl, F.A., and Quinn, J.M. 1983. Transfer of Ra-226, Pb-210 and uranium from soil to garden produce: assessment of risk. Health Phys. 44: 469-477.

United Nations Scientific Committee on the Effects of Atomic Radiation. 1982. Ionizing Radiation: Sources and Biological Effects. United Nations, New York, NY. 772 pp.

Wahlgren, M.A. and Orlandini, K.A. 1982. Comparison of the geochemical behavior of plutonium, thorium and uranium in selected North American lakes. In: Proc. Symp. Migration in the Terrestrial Environment of Long-Lived Radionuclides from the Nuclear Fuel Cycle. IAEA-SM-257. Knoxville, TN, July 23-31, 1981. pp. 757-774.

Watters, R.L., Edgington, D.N., Hakonson, T.E., Hanson, W.C., Smith, M.H., Whicker, F.W., and Wildung, R.E. 1980. Synthesis of the research literature. In: Transuranic Elements in the Environment (W.C. Hanson, ed.). DOE/TIC-22800. U.S. Department of Energy, Washington, DC. pp. 1-44.

Wedow, H. 1961. Thorium and rare earths in the Poços de Caldas zirconium district, Brazil. In: Short Papers in the Geologic and Hydrologic Sciences (Geological Survey Research, 1961), U.S. Geological Survey Prof. Paper 424-D. pp. D214-D216.

Wedow, H. 1967. The Morro do Ferro thorium and rare-earth deposit, Poços de Caldas District, Brazil. U.S. Geological Survey Bull. 1185-D. 35 pp.

Weimer, W.C., Laul, J.C., and Kutt, J.C. 1980. Prediction of the ultimate biological availability of transuranium elements in the environment. In: Contaminants and Sediments, Vol. 2. Ann Arbor Sci. Publ., Ann Arbor, MI. pp. 465-484.

Wildung, R.E. and Garland, T.R. 1974. Influence of soil plutonium concentration on plutonium uptake and distribution in shoots and roots of barley. J. Agr. Food Chem. 22: 836-838.

Wildung, R.D. and Garland, T.R. 1980. The relationship of microbial processes to the fate and behavior of transuranic elements in soils, plants, and animals. In: Transuranic Elements in the Environment (W.C. Hanson, Ed.). DOE/TIC-22800. U.S. Department of Energy, Washington, DC. pp. 300-335.

Zar, J.H. 1984. Biostatistical Analysis. Prentice-Hall, Inc., NJ.

TABLE 1

Methodologies and Detection Limits[a]

Element or Nuclide	Matrix	Sample Size	Methods[b]	Lower Limits of Detection 95% C.I.
^{232}Th	soil	7 g-dry	X-ray fluorescence (XRF)	140 μg
^{232}Th ^{230}Th, ^{228}Th	soil	1 g-dry	radiochem.; α-spec.	0.4-1.5 mBq
^{232}Th, ^{230}Th, ^{228}Th	biota	0.5-5.0 kg-fresh	radiochem.; α-spec.	0.4-1.5 mBq
REE (La-Sm)	soil	7 g	XRF	70 μg
REE (La-Sm)	soil	1 g	chem.; ICPOES	0.8-5.0 μg
REE (La-Sm)	biota	0.5-5.0 kg-fresh	chem.; ICPOES	0.8-5.0 μg
^{226}Ra	soil	290 g-dry	γ-spec.; Ge(Li)	5 Bq
^{226}Ra	biota	50 g-fresh	radiochem.; ^{222}Rn emanation	2.0 mBq
^{228}Ra	biota	50 g-fresh	radiochem.; β-γ coincidence counting	55 mBq
^{238}U	soil	7 g-dry	XRF	100 μg
^{238}U, ^{235}U, ^{234}U	soil	1 g-dry	radiochem.; α-spec.	0.4-1.5 mBq
^{238}U, ^{235}U, ^{234}U	biota	0.5-5.0 kg-fresh	radiochem.; α-spec.	0.4-1.5 mBq

[a] Lower limits of detection based on radioactivity counting were calculated using methods discussed in the Environmental Measurements Laboratory (DOE) Procedures Manual (1983).

[b] Methods abbreviations include radiochemical or chemical separation, followed by either alpha spectrometry or induced coupled plasma optical emission spectrometry.

TABLE 2

Analytical and Descriptive Characteristics of Vegetable Samples from Poços de Caldas[a]

Sample Type	N	Analytical[b] Weight (kg)	Chemical Yield Th	Chemical Yield REE	% Moisture	% Composition dry wt[d] Ca	% Composition dry wt[d] Fe	% Composition dry wt[d] P
Brown Beans	5	0.9	60±16	87±5	33±7	0.145±0.083	0.009±0.005	0.558±0.071
Carrots	6	1.8	76±13	75±14	87±31	0.316±0.098	0.006±0.008	0.325±0.160
Corn	8	2.6(8.4)[c]	49±20	83±23	22±1[c]	0.006±0.002	0.003±0.001	0.349±0.071
Couve	6	1.3	54±10	86±13	87±34	1.74 ±0.97	0.009±0.004	0.301±0.109
Manioc	7	2.1	75±20	86±6	61±11	0.061±0.018	0.001±0.000	0.088±0.043
Potatoes	8	2.7	68±15	91±7	81±11	0.013±0.005	0.004±0.003	0.197±0.046
Zucchini	4	3.2	68±9	90±12	95±21	0.370±0.110	0.008±0.002	0.534±0.183

[a] All values given represent mean quantities ± one standard deviation.

[b] Average analytical fresh weight.

[c] Corn was generally field-dried (i.e., for livestock consumption) prior to sampling. Fresh corn was found to have a moisture content of about 76%.

[d] Ca, Fe and P determinations were made by ICPOES.

TABLE 3

Physical and Chemical Properties of Farm Soils

Sampled Within the Poços de Caldas Plateau

Parameter (% Composition)	Small Farms and Plots* Mean±S.D.	Range	Larger Commercial Farms¶ Mean±S.D.	Range
Coarse sand†	6.1±2.5	2-11	5.0±1.7	3-8
Fine sand†	2.3±1.9	1-4	1.3±0.5	1-2
Silt†	19.9±4.8	11-29	17.5±3.0	14-22
Clay†	72.0±6.8	60-84	76.2±4.2	72-82
Organic C	2.23±0.44	1.39-3.10	1.99±0.15	1.85-2.21
N	0.22±0.03	0.17-0.26	0.18±0.04	0.14-0.26
SiO_2‡	22.1±5.7	8.7-29.6	21.1±2.7	17.6-24.2
Al_2O_3 ‡	31.8±2.6	27.5-37.9	31.3±1.9	29.2-33.3
Fe_2O_3 ‡	8.4±2.4	4.0-15.6	8.7±0.6	8.0-9.8
TiO_2‡	0.72±0.34	0.20-1.45	0.62±0.08	0.49-0.73
P_2O_5	0.20±0.17	0.07-0.73	0.25±0.15	0.13-0.53
pH§	5.1±0.04	4.6-5.8	6.3±0.7	5.6-7.2
Exchangeable Cations				
Ca^{+2} (meq/100g)	3.1±1.6	1.0-6.2	6.8±2.4	3.4-9.8
Mg^{+2} "	0.8±0.8	0.1-2.7	1.5±0.8	0.5-2.6
K^+ "	0.38±0.19	0.17-0.88	0.69±0.34	0.33-1.26
Na^+ "	0.07±0.03	0.03-0.12	0.11±0.09	0.01-0.27
Al^{+3} "	1.2±1.2	0-4.5	0.03±0.05	0-0.1
H^+ "	7.0±1.4	4.7-9.5	4.2±2.1	1.7-6.5
Total cations	12.6±2.6	8.4-17.2	13.3±3.3	9.6-18.5
% Base sat.	31.6±15.6	11-66	68.2±17.0	39-86

* 18 samples from 8 farms.

† Analysis performed on chemically dispersed soil (NaOH-Calgon).

‡ Based on decomposition with 50% H_2SO_4 except P_2O_5 (0.8% NaOH).

§ A soil-to-solution (water) ratio of 1:2.5 was used.

¶ 6 samples from 3 farms.

TABLE 4

Summary of Farm Soil Concentration Data for the Pocos de Caldas Plateau

Element	Soil Concentrations ($\mu g\ g^{-1}$ or $Bq\ g^{-1}$ dry)					N	p[b]
	$\bar{X}$	S.E.	Min.	Max.	Median		
^{228}Ra[a]	0.32	0.02	0.18	0.53	0.28	29	0.136
^{226}Ra[a]	0.20	0.02	0.09	0.45	0.20	29	0.231
^{232}Th	89.9	4.4	59.0	133.0	92.5	24	0.227
La	277.6	44.3	79.0	904.0	213.0	24	0.121
Ce	837.6	61.4	439.0	1,484.0	798.5	24	0.287
Nd	115.8	23.1	27.0	447.0	67.5	24	0.093

[a] Concentrations for the radium isotopes are expressed in Bq g^{-1} dry soil. Concentrations of Th and the REE are expressed in $\mu g\ g^{-1}$ dry soil.

[b] p values computed from Z scores using the Kolmogorov-Smirnov one sample test for goodness of fit to the normal distribution (i.e., $Z = /D/_{max}\sqrt{n}$, where D is the K-S test statistic). Assuming an a priori level of significance of $p \leq 0.05$ for rejecting the null hypothesis (i.e., that the underlying distribution of these elements is normal), we cannot conclude from these limited sample data sets that the elements are not normally distributed in farm soils. Significant positive skewness ($p \leq 0.01$) was noted for La and Nd and, to a lesser extent, for ^{226}Ra ($0.01 < p < 0.05$), Ce and ^{228}Ra ($p \sim 0.05$).

TABLE 5

Summary of Concentration Ratios for Edible Vegetable Samples Collected Within the Poços de Caldas Plateau

Element	N	Concentration Ratios ($x10^{-4}$)[a] $\bar{X}\pm SE$[b]	Geom. Mean[c]	95% C.I.[d]	p[e]	p(ln)[f]
Ra-228	41	466±136	148	91-242	<0.01	0.94
Ra-226	41	236±68	76	47-124	<0.01	0.97
La	43	22.5±5.9	5.4	2.9-9.8	<0.01	0.94
Nd	37	16.8±6.2	3.0	1.5-6.0	<0.01	1.00
Ce	42	9.0±2.0	2.6	1.5-4.6	<0.01	0.77
Th-232	44	1.1±0.2	0.6	0.4-0.9	0.025	0.28

[a] Concentration ratios (CR) are computed as [μg (or Bq) g^{-1} dry plant/μg (or Bq) g^{-1} dry soil] and have been multiplied by 10^4. Vegetable samples (approximate number of analyses) include corn kernels (8), potatoes (7), collard greens (6), carrots (6), manioc (tapioca, 6), brown beans (5) and squash (4).

[b] $\bar{X}\pm SE$ refers to the arithmetic mean ± the standard error ($S/\sqrt{N}$).

[c] The geometric means are calculated as: exp (arithmetic mean of the ln-transformed CR values).

[d] The 95% confidence intervals were calculated from the ln-transformed CR values and thus pertain to the geometric means.

[e] A p-value ≤ 0.05 indicates that there is a ≥ 95% probability that the sample CR is not a normally distributed variable (see footnote b, Table 4 for test procedure).

[f] These p-values, obtained from ln-transformed CR data, indicate strongly that the CR variables, when examined collectively (i.e., across all vegetable types), are lognormally distributed.

TABLE 6

Comparison of Dry-Weight CR Data from Poços de Caldas and Other Environments

Vegetable	N	CR($x10^{-4}$) as Reported				Ref.
		La	Ce	Th	Ra-226	
corn	1	1.7	1.6	<3.6	--	a
"	NG[e]	--	1-9	--	--	b
"	2	0.25	0.81	0.17	10	This work, N.Y.[c]
"	7-8	0.2-0.8	0.1-0.4	0.1-0.4	5-14	This work, P.C.[d]
potato	1	0.7	0.4	5.7	--	a
"	NG	--	20-90	--	--	b
"	1	1.9	2.6	0.6	48	This work, N.Y.
"	7-8	0.6-3.9	0.7-1.7	0.1-0.4	25-48	This work, P.C.
squash	1	6.0	2.5	14.0	--	a
"	3	19.1	37.0	12.0	619	This work, N.Y.
"	4	10.7-66.0	4.0-77.0	0.3-2.6	53-258	This work, P.C.
variety	14	--	--	2.0	--	f
"	15	--	--	0.8-4.6[h]	--	This work, N.Y.
"	~42	--	--	0.4-0.9	--	This work, P.C.
variety	13	--	--	--	80	g
"	41	--	--	--	47-124	This work, P.C.

[a] Laul et al. (1977). Field study in sandy loam soil of N. Eastham, MA, USA.

[b] Sartor et al. (1966). As referenced in Ng et al. (1982). Values given represent the range of means for Ce-144 (chloride) added to loam, clay and sandy loam soils.

[c] NYUMC (1986). Field study in Orange Country, NY, USA. Values represent the means from plants grown in a silty-clay loam.

[d] NYUMC (1980) and current work. Values for the Poços de Caldas (P.C.) samples represent the 95% C.I. about the geometric mean.

TABLE 6 (Cont'd)

[e] NG refers to not given.

[f] Bondietti et al. (1979). Value given represents the median based on analyses of soybeans, snap beans, Japanese Millet, squash, tomatoes, carrots and radishes grown in floodplain soil.

[g] McDowell-Boyer et al. (1980). Value given is the grand average of 13 sample means representing a variety of vegetables and soil substrates.

[h] 95% confidence interval about the geometric mean for the NY data. Other samples include carrots (3), green beans (1), lettuce (1), cabbage (1) and broccoli (1).

FIGURE 1

LOCATION OF SELECTED FARMS IN THE POCOS DE CALDAS PLATEAU

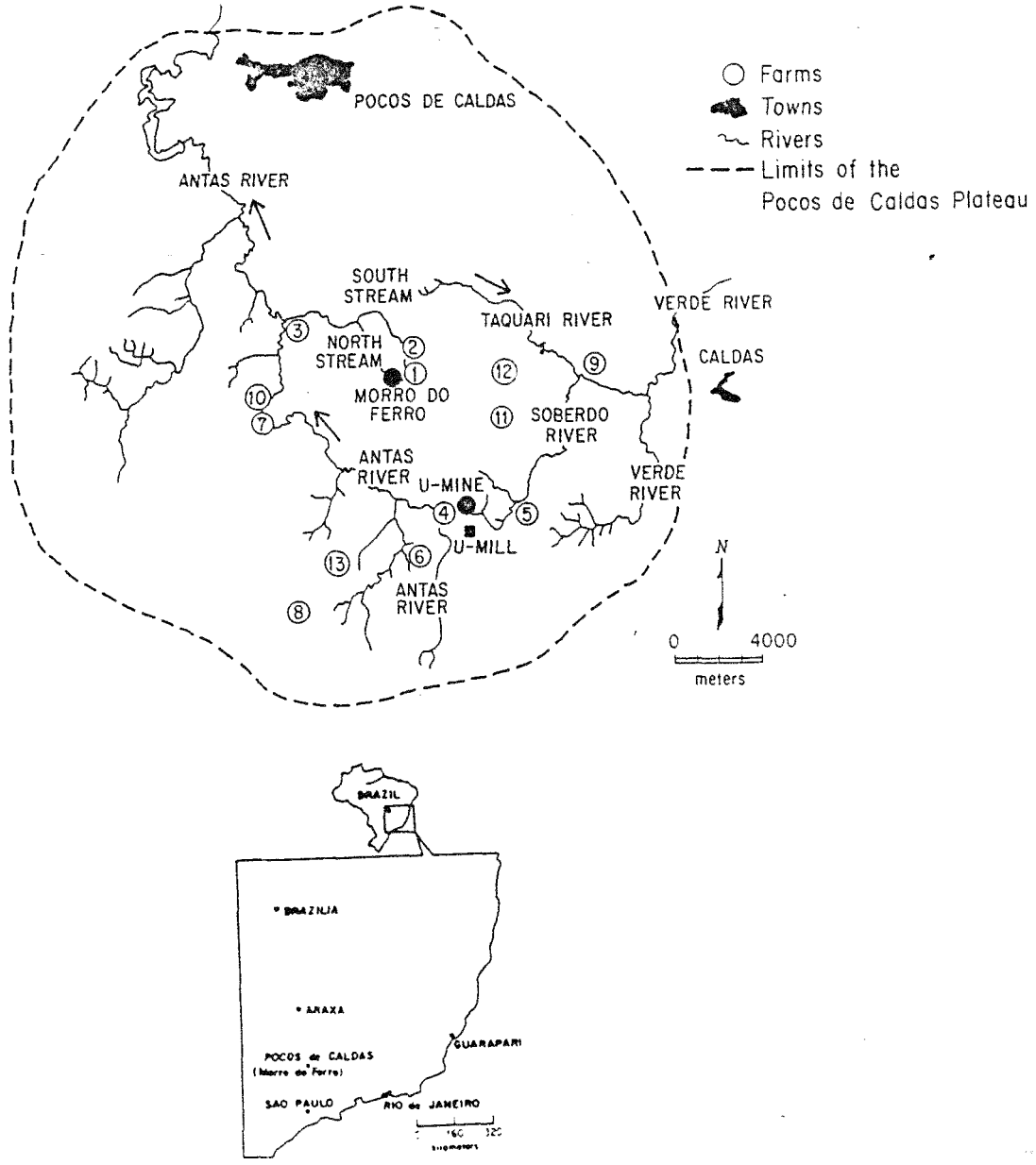


FIGURE 2

Median Concentration Ratios for ^{232}Th, ^{228}Ra, ^{226}Ra, La, Ce and Nd in Vegetables Grown on the Pocos de Caldas Plateau

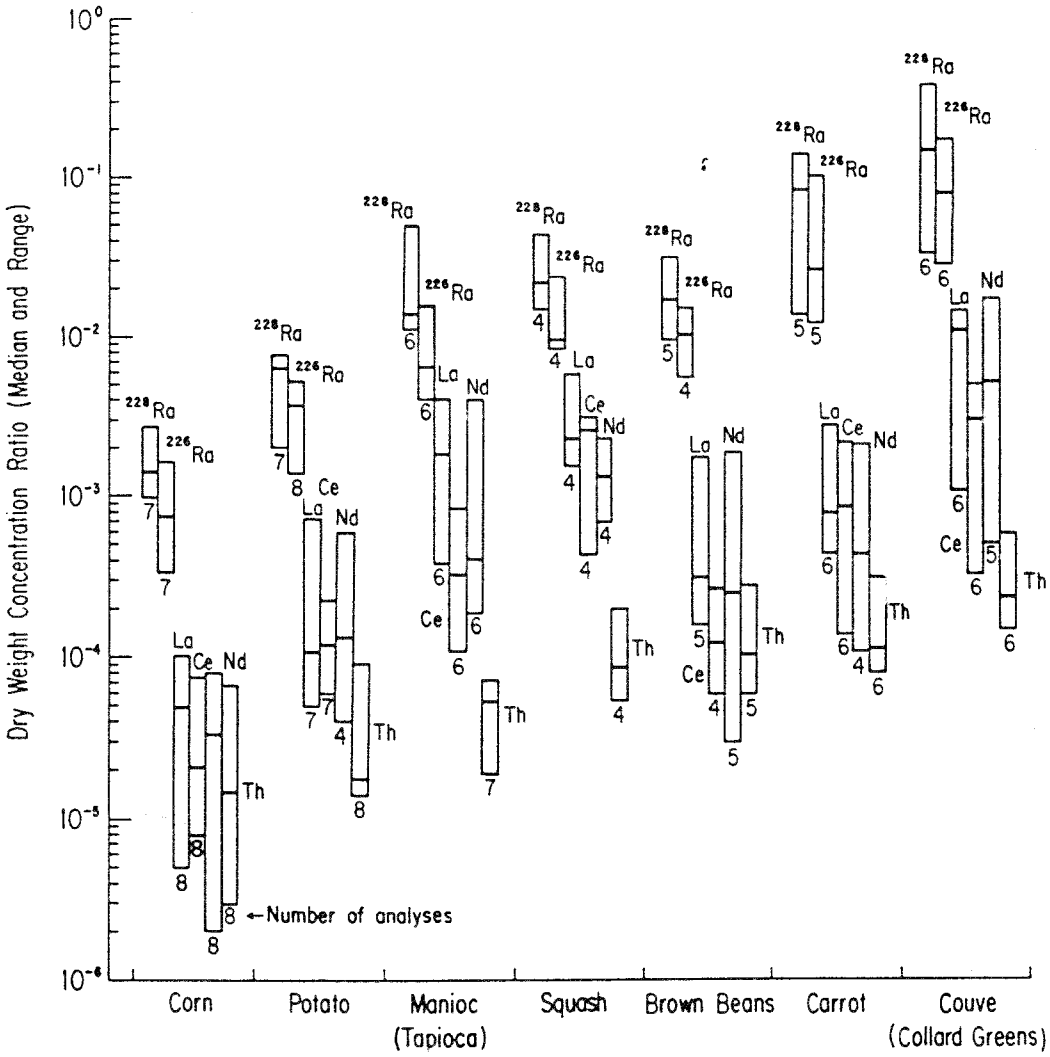
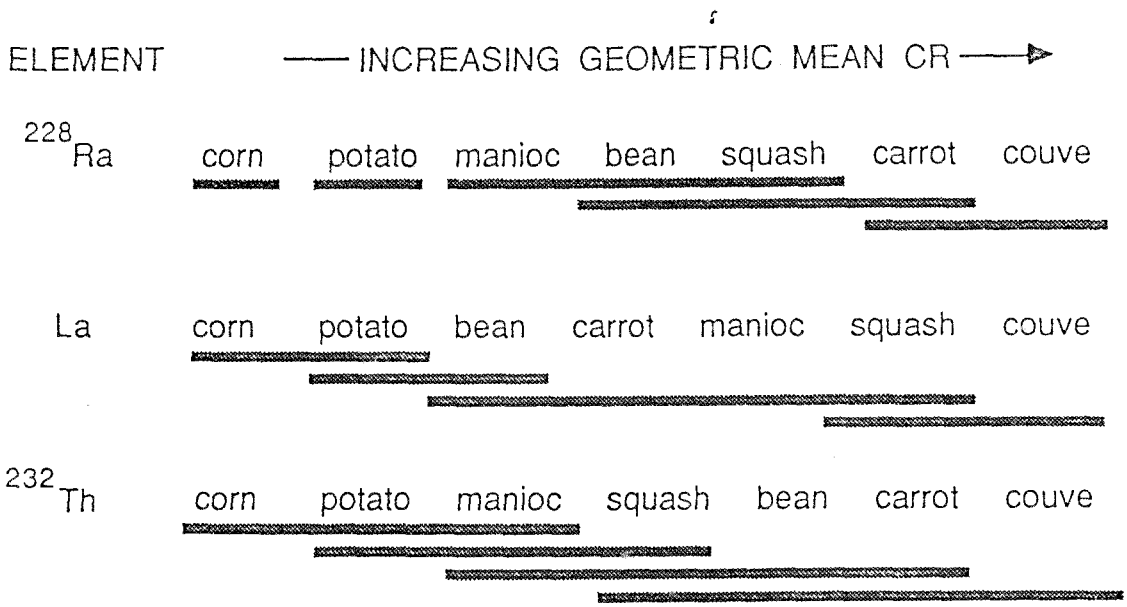


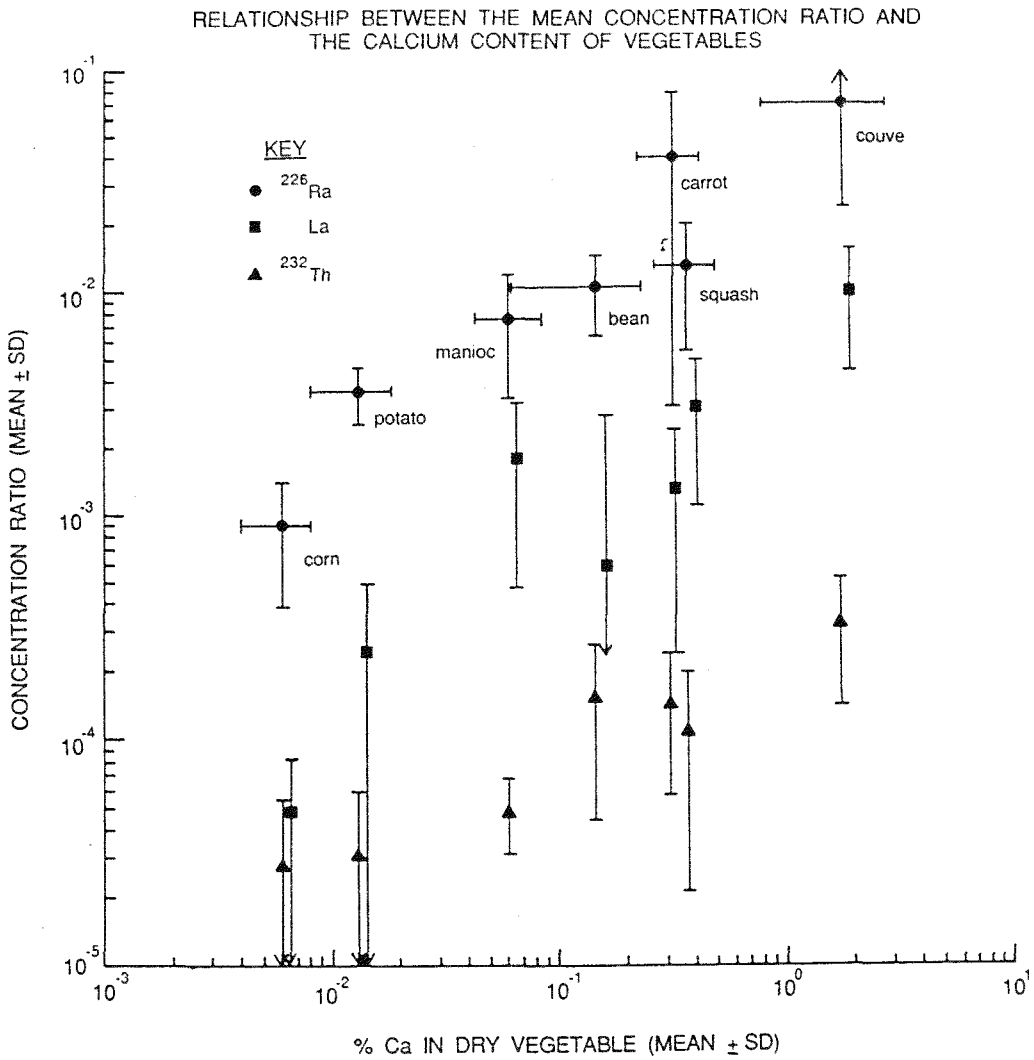
FIGURE 3

MULTIPLE COMPARISONS[1] FOR THE CONCENTRATION RATIO BETWEEN VEGETABLES



[1] Based on results of the Tukey test performed on ln-transformed CR data. Breaks in the line indicate significant differences ($p \leq 0.05$) between means, while continuity of the line indicates no significant differences.

FIGURE 4


RELATIONSHIP BETWEEN THE MEAN CONCENTRATION RATIO AND THE CALCIUM CONTENT OF VEGETABLES
KEY
226Ra
La
232Th
corn
potato
manioc
bean
carrot
squash
couve
CONCENTRATION RATIO (MEAN ± SD)
% Ca IN DRY VEGETABLE (MEAN ± SD)

PART II

Studies of the Transport Pathways of Th, U, Ra and Light Rare Earth Elements from Soil to Farm Animals

Part II: Studies of the Transport Pathways of Th, U, Ra and Light Rare Earth Elements from Soil to Farm Animals

Abstract

Field studies were conducted in areas of elevated, natural radioactivity (the Pocos de Caldas plateau, Minas Gerais, Brazil) and normal background (Orange County, New York) to assess tissue concentrations, soil-to-tissue concentration ratios (CR's), and the comparative bioavailability of isotopic Th, U, Ra and light rare earth elements or REE's (i.e., La, Ce, Nd and Sm) in adult steers, chickens and pigs. The study was undertaken because few field or laboratory data exist on the dietary transfer of these elements to farm animal tissues; and because the elements chosen for study bear many physical, chemical and biological properties which are similar to those of the actinide elements contained in high-level nuclear waste.

Since these elements are biologically nonessential and under most conditions, have characteristically large (soil/water) partition coefficients and low (plant/soil) CR's, it was shown by analysis of the N. Y. bovine diet, that soil ingestion, occuring incident to grazing, purposfully, and, or as surficial contamination on feeds, would, under most conditions, account for the majority of intake considering all possible intake pathways. Exceptions are uranium isotopes and Th-230, which, for the N. Y. cattle, were ingested primarily with a phosphate mineral feed supplement. Because the intakes of most of these elements are dominated by soil ingestion, and because the diets of steers, chickens and pigs raised in the Pocos de Caldas plateau were not precisely known, we have calculated CR's as $\mu g\ kg^{-1}$ (fresh tissue weight)/$\mu g\ kg^{-1}$(dry soil), as opposed to the more routinely used F_f ratio [$F_f = \mu g\ kg^{-1}$ (fresh muscle weight)/$\mu g\ day^{-1}$ (intake rate from feed)]. Tissues analyzed include muscle, bone, liver, kidney and lung in steers (N = 5, N. Y. and N = 3, Pocos), and muscle and bone in chickens (N = 3, Pocos) and pigs (N = 4, Pocos).

The mean CR's for muscle in the Pocos animals were very similar for U, La and Th which, as a group, decreased among the adult farm animals studied as (all x 10^{-4}): chicken (1) ≥ steer (0.7) ≥ pig (0.4). CR's for Ra-226 in muscle decreased in the same

order among these animals although mean values were 3-5 times higher than those quoted. Much higher values and greater differences were generally noted in bone/soil CR's among these elements, with CR's decreasing as: Ra >> U > La ≈ Th. Organ burden data for the N. Y. cattle indicated bone to be the major retention compartment for all analytes, accountable for 68-82% of Th-232 as well as La, for 92-98% of the U isotopes, and for 98-99% of the Ra-226. The remainder of the cattle body burdens were largely attributable to muscle. Analyses of the bovine diet and organ concentrations indicated that body burdens, at time of slaughter (24 months), represented much less than one day's intake equivalent with the exception of Ra-226 (5-10 days) illustrating the large discrimination that exists during transfer from diet to tissue.

Based on comparative (body burden/intake) ratios for the N. Y cattle, and (bone/soil) CR's for the Pocos animals, the order of element (oxidation state) bioavailability decreases among these elements as: Ra(II) >> U(VI) ≥ La(III) = Th(IV) for all animals studied. Although cattle management and diet were very different, the (tissue/soil) CR data for the Pocos range cattle were reasonably similar to those for the largely sheltered, N. Y. herd, with values agreeing to within roughly a factor of two for La, Th-232 and Ra-226 in all tissues in which comparative data were obtained with the exception of muscle, in which CR's for La and Th averaged 4.6 and 3.4 times higher, respectively, in the Pocos animals.

I.Introduction

Part II of this report includes our final measurement results for naturally occurring light rare earth elements (REE's include La, Ce, Nd and Sm), U-series and Th-series radionuclides in adult farm animal tissues, feeds and soils. Our findings on soil-to-tissue concentration ratios (CR's) and the comparative behavior of these elements in farm animals raised under natural conditions by local farmers are presented. Since uranium was included in the sequential radiochemical procedure initially developed for Th and the REE's in vegetation and later adapted to animal tissues (see Part I), we are able to report comparative data for elements with stable oxidation states of II (Ra), III (La, Ce, Nd and Sm), IV (Th) and VI (U). This work was undertaken primarily because few data exist documenting the concentrations or CR's of these naturally occurring elements in edible farm animal tissues (Ng, 1982a and 1982b), and secondarily, to obtain by analogy, information which may be useful for predicting steady-state tissue concentrations of certain transuranic elements such as Pu, Am and Cm.

Briefly, one aspect of the field study involved the sampling of soils and adult chickens, pigs and steers raised on three farms (Nos. 1, 2 and 10, Fig. 1) in an area of elevated natural background radiation known as the Pocos de Caldas plateau (State of Minas Gerais, Brazil). Although farms 1 and 2 are within watershed of the Th-REE ore body known as the Morro do Ferro (MF), previous results have indicated that soil concentrations of Th and the REE's on these farms are not different than elsewhere on the plateau (NYUMC, 1984, Linsalata et al, 1986, Linsalata et al, 1987). Surface water samples from a stream on farm 1 that is used for irrigation and drinking water purposes and which also receives runoff from the Morro do Ferro, were previously shown not to be notably elevated in Th, U, REE or Ra concentrations with respect to other surface waters in the plateau (Lei, 1984, Eisenbud et al, 1984, Lei et al, 1986, and Campos et al, 1986).

Samples of chicken (12 individuals per sample), pig and steer tissues (muscle, trabecular and cortical bone, and some internal organs from pigs and steers) were obtained from each of the three farms. With the exception of pasture grasses and water sampled from farm 1, other dietary components were not analyzed. Grasses comprize

a major dietary component for all animals sampled in Brazil.

Tissues of adult, Black Angus beef cattle (three steers and one heifer) were also obtained from a farm in Orange County, New York. (As part of developmental work, tissues were also obtained from a Black Angus steer raised in Vermont.) The New York farm produced "natural beef" and as such, all dietary components with the exception of a mineral feed supplement (eg., corn silage, dry cobs, alfalfa hay and pasture grasses) were grown on the premises. This enabled the characterization of Th, U, Ra and REE intakes via feeds as well as via soil ingestion assuming specific consumption rates. The tissues analyzed were muscle, liver, lungs, kidneys, trabecular and cortical bone.

General discriptions of the field study areas in Pocos de Caldas, Brazil, and in New York have been given in Part I of this report and in earlier Progress Reports (NYUMC, 1984, 1985 and 1986). For the farm animal studies, it was not practical to maintain the sampled individuals apart from the remainder of the farmers' livestock. As such, individuals ready for slaughter were selected following consultation with the owners to insure the animals health and to obtain information regarding management practices, age, breed and diet. This was facilitated by the small number of livestock maintained by the farmers in Pocos in New York (125-150 head).

Because of time and resource restrictions, not all of the tissues which were collected could be analyzed for all of the elements of interest. In particular, we have limited our measurements to muscle and bone for both the chicken (N=3) and the pig (N=4) samples obtained from farms in the Pocos de Caldas plateau. These tissues were selected since they represent either the major locus for deposition and retention of these elements (bone) or because they are the most relevant with respect to the eventual consumption by man (muscle). For steers sampled in Pocos (N=3), we have included measurement results for muscle and bone (both cortical and trabecular) for all elements, and for liver, lungs, and, or kidneys from some of the animals (all elements except Ra). For beef cattle obtained in the United States, the analyses are more complete in that they include muscle (N=3), bone (N=16), liver (N=5), lungs (N=5) and kidneys (N=4) for all elements except radium. Radium-226,228 data is limited to bone (N=5) with a few measurements obtained for liver (N=2), lungs (N=2) and muscle (N=1).

A. Research Objectives and Rationale

Our primary objectives were to measure the elemental and isotopic concentrations in tissues of cattle, pigs and chickens at time of slaughter resulting from chronic intake, and to begin to access the magnitude and variability of (tissue/soil) concentration ratios (CR's) for naturally occurring Ra-226,228, Th-232,230,228, U-238,234, and the REE's. These elements and isotopes were selected because of the scarcity of data concerning both transfer parameter values and the relative importance of various pathways leading to farm animal exposure (see for example, Garten, 1978, Bondietti et al, 1979, Ng, 1982a, Ng, 1982b, Trabalka and Garten, 1983, Zach and Mayoh, 1984). The environmental chemistries of the elements studied are either similar or identical to those of many of the long lived actinide elements present in high level waste discussed previously in Part I. Because the elements studied are primordial and presumably in equilibrium both geochemically and with biological components, they may serve as models or analogues for investigating some of the processes by which farm animals, through their ultimate dependence on soils, acquire these elements.

The Pocos de Caldas region was studied since soils here contain the elements of interest at levels that range from about 3-15 times those of average U. S. soils thus increasing the likelihood of detection in farm animal tissues. The field program in New York was added later in the study to allow comparisons of CR's to be made among very different cattle management practices and because intake pathway analysis could be reasonably addressed.

In traditional dose assessment equations which assume a steady-state between element intake rate and tissue concentration (NRC, 1977 and Ng, 1982a), the tissue fresh weight concentration data (meat, milk and,or eggs) for the element or radionuclide of interest is devided by an estimate of the animals' intake rate (element concentration in feed x daily ingestion of feed) to obtain a transfer coefficient in units of day kg^{-1} (termed F_f for transfer to meat as an example). These factors have been collated for various radionuclides and animal products of interest (Ng, 1982a). For dose assessment, the F_f values are multiplied by appropriate average feed consumption rates and predicted concentrations in feeds to arrive at predicted

concentrations in animal products. Dose to man is then estimated by multiplying the predicted animal product concentrations by usage factors (average human intake rate of the product) and ingestion dose rate conversion factors for the specific radionuclide and human age groups of interest (NRC, 1977).

Animal management practices in Pocos involved neither confinement of pigs, chickens and cattle nor strict feeding regimes. Cattle subsist almost exclusively on pasture and their diets are supplemented with coarse marine salt. Chickens and pigs subsist mainly on grasses but also consume unknown proportions of corn and household organic refuse. Since only one sample of pasture grass was obtained (farm 1, analyzed for Th and REE's only) we have no reliable way of estimating F_f values for the animals raised in Pocos.

As an alternative, we have calculated the ratios of the element concentrations in animal tissue (fresh weight) to concentrations in soil (dry weight). Although (tissue/soil) CR's are not routinely used, there are several reasons supporting its usage. Of primary importance is the fact that this CR is independent of the route of exposure (i.e, ingestion or inhalation intake) and should be reliable as long as the magnitude of the intakes and resulting tissue concentrations exhibit a linear dependency with soil concentrations. In other words, it should not matter whether or not the intakes are derived primarily from the inhalation of resuspended soil, or the ingestion of soil-grown feeds, soil-contaminated feeds or the direct ingestion of soil, as long they are related linearly to the concentrations within the soil substrate. When the intakes are derived primarily from non-soil related products, such as water or mineral feed supplements, as has been shown for uranium in cattle (Chapman and Hammons, 1963 and Reid et al, 1977), then the CR as used in the present context is irrelevant. The (tissue/soil) CR takes on added significance if and when the inhalation of radionuclides by farm animals contributes in a substantial way (relative to ingestion intake) to the resulting concentrations in animal products as has recently been reported by Zach (1985) for certain actinide elements.

Secondly, soil ingestion by cattle, swine and poultry among other farm animals, apparently occurs both intentionally and incidentally to feed and forage consumption.

For dairy cattle on pasture and receiving no other feeds, estimates range from 4 to 8% of the mass of dry matter intake (Healy, 1968) with lower values occuring during good pasture conditions and higher values during periods of sparse growth. Values of 1 to 2% of dry matter intake have been reported for dairy cattle on pasture which also receive supplemental feed (Fries et al, 1982a). A commonly used value for cattle for dose assessment is 0.5 kg d^{-1} $animal^{-1}$ (Whicker and Kirchner, 1987) which corresponds to 4% of dry matter intake at a typical ingestion rate of 50 kg wet feed d^{-1} (NRC, 1977 - assuming a 25% dry/fresh weight ratio). Whicker and Kirchner give a value for poultry of 0.01 kg d^{-1}. Assuming standard body weights of 2 and 450 kg for poultry and cattle respectively, soil ingestion would appear to be five times greater per kg body weight for the chicken relative to the cow. For swine, Fries et al (1982b) estimate soil ingestion at between 3 and 8% of dry matter intake when on pasture which they cite as being notably higher than their values for cattle.

In their analysis of the relative importance of radionuclide intake by cattle via soil and feeds, Zach and Mayoh (1984) conclude that assuming 0.5 kg soil d^{-1} and 12.5 kg dry feed d^{-1} are ingested (4% of dry matter intake), radionuclide intake via soil ingestion will be greater than that intake occurring via feeds when the (vegetation (dry)/soil) CR for the element of interest is below about 0.04. Whether or not the radionuclide intakes associated with soils and feeds are equally available for absorption is an unresolved question. There are data that indicate enhanced Pu absorption in mammals (by about a factor of six) following its incorporation into plant tissue (via root uptake from soil) which is then fed to the animal, relative to gavaging the same Pu compound which was initially added to soil (Wildung et al, 1979). There are also data which indicate considerable, though highly variable solubility in *in-vitro* simulated bovine fluid of what must be considered refractory Pu originating from Nevada Test Site soils (Barth, 1977). This point may be moot for some of the elements studied such as Th and the REE's since the concentrations in unwashed forage and feeds are largely a result of surficial soil contamination. In a study of the ingestion of Am and Pu in range cattle in a contaminated desert environment, Blincoe et al (1981) assigned virtually all of the ingested Pu and Am to soil ingestion incident to grazing. From our analyses of various feeds and soils from the New York farm, we will show

later in this report that for cattle, soil ingestion is probably the predominant intake pathway for several of the elements and radionuclides studied even at soil consumption rates much below 0.5 kg d^{-1}.

Clearly, the importance of the soil ingestion pathway will depend on both the amount of soil consumed and the availability of the element of interest for absorption. Based on the previous discussion and that given in Zach and Mayoh, soil intake by cattle can be quite variable, both among individuals of a herd for which management and feeding practices are the same, and expectedly more so between animals reared under different management practices. Variablity results from vegetation density and species compostion on pasture, the percentage of time the cattle are on pasture, whether or not other feeds are given, type or presence of the bedding provided in shelters, and the individual animals preference for soil or need for essential minerals contained in soil. These same factors probably influence soil intake for other farm animals as well. Depending on the magnitude of the variability of these factors among animals of the same farm and between farms, the (tissue/soil) CR would be expected to reflect this variation.

II. Methods

A. Field Sampling and Sample Preparation

Soils in Brazil were collected by auger to a depth of 15 cm in pastures from each of the three farms. At least 10 widely spaced aliquots were taken per pasture and homogenized. Soils were air dryed and sieved to remove particles and debris greater than 2 mm in diameter. In New York, the surface 5 cm were sampled from two pastures using a trowl after removing the grass mat. Ten aliquots were taken per pasture, composited, homogenized, dryed and sieved to remove debris greater than 1.4 mm in diameter. Physical and chemical characteristics were determined for all soil samples using standard methods in Brazil (Emprapa, 1981).

Samples of baled alfalfa (second and third cuttings), ground corn cobs, fresh cut corn silage, pasture grass, and a mineral feed supplement (Agway Fortamin Mineral Mix) were collected and analyzed from the New York farm. With the exception of alfalfa, the feeds collected were done so at a single point in time. With the exception of pasture

grass (hand clipped to about 2-3 cm above the soil) all samples were analyzed (after oven drying at 95° C and homogenizing) without any attempts to remove particulate matter. The grass sample was split and analyzed both before and after extensive washing by hand. One sample of pasture grass was obtained from farm 1 in Pocos and analyzed without any prior cleaning. Because the feeds were unwashed, they were analyzed repetitively (2-4 times) following homogenization to insure reproducable results.

Following animal selection, local butchers were used for slaughter and to obtain the requested organs. Whole liver, lungs and kidneys were obtained and used for analysis from steers and pigs. On occasion, 10 to 15% of the organ ash weight was removed for radium analyses with the remainder used for the sequential determinations of Th, U and the REE's. All organs and tissues were weighed fresh (including residual blood), oven dryed, and ashed in a muffle furnace at 450-600 °C. For the New York cattle, entire forequarters were obtained with meat seperated from bone. For steers and pigs, the bone samples obtained (thoracic and cervical vertebrae, ribs, femur, and, or humerus, ulna and radius) were further hand cleaned in the laboratory to remove residual soft and connective tissues but were not defatted. Between 10 and 20 kg fresh weight of chicken, pork and beef were prepared for analysis although smaller aliquots were used in the actual determinations (4-8 kg). The chicken mass was obtained by compositing meat from 12 adult individuals per farm. Seperation of meat and bone from chickens was facilitated by low temperature heating. The entire skeletons from the 12 birds were composited for analysis.

Some physical and anatomical characteristics of the Black Angus cattle from the New York farm are given in Table 1, and for steers, male pigs and chickens obtained in Brazil (all mixed breeds), in Tables 2, 3 and 4, respectively. Muscle and skeletal masses for steers and the single heifer were calculated as 40% and 10% of whole body weight, respectively (Comar, 1966). For pigs, the corresponding percentages used were 45% and 8% for muscle and skeleton, respectively (Annekov et al, 1973 and Comar, 1966). Although all of the bone samples which were analyzed are listed in these tables, the single mass value given represents the entire skeleton. With the exception of chickens, for which an aliquot of the entire skeleton was analyzed, all

bones identified simply as trabecular (cancellous bone) refer to rib composites, and those identified as cortical, to a composite of long bones including humerus, ulna, radius and femur unless otherwise specified.

B. Analytical

The radiochemical procedures, quality assurance and quality control results, and associated detection limits for the determinations of Ra-226,228, U-238,235,234, Th-232,230,228 and the REE's including La, Ce, Nd and Sm in soils and biota have been given in Part I of this report, and in earlier Progress Reports (NYUMC 1984, 1985, 1986) and publications (Linsalata et al, 1985, Linsalata et al, 1987a and Linsalata et al, 1987b).

All analyte concentrations exceeded detection limits for the sample masses used in all samples analyzed from Pocos de Caldas. The occasional exception was for Th-232 and Th-230 in bone and resulted from spectral interference from Th-228. As was noted previously in Part I of this report for vegetables, the much greater biological availability of radium isotopes (relative to thorium isotopes) results in considerable ingrowth of Th-228 from Ra-228 decay during the animals lifetime and up to the point of chemical seperation of Th from Ra. As expected based on the relative ages of the animals at sacrifice (and delay times prior to analysis), the problem was most evident in steer bones from Pocos. For cattle tissues obtained in New York, the major analytical difficulties occurred with the REE's and Ra-228 due to low concentrations coupled with relatively high detection limits. Although all results for those analytes measured are presented, we place more reliability in La concentration estimates in tissues (relative to other REE's) due to superior detection limits. Most of the tissues obtained in New York were not analyzed for radium isotopes because of the need to utilize entire organ masses for the sequential determinations of Th, U and the REE's. Since Ra-226 detection limits are superior to those for Ra-228 (Table 1, Part I) resulting in concentration estimates of relatively higher precision, we place more confidence in the Ra-226 data for the N. Y. samples and interpret our results accordingly.

All concentrations have been reported (± 1SD) using S. I. units on a tissue fresh weight basis with dry weight concentrations given for soils and feeds. All errors arising from counting samples, detector backgrounds, reagent blanks, tracers, etc. were

propagated to arrive at the final uncertainty. The (tissue/soil) CR's were calculated from individual measurements obtained from the various samples collected at each farm.

III. Results and Discussion

A. Soils

The pedological characteristics of the Pocos de Caldas soils have been given in Table 3 (Part I) of this report and in NYUMC (1986) for the New York soils. To briefly summarize those findings, soils from farms 1, 2 and 10 in Pocos are very similar with respect to particle size distribution (69-79% clay) and many of the chemical parameters given in Table 3 (Part I). Soils from these farms (ranges given) and throughout the plateau are potassic and classified as dystrophic cambisols and red-yellow dystrophic latosols. They are also lateritic exhibiting acidic pH (5-6), low SiO_2/Al_2O_3 ratios (0.5-1.0), relatively high amounts of exchangeable Al^{+3} (0.5-1.9) and H^+ (6.6-8.0) (in units of meq/100 g), and low cation exchange capacities (11-13 meq/100 g) and saturated base percentages (19-42%). In contrast, soils from the New York farm are shaley silt loams (22% clay and 51% silt) of slightly higher pH and cation exchange capacity (relative to Pocos soils) but exhibit no measurable exchangeable Al^{+3}, half the amount of exchangeable H^+, and more than a two fold higher saturated base percentage than Pocos de Caldas soils.

Activity and mass concentrations of the isotopes and elements of interest are given in Tables 5 and 6 for the New York soils and Tables 7 and 8 for the Pocos de Caldas soils. Measurements were obtained in duplicate for the two pastures sampled on the New York farm with single analyses performed on each of the three pasture samples from the three farms in Pocos. As expected, results were nearly identical for the two pastures sampled in New York with average mass concentrations ($\mu g\ g^{-1}$) decreasing as Ce (68.7) > La (32.6) ≥ Nd (28.8) > Th (9.3) > Sm (6.8) > U (3.1) (Table 6). Thorium and uranium concentrations are similar to averages given for U. S. soils (9 and 1.8 ppm, respectively, Lowder et al, 1964). Whethering of underlying shales may be responsible for the apparently higher U content of these soils than on the average. Radionuclides within the thorium and uranium series are in approximate equilibrium at

least up to and including Ra-228 and Ra-226, respectively (Table 5).

Mass concentrations of uranium and the REE's display considerable variablity (factors of 2-3) among the three farm soils sampled in Pocos de Caldas (Table 8). It is precisely for this reason and the fact that the range cattle obtained were reported to graze within farm boundaries, that we have chosen to use individual soil sample concentrations in the calculation of (tissue/soil) CR's than either averages of these samples or averages based on the more extensive soil sampling program discussed in Part I of this report. As we have observed previously (Table 4, Part I), thorium is least variable ranging from 52-62 $\mu g\ g^{-1}$ and on the average, is six times greater than in the N. Y. farm soils. Mass concentrations of Th, U and the REE's decrease in the same order as that given above for the N. Y. soils. Although uranium isotopes were only measured in farm 1 soil, we have used the average of the Th-230 (alpha spectrometry) and Ra-226 (GeLi spectrometry) activity concentrations in the remaining two samples to estimate the U-238 concentrations assuming secular equilibrium. Uranium ranges from 8 to 18 $\mu g\ g^{-1}$ and is thus 2.5 to five times greater than in the N. Y. farm soil.

B. Cattle Feeds

As previously shown in vegetables, concentrations of Th and the REE's decrease in unwashed samples of ground corn cobs, silage, alfalfa and pasture grass as: Ce > La ≥ Nd > Sm ≥ Th (Table 9) reflecting soil abundances on the N. Y. farm. Including uranium in alfalfa and grass (the only samples analyzed for U), would place it after Th in the above sequence. Based on the relatively large contributions (i.e., 30 to 50% for Th and 10 to 30% for the REE's) to the total plant concentrations which we have previously observed in filtered particulate residue portions of acid-digested feed samples which were spiked and analyzed seperately from the acid-soluble fractions (NYUMC, 1985), it was apparent that acid-insoluble silicates, present on plant surfaces, make significant contributions to the whole-plant concentrations for these elements. This is supported by the fact that Th-228/Th-232 ratios in the insoluble particulate residues were approximately unity as they are in soils. Activity ratios obtained in the acid-soluble plant filtrates were always in excess of 1.0 resulting from Th-228 ingrowth from Ra-228 decay. As an example, using the Th-232 soil data of Table 6, the percentages of soil weight/sample dry weight needed to contribute 100%

of the Th-232 activity in each sample are only 0.1%, 0.4% and 0.1% for corn cobs, alfalfa (third cut) and corn silage, respectively. These percentages are certainly not unreasonable based on data reported in Zach and Mayoh (1984) for percentages of soil in dry feed ingested by heifers and dry cows which are not on pasture (range of 0.5 to 4%).

With the exception of Ra-226 in grass (CR = 0.05), all of the (dry feed/dry soil) CR's are below 0.02 (Table 10) and notably similar among the different elements analyzed in a given sample. As might be expected based on the CR's given for corn kernels in Part I and the fact that the cob is shielded from direct soil contamination during growth, ground corn cobs which are fed to the cattle (for fattening), display the lowest CR's among the feed types analyzed (from 4×10^{-4} to 12×10^{-4} for Th and REE's), and pasture grass the highest. The two to three fold differences in CR's for Th and the REE's between the second and third cutting of alfalfa is probably a result of differences in soil contamination on the leaf surfaces. Clearly, soil contaminaton serves to occlude any differences that may exist in the uptake of these elements by plant roots and contributes substantially to the variability reported in CR's determined by field studies. The CR's for Th and REE's in washed pasture grass were two to three times less than in unwashed grass (Table 10). Based on these differences we estimate that about 500 mg of soil was present on the unwashed sample aliquot representing 0.36% of the dry weight sample mass.

A mineral feed supplement (Agway Fortamin mineral mix for livestock on silage diets) which the N. Y. cattle are allowed to consume *ad libidum* after weaning (manufacturer recommends ≤ 50 g d^{-1} based on Se content while in practice, 100 to 150 g d^{-1} is more typically consumed, L. Chase, Cornell University, personal communication) was assayed and found to contain significant quantities of isotopic Th and U and considerably less REE's (Table 9). With the exception of Ra-226 (22 mBq g^{-1}), uranium series nuclides are particularly enriched (U-238 $\approx$ U-234 = 721 mBq g^{-1} and Th-230 = 516 mBq g^{-1}). This type of disequilibrium in the uranium series has been observed previously by Reid et al (1977) and found to occur when the phosphate in the mix is derived from a wet chemical method in which radium is removed during the

precipitation of $CaSO_4$. Rare earths, Ra-226, Th-232, Th-230 and U-238 are present in the mix at 0.05, 0.54, 0.6, 12 and 19 times their respective soil concentrations.

Unwashed pasture grass from farm 1 in Pocos had fresh weight concentrations (in $\mu g\ kg^{-1}$) of 3481, 883, 536, 239 and 49 for Ce, La, Nd, Th and Sm (relative uncertainties from 10-30% at ±1SD) and a Th-230/Th-232 activity ratio of 0.5 (ratio in soil = 0.34). (Fresh weight concentrations are given because of unresolved discrepancies in dry/fresh and ash/dry weight ratios.) Converting the pasture grass concentrations given for the N. Y. farm (Table 9) to fresh weights, the ratios of the P.C./N.Y. concentrations in grass are 9.6, 4.4, 3.3, 6.8 and 1.2 for Ce, La, Nd, Th and Sm, respectively. The corresponding ratios in soils from these two farms are 7.2, 3.5, 1.5, 6.1 and 1.2, respectively, indicating perhaps fortuitously (since there is no reason to expect that the soil load would be equivalent), agreement in CR's between these locations to well within a factor of two with the exception of Nd.

C. Apportionment of intakes for beef cattle

Based upon an annualized diet for the N. Y. cattle consisting of daily intakes of 12 kg feed (dry matter with 30% silage, 30% alfalfa, 30% pasture grass and 10% cobs), 0.1 kg mineral supplement, 50 l water and variable amounts of soil (0.1-0.5 kg dry), estimates of the daily consumption of Th-232, U-238, La and Ce (in $mg\ d^{-1}$), and Th-230 and Ra-226 ($Bq\ d^{-1}$) are derived (Table 11). Intakes derived from the direct ingestion of soil (as opposed to soil contained on vegetative surfaces which is considered part of feed intake in Table 11) are shown to be predominant for Th-232 (43%-79% assuming 0.1 or 0.5 kg soil d^{-1}) and the REE's (about 45%-85%). Ingestion of the mineral supplement is the predominant route of intake for uranium isotopes (77%-92% for U-238) and for Th-230 (68%-89%). The intake of Ra-226 is probably mainly derived from dry feeds (37%-67%) with slightly smaller percentages attributed to soil ingestion (21%-57%). Because the animals consume the mineral supplement at their own discretion, we might expect that the actual intake estimates for Th-230 and uranium isotopes would exhibit considerably more variability than is indicated by the quite narrow range of values given in Table 11. At present, we have no way of estimating what this variability may be. Because of the predominance of soil in the

intake estimates for Th-232, REE's, and to a lesser extent, Ra-226, minor variations in the dry feed composition and consumption rates from those assumed will not greatly alter the intake estimates for these elements and nuclides.

Intakes via surface water consumption are estimated to be negligible for all of the above elements and nuclides albiet via indirect analyses of what may be considered similar water (fresh Hudson River water for thorium and radium isotopes, Li et al, 1978 and Linsalata, unpublished data, and New York City tap water for uranium (derived from tributaries of the Hudson and Delaware Rivers, Welford and Baird, 1967).

Order of magnitude estimates of inhalation intake given in Table 11 are calculated using a standard breathing rate of 130 m^3 d^{-1} (Comar, 1966) and assuming a particulate load in the vicinity of the nostrils of 200 μg m^3. Additional assumptions required for the calculation are the elemental concentrations of the respired particulates (assumed equal to those given for surface soils) and the fraction of the respired mass which is retained in the lung (100% assumed for conservatism). Based on these assumptions we estimate that the ratios of the daily intakes (inhalation/ingestion) are on the order of 10^{-5} to 10^{-4} for all of the analytes measured. While these results indicate that there can be no significant increase in G. I. intake resulting from mucocilliary clearance and swallowing, they provide only the first step for determining the relative importance of ingestion and inhalation vis a' vis systemic uptake. If the fractional absorption values (termed f_1 in ICRP, 1979) for Th, the REE's, U and Ra from the G. I. tract to blood are similar in the ruminant and man (f_1 values given for man are 2×10^{-4} for Th, 3×10^{-4} for the REE's, 0.05 for soluble U, and 0.002 for relatively insoluble U compounds, and 0.2 for Ra, ICRP, 1979), there is no question that ingestion would account for virtually all of the U and Ra which becomes systemic. Gut absorption for natural U has previously been estimated at about 5×10^{-3} for heifers (Chapman and Hammons, 1963) which falls at the lower end of the range of f_1 values (0.005-0.05) for man fed uranyl nitrate (Hursh et al, 1969). Whether or not U (VI) is reduced to U (IV) within the ruminant gut consequently lowering its' absorption, is unknown. Even with the very conservative assumptions that have been used here with respect to inhalation intake, if we further conservatively assume that 50% of the inhaled

Th and REE's becomes systemic, then at most, 25% of the systemic burdens could be derived from inhalation (given an f_1 of 10^{-4} for both Th and the REE's in the ruminant and the intake estimates of Table 11).

D. Concentrations, tissue distributions, and (tissue/soil) CR's in U. S. beef cattle

Among all tissues and organs analyzed from the N. Y. cattle, fresh weight analyte concentrations (mBq kg^{-1}) were both lowest and most consistent in muscle (N = 3) ranging from 0.56 to 0.67 (Th-232), 0.36 to 2.41 (Th-230), 0.52 to 1.33 (U-238), 0.59 to 1.63 (U-234) and 0.39 to 0.53 μg kg^{-1} for La (Tables 12 and 13). Mean (±1SD) concentrations (mBq kg^{-1} fresh weight except for La which is in μg kg^{-1}) for these elements in different tissues of the N. Y. cattle (animal nos. 2, 3, 4 and 5) decrease as follows:

Th-232: bone (11.8±4.8) ≥ lungs (4.2±3.6) ≈ kidneys (3.1±0.5) ≈ liver (1.7±0.9) > muscle (0.60±0.06);

Th-230: bone (95±61) ≥ kidneys (65±56) ≥ liver (38±38) ≥ lungs (16±6) > muscle (1.3±1.0);

U-238: bone (192±121) ≥ kidneys (58±30) > lungs (6.1±0.8) ≈ liver (4.1±0.4) > muscle (0.9±0.4);

U-234: bone (204±133) ≥ kidneys (61±29) > lungs (6.1±0.8) ≈ liver (4.4±0.4) > muscle (1.0±0.6);

Ra-226: bone (3,597±893) >> muscle (15±2) ≈ lungs (12±8) ≈ liver (9±1);

La: bone (7.8±3.0) ≥ lungs (3.6±1.7) ≈ liver (3.0±1.9) ≈ kidneys (2.1±1.0) > muscle (0.5±0.1).

The means and standard deviations given above are based on four samples for each tissue type with the exceptions of all analytes in muscle (3), uranium in lungs (2) and liver (1), and Ra-226 in lungs (2), liver (2), bone (3) and muscle (1). Since U-234/U-238 ratios are very close to unity in soils, feeds and tissues, we limit any further discussion of uranium isotopes to the U-238 parent. Given the nature of the study, the concentration data appear to be reasonably consistant showing considerably less variability than has been observed in other field studies involving organ distributions of both Pu and U in range cattle grazing over contaminated soils

(Smith, 1977). Tissue concentrations (and calculated body burdens- Table 14) of Th-230 exhibit the greatest variability, perhaps resulting in part, from different intake rates of the mineral supplement. Supportive of this statement is the fact that for both Th-230 and U, coefficients of variation for bone are equivalent (64%) and greatly exceed those of the other analytes (i.e., 41% for Th-232, 38% for La, 25% for Ra-226).

The order of tissue concentrations given above for the various analytes is not unexpected except perhaps for the relatively high mean Th-230 concentration in kidneys (relative to bone and liver). Relative to other tissues, the higher concentrations of uranium isotopes in bone followed by kidneys are expected based on the known metabolism of this element in mammals (Yuile, 1973). For all of these elements in mammalian systems, bone represents the major biological compartment for long term retention and storage (Durbin, 1962, Yuile, 1973, Maletskos et al, 1969, ICRP, 1972).

With respect to bone, samples of both trabecular (13 rib composite and all cervical vertebrae) and cortical bone (composite of humerus, ulna and radius) were analyzed seperately from steer 3 (in triplicate for Th and REE's and once for other elements) to determine if concentration differences exist among these bone types. For Th-230, which provides the most precise measurements for thorium isotopes due to elevated concentrations resulting from ingestion of the mineral supplement, mean concentrations (from Table 12) decreased in steer 3 as: vertebrae (138±13) > ribs (106±12) ≥ humerus, ulna, radius (80±22). The order of decreasing concentrations remains the same on an ash weight basis and when the ash weight concentrations are normalized to the bone Ca concentrations (mean Ca concentrations are 0.37±0.01, 0.39±0.02 and 0.38±0.01 g Ca g^{-1} ash, respectively). The higher concentrations of Th-230 in those bones with relatively greater surface/volume ratios conforms with the expected prevalence for Th deposition within cancellous bone (Stover, 1960 and Thomas, 1961). Data for isotopes of U, Ra, for Th-232 and for La (Tables 12 and 13) did not indicate any substantial differences in concentrations among the bones analyzed from steer 3. Because of this and since Th-230 concentrations were intermediate in ribs, only rib composites were analyzed in the remaining two N. Y. cattle.

For any given element, the relative differences in tissue mean concentrations are

most pronounced for Ra-226 in bone when compared with the various soft tissues analyzed. This is a direct consequence of the similar metabolic fates shared by Ra and Ca, specifically the ability of Ra to substitute for Ca in hydroxyapatite crystals of mineral bone. With the possible exception of Ra-226, mean concentrations of all other analytes in muscle are notably less than their respective means in other soft tissues analyzed.

Considering the tissue burdens calculated in Table 14 and given as percentages of the animals' estimated total burden in Table 15 (for animals 3, 4 and 5 assuming the tissues analyzed reflect the major storage compartments), the relative importance of muscle as a storage compartment declines (ranges given as % of total in muscle) among these elements and isotopes as: Th-232 (14.7-29.5) ≈ La (13.5-27.0) > Th-230 (4.7-7.7) ≥ U-238 (0.9-4.5) ≥ Ra-226 (1.3-1.7). The order for bone is reversed with fractional inventories (Table 15) declining as: Ra-226 (98.3-98.7) ≥ U-238 (91.6-98.3) ≥ Th-230 (86.1-92.5) ≥ Th-232 (67.8-81.5) ≈ La (65.5-81.7). Similarities in the relative distributions of Th-232 and La among cattle tissues are both striking and unexpected at least when based on organ distribution patterns observed in the rat at four days after injection (Durbin, 1962). Comparative mammalian data obtained under equilibrium conditions (i.e., at long times after the onset of chronic intake) are generally not available. Dissimilarities in organ distribution patterns between Th-230 and Th-232 are equally striking. In early studies on the metabolism and toxicity of thorium in dogs, it was shown that by greatly increasing the mass quantities of Th injected (by about 10^4), distribution patterns changed such that increases were noted in soft tissue deposition (only data for internal organs are given, not muscle) with corresponding decreases in skeletal deposition (Stover, 1960). Based on the differences in specific activities and estimated ingestion rates between Th-230 and Th-232, we estimate a mass ratio (on intake) of 5×10^4 for Th-232/Th-230. The differences noted in steer tissue distributions (Table 15) do not indicate higher percentages of Th-232 in internal organs when compared to Th-230 but they do so in muscle.

Although the relative distributions of Th-230 and Th-232 in steer tissues are shown to be different, there does not appear to be any obvious difference in the availability of these isotopes to the steer via the diet. We base this conclusion on the

finding that the Th-230/Th-232 activity ratio in the representative diet assumed (~7 from Table 11) is reflected in the ratios obtained from the body burden estimates (Table 14). The body burden ratios for three animals are 2.7, 5.8 and 8.2 (mean = 5.6). The relatively large range observed may simply be due to the individual animals preference for the mineral supplement.

Although the organ burden data are only complete for three animals (Table 14), the range of calculated body burdens are within a factor of two for Th-232 (0.38-0.74 Bq), La (0.33-0.52 mg) and Ra-226 (162-208 Bq, N=2), a factor of three for U-238 (3.4-10 Bq), and a factor of six for Th-230 (0.9-5.6 Bq). Based on the daily intake rate estimates (Table 11), these body burdens represent considerably less than one days intake equivalent for all analytes with the exception of Ra-226 (5-10 days intake equivalent). This clearly reflects the large discrimination factors for these elements which must exist in their transport from diet to beef cattle tissues.

Maximum, minimum and mean (fresh tissue/dry soil) CR's are shown in Figure 2 for Ra-226, U-238, La and Th-232. Tissue data from steer 1 (from Vermont) has also been included and the CR's calculated assuming identical soil concentrations to those given for the N. Y. farm. The CR's shown for U-238 cannot be compared with those of the other analytes since U intake is largely derived from a dietary component unrelated to soil as are the intakes of Th-230 and U-234 (not shown). The CR's for La (III) and Th (IV) are nearly identical within each tissue with the possible exception of liver in which the La mean CR is twice that of Th (8×10^{-5} vs. 4×10^{-5}) although considerable variability is shown for both the La (10x) and Th (6x) CR's for liver. Thus for La and Th, the mean CR's (all $\times 10^{-4}$) decrease in the tissues analyzed approximately as: bone (2-3) > lung (1) ≥ kidney (0.6-0.8) ≥ liver (0.4-0.8) > muscle (0.15). The similarity between La and Th CR's among different tissues are indicative of similar environmental and metabolic fates with respect to intake, uptake and retention by beef cattle.

As expected, the CR's for Ra-226 are significantly greater in bone (mean = 0.08) than in soft tissues (mean values range from 2×10^{-4} in liver to about 4×10^{-4} in muscle for one sample, with kidney values intermediate). Based on analyses of the same

samples, the CR's for Ra-226 in soft tissues other than muscle are about 2-4 times greater, and bone about 300 times greater, than those for either Th or La .

E. Concentrations and (tissue/soil) CR's for animals raised in Pocos de Caldas

Isotopic activity concentrations, activity ratios (in tissues and in soil) and mass concentrations (for REE's, Th-232 and U-238) are given in Tables 16-18, 19-21, and 22-24 for tissues from the steer, pig and chicken, respectively. From Table 17 it is apparent that the isotopic ratios (Th-232/Th-230 and Ra-228/Ra-226) in steer tissues from the different farms closely resemble the corresponding ratios in soils. This finding supports the underlying importance of soil in the transfer of these elements to cattle tissues. Daughter/parent ratios of radionuclides originating from within the same series but having very different chemical and biological properties i.e., Th-230/U-234, Ra-226/Th-230 and Ra-228/Th-232, are also given to illustrate the magnitude of disequilibria which exists among tissues and results from a combination of differences in intake rates, absorption percentages and metabolic behavior. These differences are most evident for activity ratios of Ra/Th in bone (1000-4600) and to a considerably lesser extent, in muscle (4-15). Other notable departures from equilibrium, or more precisely, from observed ratios in soil, include Th-230/U-234 ratios in bone (0.14) and kidney (0.06-0.38). Ratios in muscle (0.56-0.79) are very similar to one measured value in soil (0.69). Relative enrichment in uranium series nuclides in tissues from the farm 10 steer is apparent from the data of Table 16. Soils from this farm were highest in uranium and lowest in Th/U series isotopic ratios (Tables 7 and 8).

Among the various steer tissues analyzed regardless of type or location, activity concentrations decreased as: Ra-228 > Ra-226 > U-234 ≈ U-238 > Th-232 ≥ Th-230 with a few exceptions (Table 16). One obvious exception is muscle, in which case Th-232 activity concentrations (7-21 mBq kg^{-1}) are about equal to those of U-238 and U-234 (5-20 mBq kg^{-1}). As previously discussed, the bone data for thorium isotopes are marred by degradation in the alpha spectra caused by the great excess of Th-228 (from Ra-228 which varies from 29 to 69 Bq kg^{-1}, or 0.8 to 1.9 nCi kg^{-1} fresh). For the farm 10 steer in which bone data were obtained, thorium (and uranium) isotopes decrease among the tissues analyzed as: bone (cortical) > kidney > muscle. For the remaining two steers, uranium concentrations in kidneys (30-109 mBq kg^{-1} for U-238)

are equivalent to bone concentrations (28-122 mBq kg^{-1}). Considering the relative magnitude of the counting uncertainties, differences between primarily trabecular (ribs) and cortical bone (femur, ulna and radius) concentrations for both uranium and radium isotopes indicate a slight enrichment in cortical bone (Table 16).

Differences between these bone types are more apparent in the REE data in which for both La and Ce in two of the three steers sampled, concentrations in ribs exceed the long bones by roughly a factor of two (Table 18). No differences are seen however, among bones of the farm 2 steer. With the exception of La in muscle in the farm 1 steer, for any given REE in any given steer, soft tissue concentrations do not differ by more than about a factor of two.

Using the average bone concentration to estimate the skeletal burdens of La and Ce in the farm 1 steer, 50% of the La and 33% of the Ce burdens are in bone, with 40% of the La and 61% of the Ce in muscle. The ratio of the Ce/La body burdens is 4.8 (4.6 mg/0.96 mg), and the ratio in soil from farm 1 is 4.4. For the farm 2 steer, if we first assume that 2.6% of the La and Ce burdens are in liver (based on the N. Y. data for La) which was not analyzed, we estimate 50% of the La and only 16% of the Ce to be in bone, with 44% of the La and 78% of the Ce to be in muscle. The ratio of the Ce/La body burdens minus liver, is 5.2 mg/1.0 mg = 5.2, and the corresponding ratio in soil is 8.3. The percentage of the Pocos steers' La burden in muscle is twice that observed for the N. Y. Black Angus (mean = 22%). Unfortunately, the measurement imprecision for the remainder of the REE's is too great to allow meaningful comparisons to be made. Although the U and Th data in steer tissues from Pocos are incomplete, the available data indicate that, as with Ce and La, relative to the tissue distributions of these elements in the N.Y. cattle, the muscle burden percentages (neglecting those tissues not analyzed) are notably greater (i.e., 11, 38, and 41% for U, and 58% for Th for the farm 10 steer). Factors contributing to these differences may include contamination of the flesh samples during preparation, differences in muscle or skeletal mass/body mass ratios, and, or differences in muscle composition. (The Pocos steers, although closely matched in age with the N. Y. group, were several times smaller. Considering that their diet was derived exclusively from grazing, we would expect relatively less muscle fat. For equivalent intakes, this would result in relatively higher values of fresh

weight beef concentrations in the leaner tissue since fat would simply be acting as a diluent.)

Activity concentration data, primarily for muscle and bone in the pig, indicate as in the steer, a decline in levels as: Ra-228 > Ra-226 > U-234 ≈ U-238 > Th-232 ≥ Th-230 for bone, and as: Ra-228 > Ra-226 ≥ Th-232 > Th-230 ≈ U-234 ≈ U-234 for muscle (Table 19). Radionuclide concentrations (mBq kg^{-1}) in muscle are quite consistant among the animals varying by about a factor of two for Th-232 (4.6-10.2), Th-230 (1.5-4.0), U-234 and U-238 (2.6-3.8) and Ra-228 (93-133), and by a factor of three for Ra-226 (7-21). The muscle data for thorium and uranium isotopes show considerably less variability in pigs than was observed in steer muscle. Isotopic ratio data (Table 20) in tissues are again fairly consistant with those observed in soils with the notable exception of consistantly greater Ra-228/Ra-226 ratios in pig tissues relative to soil. This was not observed in the steer data (Table 17) and may indicate the importation of items in the pig diet having relatively high Ra-228/Ra-226 ratios.

Rare earth data for pig muscle (Table 21) are also shown to vary over a narrow range of 3.7-6.3 μg kg^{-1} for La and 9.2-24.4 for Ce. As is observed in the steer data, REE concentrations in all tissues decline as: Ce > La > Nd > Sm, reflecting soil abundances. Only one of three animals shows an enhancement in REE concentrations in trabecular versus cortical bone (farm 10 pig) while no significant differences are seen among bones from the remaining two animals.

For muscle and bone of the chicken, radionuclide and REE concentrations decrease in exactly the same order as that given above for these tissues in the pig (Tables 22 and 24) although they are notably greater. Isotopic ratios, i.e., Th-232/Th-230 and Ra-228/Ra-226, especially in bone, resemble those observed in the different farm soils (Table 23).

Comparing muscle data from the chicken, steer and the pig (Table 25), mean concentrations for all analytes decrease as: chicken ≥ steer > pig, with the exception of Ra-228 in which pig ≥ steer. For any given analyte, differences in muscle mean concentrations among the animals are within a factor of three except for Ra-226 (chicken muscle concentration is seven times that of the pig). For any given analyte in bone, differences in mean concentrations among the different animals are closer to a

factor of two except for Ra-226 in pig bone (Ra-228 was below detection limits for pig bone) which is 47 times less than that measured in the chicken and 81 times less than that in the steer (Table 25). These findings are most remarkable considering the differences in digestive physiologies, diets, ages, muscle composition (i.e., %fat) and probably the dosage (intake/kg) among these animals. With respect to bone, mean concentrations for all analytes are shown to be lowest in the pig (with the possible exception of Ce).

The (tissue/soil) CR's for Ra-226, U-238, La and Th-232 are shown in Figure 3 for bone and muscle in the chicken, pig and the steer. For the first level of comparison, that among the different elements in the same tissue, we note that the mean CR's for U, La and Th in muscle are within a factor of two of each other for any given animal, with the mean CR's for La and Th being nearly equal in each specie. The mean CR's for uranium in muscle (0.7, 0.23 and 0.65 for the chicken, pig and steer, respectively, all x 10^{-4}) are slightly less than those for La or Th in the chicken (1.2 x 10^{-4}) and the pig (0.37 x 10^{-4}) but are equivalent for the steer (0.59 x 10^{-4}). The Ra-226 mean CR's for muscle are 3 to 4.5 times the average CR's given for U, La and Th among the chicken, pig and the steer.

Relative to muscle, a far greater range in CR's is evident for bone, with mean values (all animals) decreasing in the order: Ra-226 >> U ≥ La ≥ Th. Assuming that soil (and, or locally grown feeds) is the dietary source, and that bone is the major long-term retention compartment for these elements, the relative differences in (bone/soil) CR's can be used to gauge comparative bioavailability among these elements in adult farm animals. The term bioavailable, in this context, incorporates a number of factors including dosage, G. I. absorption, tissue deposition and retention kinetics. Based on the CR's (Fig. 3), Ra is two orders of magnitude more available than U in the chicken and the steer, but only 3-4 times more available than U in the pig.

Among the different animals, the relatively low tissue Ra concentrations, hence relatively low CR's for the pig may be interpreted using data reported in an earlier study on comparative alkaline earth element uptake involving controlled-feeding, serially-sacrificed pigs (up to 177 days old) and sheep (up to 300 days old) (Hardy et. al., 1969). It was shown that sheep (a ruminant as is the steer) incorporated into the

whole body, much greater percentages of their dietary Ra (9.2%) than did pigs (0.5%), which have a digestive anatomy similar to humans. It was also shown that for the oldest pigs, only 49% of the Ra body burden was in bone, while 97% was accounted for in sheep bone. Neglecting age differences, these data indicate a factor of 36 difference in (sheep/pig) bone accumulation of Ra while the steer/pig bone CR data indicate a factor of 56 difference (Fig. 3). The Ra-226 body burden data for the N.Y. steers are in good agreement with the Hardy et al. sheep data in that about 98% of the Ra-226 burden was estimated to reside in bone (Table 15). On the other hand, the P.C. pig tissue data (muscle and bone only, Table 19), indicate much higher percentages of Ra-226 in bone (80-90%) relative to the Hardy et. al. study. Age may be an important variable since the serially-sacrificed pigs showed increasing percentage bone burden with age while no age trend was observed in sheep. Our youngest pig was 1.7 times older than the oldest sacrificed by Hardy et al., perhaps contributing to the relatively higher Ra percentages in bone.

The mean CR's for La and Th in bone are equal in the chicken and twice higher for La in the pig. Although we have plotted the CR's for Th in steer bone, the data are very few and of poor precison. Based on the equality of La and Th CR values seen in steer bone from N. Y. (Figure 2), we conclude that the bioavailability of La and Th to these farm animals cannot be very different based on either bone or muscle results. Based on the mean CR's for U in bone, it's bioavailability may be greater than that for La-Th by factors of 2, 4 and 5 for the steer, pig and chicken, respectively. Among these farm animals, the (muscle/soil) CR's for U, La and Th as a group (grand average x 10^{-4}), decline as: chicken (1) ≥ steer (0.6) ≥ pig (0.3); and for Ra-226 as: chicken (4.5) ≥ steer (2.6) > pig (0.8).

The remaining soft tissue CR data for the Pocos steers (Figure 4) indicate La CR's to decrease among the various tissues as: bone ≥ liver ≈ lung ≈ kidney ≥ muscle; and for Th as: bone (?) lung ≈ kidney ≥ muscle ≥ liver. The individual (tissue/soil) CR values (±SD) for all radionuclides (except U-234) and REE's measured are given in Appendix 1, Table 1. Although there are exceptions, CR values for isotopes of the same element (U-234 and U-238, Th-230 and Th-232, and Ra-226 and Ra-228) generally agree to within a factor of two. Thus the trends which have been discussed for the longer-lived

members would hold for the shorter-lived isotopes as well. Among the REE's, we have chosen to focus on La primarily for analytical reasons. The (tissue/soil) CR's for La, Ce, Nd and Sm are quite similar (Appendix 1, Table 1), and, although limited by measurement precision, show no obvious trends among the tissues analyzed (eg, resulting from fractionation due to the lanthanide contraction).

IV. Additional Discussion and Conclusions

Because some radionuclides eg., U-234, U-238 and Th-230, were not transferred to the N.Y. cattle primarily along the soil-plant pathway, tissue/soil CR's do not, in this case, provide a reliable means for comparing element bioavailability. A more informative approach is to devide the ratio (R) of the body burdens, eg., $(U\text{-}238/Th\text{-}232)_{bb}$ by the intake ratio, eg., $(U\text{-}238/Th\text{-}232)_i$. A result of unity would indicate no difference in bioavailability, with values greater than 1 indicating U-238 to be more available than Th-232, and those less than 1 the reverse. U-238 to Th-232 body burdens (by activity) for two steers and one heifer are 9.3, 9.2 and 13.5, respectively. Activity intake ratios are calculated to range from 4.1 (0.5 kg soil d^{-1}) to 9.3 (0.1 kg soil d^{-1}). Thus the R_{bb}/R_i values range between 1-3.3 suggesting U bioavailablity to be slightly greater than that of Th with respect to cattle. Calculating R_{bb}/R_i values for the U-238/Th-230 pair, which negates any artifacts caused by differences in the dietary source in the above analysis (i.e., both of these nuclides have the mineral supplement as their primary dietary source), one obtains a similar range of values (0.8 to 2.75) suggesting again that dietary hexavalent U (the oxidation state assumed to be predominant in the supplement and in the nonresistate or leachable component of ingested surface soils) is at most, only three times more available than quadravalent Th relative to whole body content in cattle. An identical result was obtained by comparing bone/soil CR's in the Pocos steers. R_{bb}/R_i ratios for the La/Th pair in the N. Y. cattle (N=3), are 0.5, 0.9 and 1.26 (discrete values are given since the R_i term is independent of dietary item consumption rates) suggesting, as was indicated by the nearly identical tissue/soil CR's in either the Pocos or N. Y. cattle, similar fates

for La and Th in their transport from soil to cattle tissues. For the two N. Y. cattle in which Ra-226 data are available, R_{bb}/R_i ratios for Ra-226/Th-232 range from 100 to 200 and from 78 to 110 for Ra-226/Th-230, suggesting the bioavailability of Ra to be about two orders of magnitude greater than Th with respect to whole body content. We conclude that the order of element (oxidation state) bioavailability relative to whole body content for market-ready Black Angus beef cattle under a natural, chronic intake regime is: Ra(II) >> U(VI) ≥ La(III) = Th(IV).
Based on the tissue/soil CR data for the Pocos steers (Fig. 4), one would arrive at this same conclusion, with the possible modification of La(III) > Th(IV), although this hinges on questionable bone data for Th.

Do tissue/soil CR's present a reasonable alternative for predicting radionuclide concentrations in certain farm animal products for those elements which are both uniformly distributed and strongly associated with soil? The data presented in this report or elsewhere in the literature is insufficient to answer this question. We can say however, that the range of values determined for essentially all of the analytes in various tissue types is no greater, and in many cases, (i.e., muscle/soil CR's for La and Th in N. Y. steers) considerably less than that observed for these same elements when calculating plant/soil CR's which are routinely used for dose assesment purposes (see Part 1 of this report). Although the N. Y. and Pocos cattle, management techniques, and environments are different in many respects, the tissue/soil CR data appear to be in reasonable agreement. As examples, the ratios of the mean CR's (i.e., Pocos/N. Y.) for La are 1.6, 2.2, 1.6, 2.5 and 4.6 for bone, liver, lung, kidney and muscle. For Th-232, the ratios are 0.4, 1.2, 1.0 and 3.4 for liver, lung, kidney and muscle. For Ra-226, the ratios are 2.0 and 0.7 for bone and muscle. The fact that the CR's are generally higher for the Pocos cattle may reflect a relatively greater soil intake dose for these animals which are on pasture 100% of the time. Although the small number of samples prevents statistical analysis, it does not appear that the variability in CR's is greater between herds than within herds. Clearly, there is a need to obtain data from other environments to assess the magnitude of variability in the CR's.

REFERENCES

Annekov, B.N., Dibobes, I.K., and Aleksakhin, R.M. 1973. The radiobiology and radioecology of farm animals. AEC-tr-7523 (translation series). USAEC. NTIS, Springfield, VA.

Barth, J. 1977. Application of the artificial rumen and simulated bovine gastrointestinal fluids procedure in the study of the bioavailability of the transuranics. In: Transuranics in Natural Environments (M.G. White and P.B. Dunaway, eds.). USERDA, Las Vegas, NV. pp. 419-433.

Blincoe, C., Bohman, V.R., and Smith, D.D. 1981. The ingestion of plutonium and americium by range cattle. Health Phys. 41: 285-291.

Bondietti, E.A., Trabalka, J.R., Garten, C.T., and Killough, G.G. 1979. Biogeochemistry of actinides: A nuclear fuel cycle perspective. In: Radioactive Waste in Geological Storage (S. Fried, ed.). American Chemical Society Symp. Series 100. pp. 241-265.

Campos, M.J., Penna-Franca, E., Lobão, N., Trindade, H., and Sachett, I. 1986. Migration of radium from the thorium ore deposit of Morro do Ferro, Poços de Caldas, Brazil. J. Environ. Radioactivity 3: 145-161.

Chapman, T.S. and Hammons, S., Jr. 1963. Some observations concerning uranium content of ingesta and excreta of cattle. Health Phys. 9: 79-81.

Comar, C.L. 1966. Radioactive materials in animals: Entry and metabolism. In: Radioactivity and Human Diet (R.S. Russell, ed.). Pergamon Press, NY. pp. 127-157.

Durbin, P.W. 1962. Distribution of the transuranic elements in mammals. Health Phys. 8: 665-671.

Eisenbud, M., Krauskopf, K., Penna Franca, E., Lei, W., Ballad, R., Linsalata, P., and Fujimori, K. 1984. Natural analogues for the transuranic actinide elements. Environ. Geol. Water Sci. 6 (1): 1-9.

Empresa Brasileira da Pesquisa Agropecuaria (EMBRAPA). 1981. Manual of Methods for Soil Analysis. Rio de Janeiro Servico Nacional de Levantamento e Conservaçao (SNLCS).

Fries, G.F., Marrow, G.S., and Snow, P.A. 1982a. Soil ingestion by dairy cattle. J. Dairy Sci. 65: 611-618.

Fries, G.F., Marrow, G.S., and Snow, P.A. 1982b. Soil ingestion by swine as a route of contaminant exposure. Environ. Toxicol. Chem. 1: 201-204.

Garten, C.T., Jr. 1978. A review of parameter values used to assess the transport of plutonium, uranium and thorium in terrestrial food

chains. Environ. Res. 17: 437-452.

Hardy, E., Rivera, J., Fisenne, I., Pond, W., and Hogue, D. 1969. Comparative utilization of dietary Ra-226 and other alkaline earths by pigs and sheep. In: Radiation Biology of the Fetal and Juvenile Mammals (Proc. Ninth Annual Hanford Biology Symp., Richland, WA, May 5-8), pp. 183-190.

Healy, W.B. 1968. Ingestion of soil by dairy cows. N.Z. J. Agric. Res. 11: 487-499.

Hursh, J.B., Neuman, W.F., Toribara, T., Wilson, H., and Waterhouse, C. 1969. Oral ingestion of uranium by man. Health Phys. 17: 619-621.

ICRP, International Commission on Radiological Protection. 1972. The Metabolism of Plutonium and Other Actinides. ICRP Publ. 19. Pergamon Press, New York, NY.

ICRP, International Commission on Radiological Protection. 1979. Limits for Intakes of Radionuclides by Workers. ICRP Publ. 30, Part 1. Pergamon Press, New York, NY.

Lei, W. 1984. Thorium Mobilization in a Terrestrial Environment. Ph.D. Dissertation, New York University, New York, NY. 414 pp.

Lei, W., Linsalata, P., Penna Franca, E., and Eisenbud, M. 1986. Distribution and mobilization of cerium, lanthanum and neodymium in the Morro do Ferro Basin, Brazil. Chem. Geol. 55(No. 3/4): 313-322.

Li, Y.H., Mathieu, G., Biscaye, P., and Simpson, H.J. 1977. The flux of Ra-226 from estuarine and continental shelf sediments. Earth Planet. Sci. Lett. 37: 237-241.

Linsalata, P., Eisenbud, M., and Penna Franca, E. 1985. Thorium and the light rare earth elements in soils, crops and domestic animals from abnormally high and typical radiation background areas. In: Proc. of the Eighteenth Midyear Topical Symposium of the Health Physics Society - Environmental Radiation '85 (Colorado Springs, CO; January 6-10, 1985). pp. 535-542.

Linsalata, P., Penna Franca, E., and Eisenbud, M. 1986. Ingestion estimates of thorium and the light rare earth elements based on measurements of human feces. Health Phys. 50 (1): 163-167.

Linsalata, P., Penna Franca, E., Sachett, I., Castro, M.B., Lobão, N., Ballad, R., Lei, W., Ford, H., Morse, R.S., and Eisenbud, M. 1987a. Radium, thorium and the light rare earth elements in soils and vegetables grown in an area of high natural radioactivity. In: Environmental Research for Actinide Elements, CONF 841142. NTIS, Springfield, VA. pp. 131-146.

Linsalata, P., Penna Franca, E., Eisenbud, M., Morse, R.S., Ford, H., de Castro, M.B., Sachett, I., Lobão, N., and Carlos, M. 1987b. An

assessment of soil-to-plant concentration ratios for some natural analogues of the transuranic elements. Health Phys. (accepted for publication).

Lowder, W.M., Condon, W.J., and Beck, H.L. 1964. Field spectrometric investigations of environmental radiation in the U.S.A. In: The Natural Radiation Environment (J.A.S. Adams and W.M. Lowder, eds.). Univ. Chicago Press, Chicago, IL. pp. 597-616.

Maletskos, C.J., Keane, A.T., Telles, N.C., and Evans, R.D. 1969. Retention and absorption of ^{224}Ra and ^{234}Th and some dosimetric considerations of ^{224}Ra in human beings. In: Delayed Effects of Bone-Seeking Radionuclides (C.W. Mays, W.S. Jee, R.D. Lloyd, B.J. Stover, J.H. Dougherty, and G.N. Taylor, eds.). University of Utah Press, Salt Lake City, UT. pp. 29-49.

New York University Medical Center. 1984. Studies of Transport Pathways of Th, U REE's and Radium Isotopes from Soil to Farm Animals. Annual Progress Report to DOE/OHER, Jan., 1974. Available from: Office of Scientific & Technical Information, Oak Ridge Associated Universities, P.O. Box 32, Oak Ridge, TN 37831. 71 pp.

New York University Medical Center. 1985. Studies of Transport Pathways of Th, U, REE's and Radium Isotopes from Soil to Farm Animals. Annual Progress Report to DOE/OHER, Jan., 1985. Available from: Office of Scientific & Technical Information, Oak Ridge Associated Universities, P.O. Box 32, Oak Ridge, TN 37831. 200 pp.

New York University Medical Center. 1986. Studies of Transport Pathways of Th, U, Rare Earths, Ra-228 and Ra-226 from Soil to Plants and Farm Animals. Annual Progress Report to DOE/OHER, Feb., 1986. Available from: Office of Scientific & Technical Information, Oak Ridge Associated Universities, P.O. Box 32, Oak Ridge, TN 37831. 120 pp.

Ng, Y.C., Colsher, C.S., and Thompson, S.E. 1982a. Soil-to-plant concentration factors for radiological assessments. Lawrence Livermore National Laboratory, NUREG/CR-2975. UCID-19463. 133 pp.

Ng, Y.C. 1982b. A review of transfer factors for assessing the dose from radionuclides in agricultural products. Nucl. Saf. 23: 57-71.

Reid, D.F., Sackett, W.M. and Spalding, R.F. 1977. Uranium and radium in livestock feed supplements. Health Phys. 32: 535-540.

Smith, D.D. 1977. Review of grazing studies on plutonium-contaminated rangelands. In: Transuranics in Natural Environments (W.G. White and P.B. Dunaway, eds.). USERDA, Las Vegas, NV. pp. 407-417.

Stover, B. 1960. Thorium studies in beagles. In: Proc. of the Rochester Conference on Thorium Toxicity. Rochester, NY. pp. 51-56.

Thomas, R.G. 1961. Distribution and excretion of thorium with emphasis upon route of injection and amount of carrier present. University

of Rochester. UR-592. Atomic Energy Project Library, P.O. Box 287, Rochester, NY. 27 pp.

Trabalka, J.R. and Garten, C.T., Jr. 1983. Behavior of the long-lived synthetic elements and their natural analogs in food chains. Advances in Radiation Biology 10. Academic Press, Inc., New York, NY. pp. 39-104.

USNRC, United Stated Nuclear Regulatory Commission. 1977. Calculation of annual doses to man from routine releases of reactor effluents for the purposes of evaluating compliance with 10CFR Part 50, App. 1, Rev. 1. Regulatory Guide 1.109. USNRC, Washington, DC.

Welford, G.A. and Baird, R. 1967. Uranium levels in human diet and biological materials. Health Phys. 13: 1321.

Whicker, F.W. and Kirchner, T.B. 1987. Pathway: A dynamic model to predict radionuclide ingestion after fallout deposition. Health Phys. 52: 717-738.

Wildung, R.E., Garland, T., and Cataldo, D.A. 1979. Environmental processes leading to the presence of organically bound plutonium in plant tissues consumed by animals. In: International Symposium on Biological Implications of Radionuclides Released from Nuclear Industries. IAEA-SM-237/37. IAEA, Vienna.

Yuile, C.L. 1973. Animal experiments. In: Uranium, Plutonium and the Transplutonic Elements (H.C. Hodge, J.N. Stannard, and J.B. Hursh, eds.). Springer-Verlag, New York, NY. pp. 165-196.

Zach, R. and Mahoh, K.R. 1984. Soil ingestion by cattle: A neglected pathway. Health Phys. 46: 426-431.

Zach, R. 1985. Contribution of inhalation by food animals to man's ingestion dose. Health Phys. 49: 737-745.

Table 1

Characteristics of Beef Cattle Selected from New York

Animal No.	Animal type	Age (months)	Weight (kg)	Location	Sample No.	Organ	Total Organ Weight (kg)
1	Steer	24-36	215	Vermont	BT-3	liver	2.37
					BT-4	lungs	1.58
					BT-2T-A	bone (femur end)	21.50*
					BT-2T-B	bone (femur end)	
					BT-2C-A	bone (femur shaft)	
					BT-2C-B	bone (femur shaft)	
2	Steer	24	484	New York	BT-13	kidneys	0.88
					BT-11	liver	5.01
					BT-12	lungs	2.29
					BT-14	bone (humerus, ulna, & radius)	48.40*
3	Steer	24	453	New York	BT-22	flesh	181.20
					BT-21	kidneys	0.85
					BT-20	liver	4.89
					BT-19	lungs	2.33
					BT-23-B1	bone (ribs)	45.30*
					BT-23-B2	bone (ribs)	
					BT-23-B3	bone (ribs)	
					BT-23-C1	bone (vert.)	
					BT-23-C2	bone (vert.)	
					BT-23-C3	bone (vert.)	
					BT-23-A1	bone (humerus, ulna & radius)	
					BT-23-A2	bone (humerus, ulna & radius)	
					BT-23-A3	bone (humerus, ulna & radius)	
4	Heifer	42	453	New York	BT-25	flesh	181.20
					BT-28	kidneys	0.74
					BT-26	liver	3.91
					BT-27	lungs	2.36
					BT-30-A	bone (ribs)	45.30*
5	Steer	24	496	New York	BT-50	flesh	198.40
					BT-51	kidneys	1.04
					BT-52	liver	5.68
					BT-53	lungs	2.71
					BT-54	bone (ribs)	49.60*

* Refers to entire skeletal mass

Table 2

Characteristics of Farm Animals Selected from Pocos de Caldas, Brazil

Animal No.	Animal type	Age (months)	Weight (kg)	Location	Sample No.	Organ	Weight (kg)
10	Steer	30	160	Farm 1	BT-44	flesh	64.00
					BT-49	kidneys	0.55
					BT-46	liver	2.63
					BT-47	lungs	2.08
					BT-48	bone (ribs)	16.00*
					BT-45	bone (femur, ulna, radius)	
11	Steer	27	105	Farm 2	BT-69	flesh	42.00
					BT-62	kidneys	0.61
					BT-64	lungs	1.98
					BT-60	bone (ribs)	10.50*
					BT-58	bone (femur, ulna, radius)	
14	Steer	20	90	Farm 10	BT-73	flesh	36.00
					BT-68	kidneys	0.79
					BT-67	bone (ribs)	9.00*
					BT-66	bone (femur, ulna, radius)	

* Refers to entire skeletal mass

Table 3

Characteristics of Farm Animals Selected from Pocos de Caldas, Brazil

Animal No.	Animal type	Age (months)	Weight (kg)	Location	Sample No.	Organ	Weight (kg)
7	Pig	30	60	Farm 1	BT-38	flesh	27.00
					BT-41	trab. bone	4.80*
					BT-43	cortical bone	
5	Pig	12	10	Farm 2-a	BT-33	flesh	NA
					BT-32	bone	NA
6	Pig	14	45	Farm 2-b	BT-37	flesh	20.25
					BT-36	trab. bone	3.60*
					BT-35	cortical bone	
12	Pig	10	38	Farm 10	BT-70	flesh	17.10
					BT-77	liver	1.16
					BT-76	lungs	1.06
					BT-59	trab. bone	3.00*
					BT-61	cortical bone	

* Refers to entire skeletal mass

Table 4

Characteristics of Farm Animals Selected from Pocos de Caldas, Brazil

Animal No.	Animal type	Age (months)	Weight (kg)	Location	Sample No.	Organ	Weight (kg)
8	Chicken	3	1	Farm 1	BT-40	flesh	NA
					BT-34	bone	NA
9	Chicken	3	1	Farm 2	BT-42	flesh	NA
					BT-39	bone	NA
13	Chicken	3	1	Farm 10	BT-72	flesh	NA
					BT-65	bone	NA

Table 5

Radionuclide Concentrations† in Composite Soil Samples from a Farm in New York (Bq/kg dry wt ± SD)

Sample No.	Th-232	Th-230	Th-228	U-238	U-235	U-234	Ra-226	Ra-228
BS-1A	38.5 ± 2.2	44.8 ± 2.6	40.7 ± 2.6	40.3 ± 2.6	2.7 ± 0.5	34.8 ± 2.2	45.1 ± 6.7	34.8 ± 13.0
BS-1B	36.6 ± 2.2	43.7 ± 2.6	38.9 ± 2.6	NA	NA	NA	NA	NA
BS-2A	36.6 ± 2.2	38.9 ± 2.2	36.3 ± 2.2	34.0 ± 2.2	1.4 ± 0.4	33.7 ± 2.2	35.9 ± 6.7	31.8 ± 13.3
BS-2B	38.9 ± 2.2	44.7 ± 2.6	37.7 ± 2.2	NA	NA	NA	NA	NA
Mean ± SD	37.6 ± 1.2	43.0 ± 2.8	38.4 ± 1.9	37.2 ± 4.4	2.0 ± 0.9	34.2 ± 0.8	40.5 ± 6.5	33.3 ± 2.1

† Based on radiochemical analyses and alpha spectrometry (Th and U isotopes) or gamma spectrometry (Ra isotopes)

Table 6

Mass Concentrations† of Rare Earth Elements, Th and U in Farm Soils from New York (µg/g dry wt. ± SD)

Sample No.	La	Ce	Nd	Sm	Th	U
BS-1A	32.4 ± 0.9	63.5 ± 2.1	28.3 ± 6.6	6.9 ± 0.2	9.5 ± 0.6	3.3 ± 0.2
BS-1B	31.9 ± 0.8	65.4 ± 2.0	21.6 ± 6.8	6.4 ± 0.2	9.1 ± 0.6	NA
BS-2A	31.9 ± 0.8	70.0 ± 2.2	NA	7.3 ± 0.2	9.1 ± 0.6	2.8 ± 0.2
BS-2B	34.0 ± 0.8	75.9 ± 8.9	36.6 ± 8.7	6.6 ± 0.4	9.6 ± 0.6	NA
Mean ± SD	32.6 ± 1.0	68.7 ± 5.5	28.8 ± 7.5	6.8 ± 0.4	9.3 ± 0.3	3.1 ± 0.4

† Based on ICPOES (REE's) or alpha spectrometry (Th and U)

Table 7

Radionuclide Concentrations† in Composite Soil Samples from Pocos de Caldas (Bq/kg dry wt ± SD)

Location	Sample No.	Th-232	Th-230	Th-228	U-238	U-235	U-234	Ra-226	Ra-228
Farm 1	PCS-11	230 ± 13	78 ± 8	253 ± 14	100 ± 10	4.0 ± 1.0	113 ± 11	96 ± 11	244 ± 24
Farm 2	PCS-6	211 ± 15	155 ± 11	NA	NA	NA	NA	207 ± 15	315 ± 41
Farm 10	PCS-24	249 ± 8	211 ± 7	NA	NA	NA	NA	241 ± 15	285 ± 26

† Based on radiochemical analyses and alpha spectrometry (Th and U isotopes) or gamma spectrometry (Ra isotopes)

Table 8

Mass Concentrations† of Rare Earth Elements, Th and U in Farm Soils from Pocos de Caldas (µg/g dry wt. ± SD)

Location	Sample No.	La	Ce	Nd	Sm	Th	U
Farm 1	PCS-11	113 ± 5	498 ± 23	43 ± 6	8.4 ± 0.6	57 ± 3	8.1 ± 0.8
Farm 2	PCS-6	92 ± 12	764 ± 33	33 ± 5	4.4 ± 0.4	52 ± 4	14.7 ± 3.0 ††
Farm 10	PCS-24	256 ± 11	894 ± 39	109 ± 6	11.7 ± 0.6	62 ± 2	18.3 ± 1.7 ††

† Based on ICPOES (REE's) or alpha spectrometry (Th and U)
†† Based on mean of Ra-226 and Th-230 concentrations, assuming secular equilibrium

Table 9

Mean Radionuclide and REE Concentrations in Cattle Feeds from a Farm in New York *

Sample Type	N†	mBq/kg dry wt ± SD					µg/kg dry wt. ± SD			
		Th-232	Th-230	Th-228	U-238	Ra-226	La	Ce	Nd	Sm
ground corn cobs	4	43 ± 5	56 ± 7	48 ± 2	NA	NA	35 ± 2	81 ± 3	NA	7 ± 1
corn silage	4	118 ± 19	126 ± 10	144 ± 14	NA	NA	167 ± 33	287 ± 75	119 ± 43	32 ± 6
alfalfa hay (third cut)	2	150 ± 5	166 ± 7	NA	NA	NA	305 ± 9	370 ± 20	286 ± 7	115 ± 4
alfalfa hay (second cut)	1	58 ± 4	66 ± 5	NA	58 ± 4	440 ± 80	134 ± 7	162 ± 12	115 ± 22	26 ± 2
pasture grass (unwashed)	1	422 ± 35	422 ± 35	NA	509 ± 66	2,075 ± 218	593 ± 34	1,069 ± 63	477 ± 75	115 ± 3
pasture grass (washed)	1	142 ± 9	123 ± 8	NA	173 ± 14	NA	225 ± 12	335 ± 22	174 ± 24	44 ± 3
mineral feed supplement (per gram dry wt.)††	2	24 ± 1	516 ± 4	13 ± 1	721 ± 133	22 ± 2	2.1 ± 0.1	2.4 ± 0.3	1.5 ± 0.3	0.4 ± 0.1

* Samples are unwashed unless otherwise indicated.
† The number of samples refers to different aliquots of the same sample.
†† Agway fortamin mineral mix for livestock.

Table 10

Soil-to-Crop Concentration Ratios for the New York Farm*

Crop	Dry weight concentration ratios for unwashed crops** (x 10E-4)							
	N	La	Ce	Nd	Sm	Th	U-238	Ra-226
Alfalfa***								
• Third cutting	2	95	57	115	174	40	NA	NA
• Second cutting	1	42	25	46	39	16	16	109
Corn cobs††	4	11	11	NA	10	12	NA	NA
Corn silage††	4	51	40	33	47	32	NA	NA
Pasture grass†††								
• Unwashed	1	184	160	166	162	112	137	512
• Washed	1	70	50	60	62	38	47	NA

* Soil and crops are from the same farm in which cattle were raised. The number of analyses refer to analytic replicates of the same sample taken at one point in time.

** Concentration ratios calculated from mean concentrations in plant (Table 9) and mean concentrations in dry soil (Tables 5 and 6). The uncertainties associated with the CR values are generally between 10% (corn cobs) and 25% (silage).

*** Alfalfa was grown in soils BS-1A and BS-1B (Table 6)

† NA = Not Analyzed

†† Corn was grown in soils BS-2A and BS-2B (Table 6)

††† Approximately one Kg (fresh wt) of pasture grass was hand-clipped to about 3 cm above the soil from an area of about 25 square meters.

Table 11

Parameters for Estimating Daily Intake of

Th, U, Ra and the REE's in Beef Cattle

Pathway	Assumed Consumption (kg-dry d^{-1})	Estimated Daily Intake (mg d^{-1})				Bq d^{-1}	
		Th-232	U-238	La	Ce	Th-230	Ra-226
Ingestion							
Soil	0.1-0.5	0.9-4.6	0.3-1.6	3.3-16.3	6.9-34.4	4.3-21.5	4.1-20.3
Feed	12.0	0.6	0.2	3.6	6.1	2.4	∿13
Mineral Supplement	0.1	0.6	5.9	0.2	0.2	51.6	2.2
Water (ℓ d^{-1})	50[2]	$<10^{-3}$	$\sim 10^{-3}$ [1]	NA[3]	NA	$\sim 10^{-3}$	$\sim 10^{-2}$
Total Ingestion		2.1-5.8	6.4-7.7	7.1-20.1	13.2-40.7	58.3-75.5	19.3-35.5
% Derived from Soil		43-79	5-21	46-81	52-85	7-28	21-57
% Derived from Mineral Suppl.		10-29	77-92	1-3	0.5-1.5	68-89	6-11
Inhalation (m^3 d^{-1})	130[2]	$2x10^{-4}$	$8x10^{-5}$	$9x10^{-4}$	$2x10^{-3}$	$1x10^{-3}$	$1x10^{-3}$

[1] Based on NYC tap water mean value of 0.032 μg/ℓ (Welford and Baird, 1967).

[2] From Comar, 1966. Inhalation intake assumes animal is exposed to 200 μg soil m^{-3} air.

[3] NA refers to not available. Because of solubility limitations, REE's are not expected to contribute significantly to total intakes via drinking water.

Table 12

Isotopic Concentrations in Cattle Tissues (mBq/kg fresh wt. ± SD) from New York

Animal No.	Tissue type	Th-232 ± SD	Th-230 ± SD	U-238 ± SD	U-234 ± SD	Ra-226 ± SD	Ra-228 ± SD
1	liver	0.70 ± 0.15	2.92 ± 0.30	NA	NA	NA	NA
	lungs	1.04 ± 0.22	3.81 ± 0.44	NA	NA	NA	NA
	trab. bone	2.76 ± 1.50	11.43 ± 5.05	NA	NA	NA	NA
	trab. bone	4.02 ± 1.97	16.55 ± 3.94	NA	NA	NA	NA
	cortical bone	9.14 ± 3.05	7.85 ± 5.16	NA	NA	NA	NA
	cortical bone	14.08 ± 3.52	2.35 ± 5.87	NA	NA	NA	NA
2	kidneys	3.59 ± 0.81	145.78 ± 7.40	55.50 ± 5.18	62.53 ± 5.55	NA	NA
	liver	2.22 ± 0.37	87.69 ± 4.07	NA	NA	NA	NA
	lungs	0.59 ± 0.26	22.57 ± 1.85	NA	NA	NA	NA
	cortical bone	16.51 ± 6.61	165.14 ± 16.51	346.80 ± 49.54	379.83 ± 49.54	2,742 ± 115	3,304 ± 596
3	flesh	0.56 ± 0.07	2.41 ± 0.15	1.33 ± 0.19	1.63 ± 0.22	15 ± 2	126 ± 78
	kidneys	2.78 ± 0.37	42.92 ± 1.48	19.24 ± 1.85	21.83 ± 1.85	NA	NA
	liver	2.41 ± 0.11	48.47 ± 0.78	NA	NA	9 ± 3	<174
	lungs	5.07 ± 0.26	15.39 ± 0.44	NA	NA	6 ± 4	<396
	trab.bone-ribs	14.03 ± 6.24	101.34 ± 12.47	155.91 ± 15.59	140.32 ± 15.59	4,989 ± 624	7,172 ± 2,339
	trab.bone-ribs	7.78 ± 1.56	119.83 ± 62.25	NA	NA	NA	NA
	trab.bone-ribs	12.44 ± 3.11	97.98 ± 9.33	NA	NA	NA	NA
	trab.bone-vert.	23.60 ± 5.55	152.72 ± 19.44	111.07 ± 13.88	166.60 ± 13.88	4,304 ± 139	7,358 ± 2,777
	trab.bone-vert.	6.94 ± 2.78	131.81 ± 9.71	NA	NA	NA	NA
	trab.bone-vert.	8.33 ± 2.78	129.04 ± 8.33	NA	NA	NA	NA
	cortical bone	18.53 ± 2.85	105.51 ± 8.55	141.15 ± 18.53	142.58 ± 18.53	4,277 ± 570	5,418 ± 285
	cortical bone	8.55 ± 2.85	65.59 ± 5.70	NA	NA	NA	NA
	cortical bone	11.41 ± 2.85	68.48 ± 5.71	NA	NA	NA	NA
4	flesh	0.67 ± 0.11	1.11 ± 0.11	0.52 ± 0.11	0.59 ± 0.11	NA	NA
	kidneys	3.48 ± 0.56	50.10 ± 2.44	64.75 ± 3.33	69.19 ± 3.70	NA	NA
	liver	1.70 ± 0.19	11.66 ± 0.52	4.07 ± 0.37	4.44 ± 0.37	8 ± 3	<252
	lungs	8.81 ± 0.52	16.54 ± 0.78	6.66 ± 0.74	6.66 ± 0.74	17 ± 5	<377
	trab.bone-ribs	13.07 ± 3.53	88.13 ± 10.28	220.34 ± 29.38	220.34 ± 29.38	3,525 ± 147	15,717 ± 4,847
5	flesh	0.56 ± 0.07	0.36 ± 0.16	0.78 ± 0.11	0.74 ± 0.15	NA	NA
	kidneys	2.52 ± 0.30	19.87 ± 1.00	91.39 ± 5.18	92.13 ± 5.18	NA	NA
	liver	0.34 ± 0.06	4.11 ± 0.22	NA	NA	NA	NA
	lungs	2.29 ± 0.15	8.18 ± 0.33	5.55 ± 0.37	5.55 ± 0.37	NA	NA
	trab. bone-ribs	5.15 ± 2.03	17.20 ± 3.66	63.65 ± 4.06	66.36 ± 5.42	NA	NA

Table 13

Mass Concentrations in Cattle Tissues (µg/kg fresh wt. ± SD) from New York

Animal No.	Tissue type	La ± SD	Ce ± SD	Nd ± SD	Sm ± SD	Th-232 ± SD	U-238 ± SD
1	liver	1.06 ± 0.10	1.68 ± 1.31	NA	0.02 ± 0.08	0.17 ± 0.04	NA
	lungs	2.49 ± 0.15	0.91 ± 1.69	NA	0.09 ± 0.15	0.26 ± 0.06	NA
	trab. bone	1.56 ± 1.28	31.96 ± 17.05	NA	1.92 ± 0.85	0.68 ± 0.37	NA
	trab. bone	4.05 ± 2.13	34.07 ± 19.16	NA	-0.21 ± 1.70	1.00 ± 0.49	NA
	cortical bone	3.17 ± 4.43	66.52 ± 34.84	NA	1.27 ± 2.22	2.27 ± 0.76	NA
	cortical bone	10.46 ± 1.90	44.40 ± 44.40	NA	0.32 ± 1.27	3.49 ± 0.87	NA
2	kidneys	3.48 ± 0.30	7.94 ± 2.47	-1.83 ± 3.14	0.87 ± 0.26	0.89 ± 0.20	4.51 ± 0.42
	liver	4.81 ± 0.22	7.22 ± 0.62	2.75 ± 0.67	0.61 ± 0.04	0.55 ± 0.09	NA
	lungs	4.21 ± 0.23	7.39 ± 1.04	1.81 ± 0.46	0.17 ± 0.08	0.15 ± 0.06	NA
	cortical bone	11.16 ± 1.34	37.94 ± 15.18	-2.68 ± 8.93	2.68 ± 0.89	4.10 ± 1.64	28.16 ± 4.02
3	flesh	0.39 ± 0.07	1.33 ± 0.37	0.24 ± 0.48	0.09 ± 0.06	0.14 ± 0.02	0.11 ± 0.02
	kidneys	1.31 ± 0.58	3.50 ± 3.05	0.15 ± 4.74	0.63 ± 0.33	0.69 ± 0.09	1.56 ± 0.15
	liver	4.14 ± 0.20	6.16 ± 0.56	3.45 ± 0.77	0.94 ± 0.06	0.60 ± 0.03	NA
	lungs	1.44 ± 0.20	3.45 ± 1.02	0.50 ± 1.22	0.31 ± 0.14	1.26 ± 0.06	NA
	trab.bone-ribs	5.06 ± 7.16	-15.17 ± 46.35	-2.11 ± 44.67	-32.87 ± 54.78	3.48 ± 1.55	12.66 ± 1.27
	trab.bone-ribs	11.78 ± 6.73	-23.98 ± 35.33	29.44 ± 45.43	-0.42 ± 5.05	1.93 ± 0.39	NA
	trab.bone-ribs	13.87 ± 6.73	-6.30 ± 38.67	23.12 ± 62.21	0.84 ± 4.20	3.09 ± 0.77	NA
	trab.bone-vert.	4.50 ± 6.38	-48.78 ± 33.77	9.76 ± 40.53	10.51 ± 12.01	5.85 ± 1.38	9.02 ± 1.13
	trab.bone-vert.	10.88 ± 6.00	-16.13 ± 33.38	25.88 ± 42.75	-0.38 ± 3.75	1.72 ± 0.69	NA
	trab.bone-vert.	8.63 ± 6.00	-21.38 ± 30.75	18.38 ± 50.25	-0.38 ± 3.75	2.06 ± 0.69	NA
	cortical bone	4.62 ± 6.17	-88.63 ± 34.68	10.40 ± 38.53	-0.77 ± 4.24	4.60 ± 0.71	11.46 ± 1.51
	cortical bone	12.72 ± 7.32	-8.09 ± 33.91	18.11 ± 44.70	1.16 ± 5.39	2.12 ± 0.71	NA
	cortical bone	12.72 ± 6.17	-22.75 ± 35.47	20.82 ± 38.17	-3.86 ± 3.86	2.83 ± 0.71	NA
4	flesh	0.49 ± 0.09	-0.03 ± 0.54	NA	0.01 ± 0.05	0.17 ± 0.03	0.04 ± 0.01
	kidneys	1.59 ± 0.56	3.64 ± 3.60	0.48 ± 3.49	0.04 ± 0.51	0.86 ± 0.14	5.26 ± 0.27
	liver	2.71 ± 0.19	2.80 ± 0.70	2.47 ± 1.17	0.26 ± 0.09	0.42 ± 0.05	0.33 ± 0.03
	lungs	5.37 ± 0.36	6.35 ± 1.18	4.59 ± 2.96	0.47 ± 0.11	2.18 ± 0.13	0.54 ± 0.06
	trab.bone-ribs	4.76 ± 2.38	-3.97 ± 15.88	NA	1.19 ± 1.59	3.24 ± 0.87	17.89 ± 2.39
5	flesh	0.53 ± 0.19	0.83 ± 1.10	-0.38 ± 1.66	-0.01 ± 0.13	0.14 ± 0.02	0.06 ± 0.01
	kidneys	1.87 ± 0.31	1.20 ± 1.79	1.23 ± 2.00	0.26 ± 0.24	0.62 ± 0.07	7.42 ± 0.42
	liver	0.40 ± 0.06	0.53 ± 0.32	0.24 ± 0.36	0.08 ± 0.04	0.08 ± 0.01	NA
	lungs	3.40 ± 0.17	5.49 ± 0.70	1.76 ± 0.80	0.30 ± 0.07	0.57 ± 0.04	0.45 ± 0.03
	trab. bone-ribs	5.65 ± 4.64	9.60 ± 27.30	NA	-0.31 ± 3.35	1.28 ± 0.50	5.17 ± 0.33

Table 14

Tissue Burdens for New York Cattle

		mBq. ± SD				µg ± SD
Animal No.	Tissue type	Th-232 ± SD	Th-230 ± SD	U-238 ± SD	Ra-226 ± SD	La ± SD
3	flesh	101.47 ± 12.68	436.69 ± 27.18	241.00 ± 34.43	2718 ± 362	70.67 ± 12.68
	kidneys	2.36 ± 0.31	36.44 ± 1.26	16.33 ± 1.57	9 ± 4	1.11 ± 0.49
	liver	11.76 ± 0.54	236.92 ± 3.80	19.89 ± 1.81 *	42 ± 13	20.24 ± 0.98
	lungs	11.84 ± 0.60	35.94 ± 1.04	15.55 ± 1.73 *	14 ± 9	3.36 ± 0.47
	mean - bone	561.72 ± 252.77	4,893.76 ± 1,307	6,162.61 ± 1,035.11	204,913 ± 18,281	426.73 ± 172.59
	TOTAL	689 ± 253	5,640 ± 1,307	6,455 ± 1,035	207,696 ± 18,284	522 ± 173
4	flesh	121.40 ± 19.93	201.13 ± 19.93	94.22 ± 19.93	2718 ± 362 ††	88.79 ± 16.31
	kidneys	2.58 ± 0.41	37.19 ± 1.81	48.06 ± 2.47	8 ± 4 ††	1.18 ± 0.42
	liver	6.66 ± 0.72	45.58 ± 2.03	15.92 ± 1.45	30 ± 12	10.60 ± 0.74
	lungs	20.74 ± 1.22	38.96 ± 1.83	15.69 ± 1.74	40 ± 12	12.65 ± 0.85
	trab.bone-ribs	592.07 ± 159.91	3,992.29 ± 465.68	9,981.40 ± 1,330.91	159,683 ± 6,659	215.63 ± 107.81
	TOTAL	743 ± 161	4,315 ± 466	10,155 ± 1,331	162,479 ± 6,669	329 ± 109
5	flesh	111.10 ± 13.89	71.42 ± 31.74	154.75 ± 21.82	NA	105.15 ± 37.70
	kidneys	2.62 ± 0.31	20.66 ± 1.04	95.05 ± 5.39	NA	1.94 ± 0.32
	liver	1.91 ± 0.32	23.33 ± 1.26	23.12 ± 2.10 †	NA	2.27 ± 0.34
	lungs	6.22 ± 0.40	22.16 ± 0.90	15.04 ± 1.00	NA	9.21 ± 0.46
	trab. bone-ribs	255.44 ± 100.69	853.12 ± 181.54	3,157.04 ± 201.38	NA	280.24 ± 230.14
	TOTAL	377 ± 102	991 ± 184	3,445 ± 203	NA	399 ± 233

† Liver value for animal No. 5 based on measurement from animal No. 4

* U-238 liver and lung values for animal No. 3 based on measurements for animal No. 4

†† Ra-226 flesh and kidney values for animal No. 4 based on measurements for animal No. 3

Table 15

Percent Organ Distribution of Isotopes in New York Cattle

Animal No.	Tissue type	Th-232 ± SD	Th-230 ± SD	U-238 ± SD	Ra-226 ± SD	La ± SD
3	flesh	14.7% ± 5.7%	7.7% ± 1.8%	3.7% ± 0.8%	1.30% ± 0.2%	13.5% ± 5.1%
	kidneys	0.3% ± 0.1%	0.6% ± 0.1%	0.3% ± 0.1%	< 0.01% ± 0.0%	0.2% ± 0.1%
	liver	1.7% ± 0.6%	4.2% ± 1.0%	0.3% ± 0.1% *	0.20% ± 0.0%	3.9% ± 1.3%
	lungs	1.7% ± 0.6%	0.6% ± 0.1%	0.2% ± 0.1% *	0.01% ± 0.0%	0.6% ± 0.2%
	mean - bone	81.5% ± 47.3%	86.8% ± 30.7%	95.5% ± 22.2%	98.66% ± 12.4%	81.7% ± 42.7%
4	flesh	16.3% ± 4.4%	4.7% ± 0.7%	0.9% ± 0.2%	1.67% ± 0.2% ††	27.0% ± 10.2%
	kidneys	0.3% ± 0.1%	0.9% ± 0.1%	0.5% ± 0.1%	< 0.01% ± 0.0% ††	0.4% ± 0.2%
	liver	0.9% ± 0.2%	1.1% ± 0.1%	0.2% ± 0.0%	0.02% ± 0.0%	3.2% ± 1.1%
	lungs	2.8% ± 0.6%	0.9% ± 0.1%	0.2% ± 0.0%	0.20% ± 0.0%	3.8% ± 1.3%
	trab.bone-ribs	79.7% ± 27.6%	92.5% ± 14.7%	98.3% ± 18.4%	98.28% ± 5.7%	65.5% ± 39.3%
5	flesh	29.5% ± 8.8%	7.2% ± 3.5%	4.5% ± 0.7%	NA	26.4% ± 18.1%
	kidneys	0.7% ± 0.2%	2.1% ± 0.4%	2.8% ± 0.2%	NA	0.5% ± 0.4%
	liver	0.5% ± 0.2%	2.4% ± 0.5%	0.7% ± 0.1% †	NA	0.6% ± 0.4%
	lungs	1.6% ± 0.4%	2.2% ± 0.4%	0.4% ± 0.0%	NA	2.3% ± 1.3%
	trab. bone-ribs	67.8% ± 32.4%	86.1% ± 24.3%	91.6% ± 7.9%	NA	70.2% ± 70.7%

† Liver value for animal No. 5 based on measurement from animal No. 4
* U-238 liver and lung values for animal No. 3 based on measurements for animal No. 4
†† Ra-226 flesh and kidney values for animal No. 4 based on measurements for animal No. 3

Table 16

Isotopic Activity Concentrations in Steer Tissues (mBq/kg fresh wt. ± SD) from Pocos de Caldas

Location	Tissue type	Th-232 ± SD	Th-230 ± SD	U-238 ± SD	U-234 ± SD	Ra-226 ± SD	Ra-228 ± SD
Farm 1	flesh	6.66 ± 0.37	2.96 ± 0.37	4.92 ± 0.30	5.03 ± 0.30	30 ± 1	100 ± 11
	kidneys	24.05 ± 1.85	11.84 ± 1.48	29.60 ± 2.59	31.45 ± 2.59	NA	NA
	liver	3.52 ± 0.33	3.26 ± 0.37	NA	NA	NA	NA
	lungs	23.53 ± 1.18	10.80 ± 0.78	NA	NA	NA	NA
	trab. bone	NA	NA	27.66 ± 4.61	27.66 ± 5.76	10,948 ± 35	35,496 ± 922
	cortical bone	NA	NA	36.89 ± 5.76	35.73 ± 6.92	14,409 ± 1,383	37,809 ± 10,605
Farm 2	flesh	21.46 ± 0.74	14.43 ± 0.74	19.98 ± 1.11	18.87 ± 0.74	59 ± 7	111 ± 7
	kidneys	20.35 ± 1.85	14.06 ± 1.48	108.78 ± 6.66	118.40 ± 7.03	NA	NA
	lungs	27.38 ± 1.48	16.28 ± 1.11	NA	NA	NA	NA
	trab. bone	NA	NA	91.90 ± 7.80	90.16 ± 7.80	29,997 ± 2,774	60,947 ± 11,010
	cortical bone	8.84 ± 11.05	NA	121.59 ± 11.05	143.70 ± 11.05	35,925 ± 6,522	41,342 ± 7,461
Farm 10	flesh	7.77 ± 0.37	5.18 ± 0.37	8.51 ± 0.37	9.25 ± 0.37	44 ± 7	78 ± 11
	kidneys	12.58 ± 1.11	10.36 ± 1.11	130.61 ± 5.55	168.35 ± 7.03	NA	NA
	trab. bone	NA	NA	255.33 ± 20.43	306.40 ± 30.64	60,157 ± 5,822	28,700 ± 14,707
	cortical bone	21.27 ± 6.38	55.30 ± 11.70	265.85 ± 31.90	382.82 ± 31.90	61,357 ± 3,084	69,545 ± 12,548

Table 17

Isotopic Activity Ratios in Steer Tissues and Soil from Pocos de Caldas

Location	Tissue type	Th-232/Th-230	U-234/U-238	Ra-228/Ra-226	Th-230/U-234	Ra-226/Th-230	Ra-228/Th-232
Farm 1	flesh	2.25	1.02	3.38	0.59	10	15
	kidneys	2.03	1.06	NA	0.38	NA	NA
	liver	1.08	NA	NA	NA	NA	NA
	lungs	2.18	NA	NA	NA	NA	NA
	trab. bone	NA	1.00	3.24	NA	NA	NA
	cortical bone	NA	0.97	2.62	NA	NA	NA
	• soil PCS-11	2.93	1.14	2.54	0.69	1.23	1.06
Farm 2	flesh	1.49	0.94	1.88	0.76	4	5
	kidneys	1.45	1.09	NA	0.12	NA	NA
	lungs	1.68	NA	NA	NA	NA	NA
	trab. bone	NA	0.98	2.03	NA	NA	NA
	cortical bone	NA	1.18	1.15	NA	NA	4,675
	• soil PCS-6	1.36	NA	1.52	NA	1.33	1.49
Farm 10	flesh	1.50	1.09	1.75	0.56	9	10
	kidneys	1.21	1.29	NA	0.06	NA	NA
	trab. bone	NA	1.20	0.48	NA	NA	NA
	cortical bone	0.38	1.44	1.13	0.14	1,110	3,270
	• soil PCS-24	1.18	NA	1.18	NA	1.14	1.14

Table 18

Mass Concentrations in Steer Tissues (µg/kg fresh wt ± SD) from Pocos de Caldas

Location	Tissue type	La ± SD	Ce ± SD	Nd ± SD	Sm ± SD	Th-232 ± SD	U-238 ± SD
Farm 1	flesh	5.97 ± 0.28	43.73 ± 2.00	2.07 ± 1.01	0.22 ± 0.09	1.65 ± 0.09	0.40 ± 0.02
	kidneys	23.20 ± 1.50	93.60 ± 6.70	2.30 ± 5.70	0.67 ± 0.33	5.96 ± 0.46	2.40 ± 0.21
	liver	20.20 ± 0.80	42.60 ± 2.30	4.90 ± 2.00	0.71 ± 0.28	0.87 ± 0.08	NA
	lungs	18.34 ± 1.17	71.57 ± 4.67	1.46 ± 2.93	0.36 ± 0.26	5.84 ± 0.29	NA
	trab. bone	42.67 ± 3.74	142.03 ± 23.67	10.59 ± 29.28	-2.80 ± 1.87	NA	2.25 ± 0.37
	cortical bone	16.82 ± 3.74	46.73 ± 24.92	-5.30 ± 28.97	-1.56 ± 4.36	NA	3.00 ± 0.47
Farm 2	flesh	10.78 ± 0.40	98.66 ± 3.69	6.22 ± 1.03	0.77 ± 0.11	5.32 ± 0.18	1.62 ± 0.09
	kidneys	22.90 ± 1.40	38.10 ± 4.00	NA	0.91 ± 0.31	5.05 ± 0.46	8.83 ± 0.54
	lungs	14.50 ± 0.70	85.60 ± 4.30	5.47 ± 1.45	0.89 ± 0.13	6.79 ± 0.37	NA
	trab. bone	53.89 ± 3.75	86.70 ± 18.75	NA	-3.98 ± 1.87	NA	7.46 ± 0.63
	cortical bone	44.81 ± 3.88	80.66 ± 20.91	40.33 ± 32.86	4.18 ± 2.39	2.19 ± 2.74	9.87 ± 0.90
Farm 10	flesh	6.08 ± 0.27	29.87 ± 1.42	5.22 ± 1.51	-0.02 ± 0.11	1.93 ± 0.09	0.69 ± 0.03
	kidneys	9.00 ± 0.60	22.60 ± 2.80	NA	0.05 ± 0.23	3.12 ± 0.28	10.61 ± 0.45
	trab. bone	77.29 ± 11.04	193.23 ± 27.60	NA	NA	NA	20.73 ± 1.66
	cortical bone	40.24 ± 2.87	89.09 ± 20.12	NA	2.01 ± 2.30	5.27 ± 1.58	21.59 ± 2.59

Table 19

Isotopic Activity Concentrations in Pig Tissues (mBq/kg fresh wt. ± SD) from Pocos de Caldas

Location	Tissue type	Th-232 ± SD	Th-230 ± SD	U-238 ± SD	U-234 ± SD	Ra-226 ± SD	Ra-228 ± SD
Farm 1	flesh	10.18 ± 0.48	3.03 ± 0.22	3.85 ± 0.37	3.70 ± 0.33	11 ± 0	133 ± 7
	trab. bone	86.97 ± 6.29	32.04 ± 4.01	154.49 ± 11.44	160.21 ± 11.44	223 ± 46	1,774 ± 458
	cortical bone	55.78 ± 6.97	27.89 ± 5.42	178.19 ± 15.49	154.95 ± 15.49	651 ± 70	3,254 ± 1,162
Farm 2-a	flesh	4.55 ± 0.26	3.96 ± 0.22	NA	NA	NA	NA
	bone	17.15 ± 3.03	25.23 ± 3.03	141.27 ± 20.18	131.18 ± 20.18	NA	NA
Farm 2-b	flesh	8.51 ± 0.41	3.00 ± 0.22	3.48 ± 0.37	3.52 ± 0.41	7 ± 1	137 ± 4
	trab. bone	30.51 ± 2.84	13.48 ± 2.13	44.70 ± 7.09	43.99 ± 7.80	341 ± 14	<1348
	cortical bone	16.74 ± 2.09	9.07 ± 1.40	41.86 ± 6.98	41.86 ± 6.98	398 ± 70	<2163
Farm 10	flesh	7.40 ± 0.37	1.48 ± 0.37	2.74 ± 0.15	2.63 ± 0.15	22 ± 7	93 ± 11
	liver	1.04 ± 0.19	3.70 ± 0.41	1.59 ± 0.33	1.78 ± 0.33	NA	NA
	lungs	6.11 ± 0.48	3.26 ± 0.41	3.70 ± 0.37	3.33 ± 0.37	NA	NA
	trab. bone	11.41 ± 2.45	6.52 ± 2.45	37.50 ± 5.71	41.57 ± 5.71	236 ± 49	<1712
	cortical bone	6.45 ± 1.80	7.20 ± 2.94	142.20 ± 18.96	132.72 ± 18.96	777 ± 209	<1612

Table 20

Isotopic Activity Ratios in Pig Tissues and Soil from Pocos de Caldas

Location	Tissue type	Th-232/Th-230	U-234/U-238	Ra-228/Ra-226	Th-230/U-234	Ra-226/Th-230	Ra-228/Th-232
Farm 1	flesh	3.35	0.96	12.00	0.82	4	13
	trab. bone	2.71	1.04	7.95	0.20	7	20
	cortical bone	2.00	0.87	5.00	0.18	23	58
	• soil PCS-11	2.93	1.14	2.54	0.69	1.23	1.06
Farm 2-a	flesh	1.15	NA	NA	NA	NA	NA
	bone	0.68	0.93	NA	0.19	NA	NA
	• soil PCS-6	1.36	NA	1.52	NA	1.33	1.49
Farm 2-b	flesh	2.84	1.01	18.50	0.85	2	16
	trab. bone	2.26	0.98	NA	0.31	25	NA
	cortical bone	1.85	1.00	NA	0.22	44	NA
	• soil PCS-6	1.36	NA	1.52	NA	1.33	1.49
Farm 10	flesh	5.00	0.96	4.17	0.56	15	13
	liver	0.28	1.12	NA	2.08	NA	NA
	lungs	1.88	0.90	NA	0.98	NA	NA
	trab. bone	1.75	1.11	NA	0.16	36	NA
	cortical bone	0.89	0.93	NA	0.05	108	NA
	• soil PCS-24	1.18	NA	1.18	NA	1.14	1.14

Table 21

Mass Concentrations in Pig Tissues (µg/kg fresh wt ± SD) from Pocos de Caldas

Location	Tissue type	La ± SD	Ce ± SD	Nd ± SD	Sm ± SD	Th-232 ± SD	U-238 ± SD
Farm 1	flesh	6.30 ± 0.37	24.45 ± 1.49	2.28 ± 2.08	0.38 ± 0.06	2.52 ± 0.12	0.31 ± 0.03
	trab. bone	37.11 ± 3.09	327.85 ± 23.20	NA	2.78 ± 1.55	21.57 ± 1.56	12.54 ± 0.93
	cortical bone	33.50 ± 2.09	364.34 ± 23.03	-5.44 ± 22.82	-1.68 ± 2.09	13.83 ± 1.73	14.47 ± 1.26
Farm 2-a	flesh	3.71 ± 0.23	9.24 ± 0.68	1.95 ± 1.14	0.33 ± 0.05	1.13 ± 0.06	NA
	bone	43.64 ± 5.45	111.82 ± 32.73	24.55 ± 40.91	2.45 ± 2.45	4.25 ± 0.75	11.47 ± 1.64
Farm 2-b	flesh	4.92 ± 0.30	18.41 ± 1.22	1.53 ± 1.36	0.11 ± 0.05	2.11 ± 0.10	0.28 ± 0.03
	trab. bone	19.18 ± 3.84	57.53 ± 17.26	15.34 ± 21.09	2.49 ± 2.11	7.57 ± 0.70	3.63 ± 0.58
	cortical bone	16.97 ± 1.89	43.37 ± 13.20	24.51 ± 18.86	2.45 ± 1.32	4.15 ± 0.52	3.40 ± 0.57
Farm 10	flesh	4.02 ± 0.16	10.85 ± 0.64	2.30 ± 0.65	0.20 ± 0.05	1.84 ± 0.09	0.22 ± 0.01
	liver	1.48 ± 0.29	0.64 ± 1.61	0.80 ± 1.85	0.08 ± 0.20	0.26 ± 0.05	0.13 ± 0.03
	lungs	5.70 ± 0.40	12.70 ± 1.80	1.40 ± 2.00	0.37 ± 0.30	1.51 ± 0.12	0.30 ± 0.03
	trab. bone	50.67 ± 4.41	79.31 ± 19.83	NA	2.42 ± 2.64	2.83 ± 0.61	3.04 ± 0.46
	cortical bone	7.69 ± 3.07	15.12 ± 20.50	15.12 ± 20.75	-1.28 ± 3.33	1.60 ± 0.45	11.55 ± 1.54

Table 22

Isotopic Activity Concentrations in Chicken Tissues (mBq/kg fresh wt. ± SD) from Pocos de Caldas

Location	Tissue type	Th-232 ± SD	Th-230 ± SD	U-238 ± SD	U-234 ± SD	Ra-226 ± SD	Ra-228 ± SD
Farm 1	flesh	27.71 ± 1.04	5.22 ± 0.41	6.03 ± 0.52	6.44 ± 0.56	37 ± 1	141 ± 4
	bone	71.76 ± 6.52	NA	221.79 ± 13.05	260.93 ± 13.05	11,677 ± 1,174	39,922 ± 7,632
Farm 2	flesh	40.70 ± 1.11	10.92 ± 0.52	13.51 ± 0.96	12.91 ± 0.93	59 ± 0	289 ± 52
	bone	114.19 ± 16.31	65.25 ± 8.16	203.91 ± 24.47	220.23 ± 32.63	11,664 ± 897	21,044 ± 3,752
Farm 10	flesh	14.06 ± 0.74	12.95 ± 0.74	17.02 ± 0.74	15.91 ± 0.74	163 ± 4	355 ± 11
	bone	25.26 ± 13.07	NA	304.89 ± 26.13	322.31 ± 26.13	38,764 ± 2,004	47,475 ± 6,098

Table 23

Isotopic Activity Ratios in Chicken Tissues and Soil from Pocos de Caldas

Location	Tissue type	Th-232/Th-230	U-234/U-238	Ra-228/Ra-226	Th-230/U-234	Ra-226/Th-230	Ra-228/Th-232
Farm 1	flesh	5.31	1.07	3.76	0.81	7	5
	bone	NA	1.18	3.42	NA	NA	556
	• soil PCS-11	2.93	1.14	2.54	0.69	1.23	1.06
Farm 2	flesh	3.73	0.96	4.88	0.85	5	7
	bone	1.75	1.08	1.80	0.30	179	184
	• soil PCS-6	1.36	NA	1.52	NA	1.33	1.49
Farm 10	flesh	1.09	0.93	2.18	0.81	13	25
	bone	NA	1.06	1.22	NA	NA	1,879
	• soil PCS-24	1.18	NA	1.18	NA	1.14	1.14

Table 24

Mass Concentrations in Chicken Tissues (µg/kg fresh wt ± SD) from Pocos de Caldas

Location	Tissue type	La ± SD	Ce ± SD	Nd ± SD	Sm ± SD	Th-232 ± SD	U-238 ± SD
Farm 1	flesh	14.90 ± 0.90	43.40 ± 2.80	2.00 ± 1.20	0.53 ± 0.10	6.87 ± 0.26	0.49 ± 0.04
	bone	37.02 ± 3.53	208.04 ± 19.39	22.92 ± 31.73	NA	17.80 ± 1.62	18.01 ± 1.06
Farm 2	flesh	13.90 ± 0.90	52.80 ± 3.40	4.20 ± 1.00	0.60 ± 0.10	10.09 ± 0.28	1.10 ± 0.08
	bone	32.85 ± 4.19	123.45 ± 22.71	29.32 ± 47.62	2.42 ± 1.76	28.32 ± 4.05	16.56 ± 1.99
Farm 10	flesh	18.06 ± 0.71	42.92 ± 2.29	13.14 ± 1.66	1.32 ± 0.18	3.49 ± 0.18	1.38 ± 0.06
	bone	54.15 ± 3.53	230.73 ± 18.83	29.19 ± 28.96	4.24 ± 1.65	6.27 ± 3.24	24.76 ± 2.12

Table 25

Summary of Radionuclide and REE Concentrations in Muscle and Bone of Farm Animals Raised in Poços de Caldas

	mBq kg^{-1} fresh (mean±SD)						μg kg^{-1} fresh (mean±SD)	
	Th-232	Th-230	U-238	U-234	Ra-226	Ra-228	La	Ce
Muscle								
steer	12.0±8.2	7.5±6.1	11.1±7.9	11.1±7.1	44±14	96±17	7.6±2.7	57.4±36.4
pig	7.7±2.4	2.9±1.0	3.4±0.6	3.3±0.6	13±8	121±24	4.7±1.2	15.7±7.1
chicken	27.5±13.3	9.7±4	12.2±5.6	11.8±4.8	86±67	262±110	15.6±2.2	46.3±5.6
Bone								
steer	NA[1]	NA	133±105	164±148	34,467±21,733	45,617±15,951	46±20	106±52
pig	32±29	17±11	106±61	101±56	439±225	NA	30±16	143±142
chicken	70±44	NA	244±54	268±51	20,733±15,646	36,133±13,646	41±11	187±57

[1] NA refers to not analyzed.

FIGURE 1

LOCATION OF SELECTED FARMS IN THE POCOS DE CALDAS PLATEAU

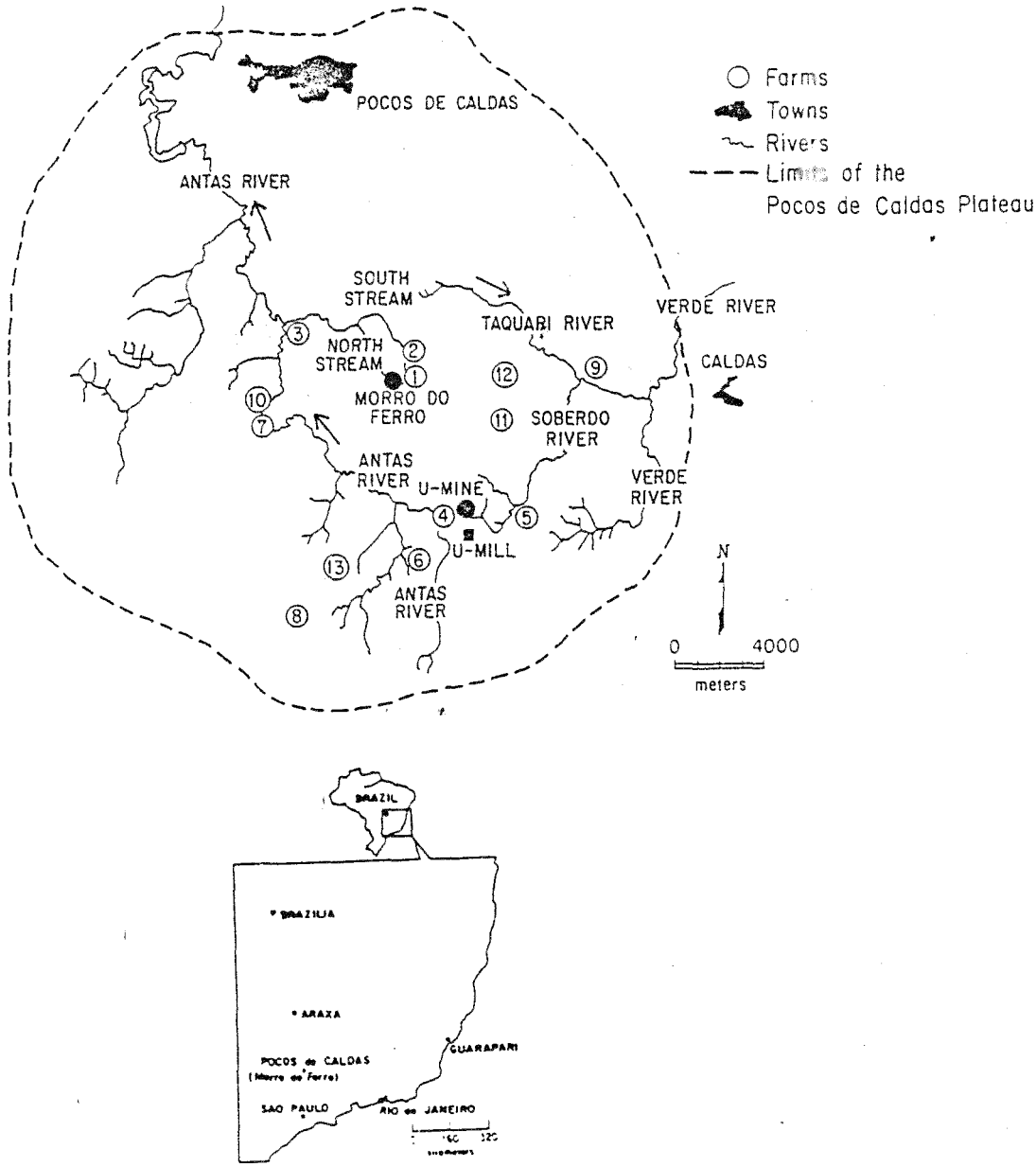


FIGURE 2

Tissue / Soil Concentration Ratios for ^{226}Ra, La, and ^{232}Th in Beef Cattle Raised in New York

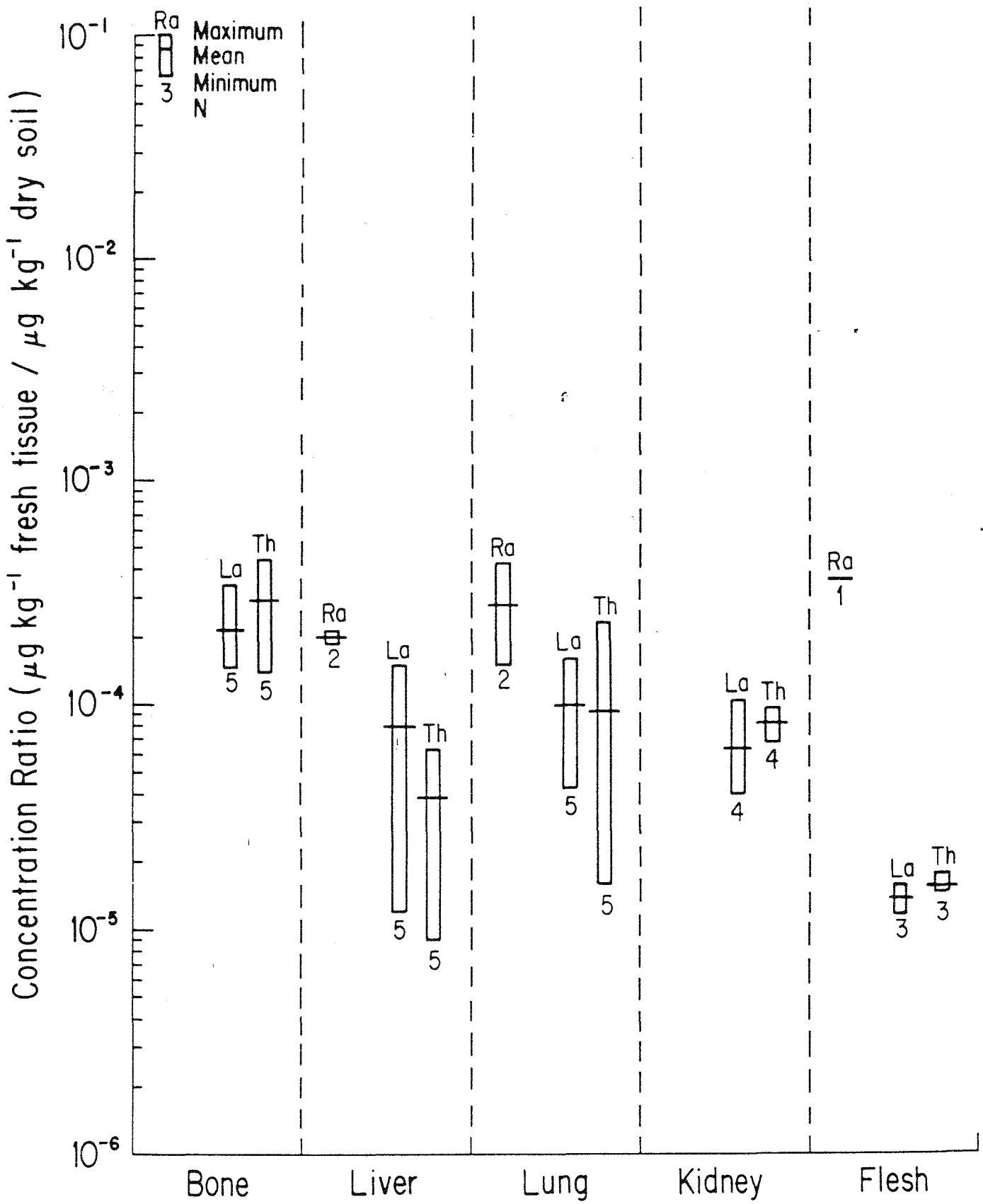


FIGURE 3

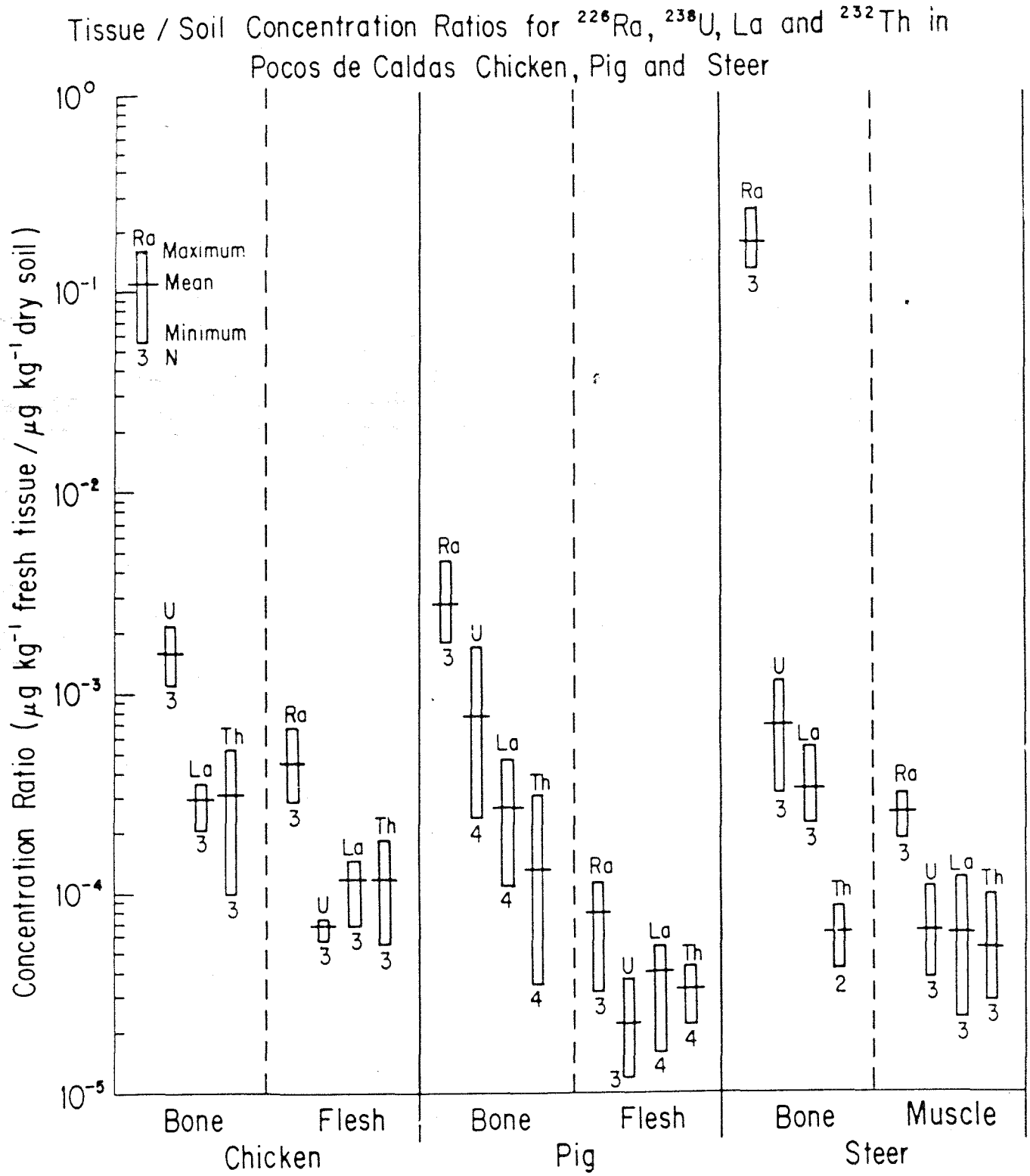
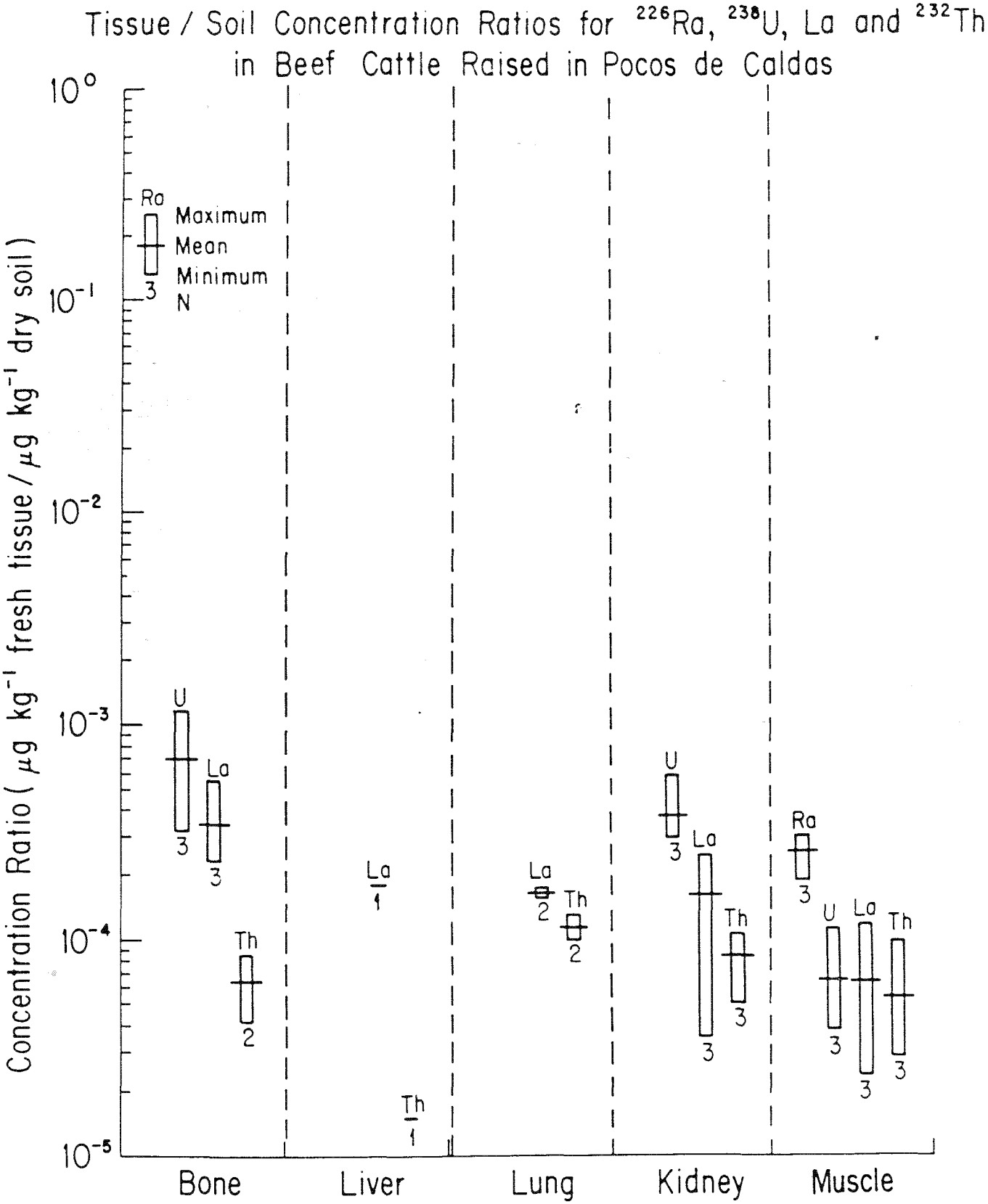

Tissue / Soil Concentration Ratios for ^{226}Ra, ^{238}U, La and ^{232}Th in Pocos de Caldas Chicken, Pig and Steer
Concentration Ratio ($\mu g\ kg^{-1}$ fresh tissue / $\mu g\ kg^{-1}$ dry soil)
10^{0}
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
Ra
Maximum
Mean
Minimum
N
U
La
Th
Bone
Flesh
Chicken
Pig
Steer
Muscle

FIGURE 4


Tissue / Soil Concentration Ratios for 226Ra, 238U, La and 232Th
in Beef Cattle Raised in Pocos de Caldas
Concentration Ratio (μg kg⁻¹ fresh tissue / μg kg⁻¹ dry soil)
10⁰
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
Ra
Maximum
Mean
Minimum
N
3
U
La
Th
Bone
Liver
Lung
Kidney
Muscle

Animal Tissue to Soil Concentration Ratios (mBq per kg fresh sample/mBq per kg dry soil) for Pocos de Caldas Steer

Location	Tissue type	Th-232 ± SD	U-238 ± SD	Ra-226 ± SD	Ra-228 ± SD	Th-230 ± SD
Farm 1	flesh	2.90E-05 ± 2.22E-06	4.93E-05 ± 2.76E-07	3.08E-04 ± 3.84E-05	4.09E-04 ± 1.54E-04	3.77E-05 ± 6.02E-06
	kidneys	1.05E-04 ± 9.75E-06	2.97E-04 ± 2.40E-06	NA	NA	1.51E-04 ± 2.41E-05
	liver	1.53E-05 ± 1.66E-06	NA	NA	NA	4.15E-05 ± 6.26E-06
	lungs	1.02E-04 ± 7.45E-06	NA	NA	NA	1.38E-04 ± 1.69E-05
	trab. bone	NA	2.77E-04 ± 4.26E-06	1.14E-01 ± 1.30E-02	1.45E-01 ± 3.75E-02	NA
	cortical bone	NA	3.70E-04 ± 5.32E-06	1.50E-01 ± 2.24E-02	1.55E-01 ± 1.17E-01	NA
Farm 2	flesh	1.02E-04 ± 8.63E-06	1.10E-04 ± 2.33E-05	2.86E-04 ± 4.13E-05	3.53E-04 ± 5.17E-05	9.29E-05 ± 8.17E-06
	kidneys	9.71E-05 ± 1.16E-05	6.01E-04 ± 1.28E-04	NA	NA	9.05E-05 ± 1.15E-05
	lungs	1.31E-04 ± 1.23E-05	NA	NA	NA	1.05E-04 ± 1.03E-05
	trab. bone	NA	5.08E-04 ± 1.12E-04	1.45E-01 ± 1.70E-02	1.94E-01 ± 4.32E-02	NA
	cortical bone	4.22E-05 ± 5.28E-05	6.72E-04 ± 1.50E-04	1.73E-01 ± 3.39E-02	1.31E-01 ± 2.93E-02	NA
Farm 10	flesh	3.12E-05 ± 1.77E-06	3.77E-05 ± 3.87E-06	1.85E-04 ± 3.29E-05	2.73E-04 ± 4.62E-05	2.46E-05 ± 1.94E-06
	kidneys	5.06E-05 ± 4.73E-06	5.79E-04 ± 5.91E-05	NA	NA	4.92E-05 ± 5.52E-06
	trab. bone	NA	1.13E-03 ± 1.39E-04	2.50E-01 ± 2.88E-02	1.01E-01 ± 5.24E-02	NA
	cortical bone	8.55E-05 ± 2.58E-05	1.18E-03 ± 1.79E-04	2.55E-01 ± 2.04E-02	2.44E-01 ± 4.94E-02	2.63E-04 ± 5.62E-05

Animal Tissue to Soil Concentration Ratios (µg per kg fresh sample/µg per kg dry soil) for Pocos de Caldas Steer

Location	Tissue type	La ± SD	Ce ± SD	Nd ± SD	Sm ± SD
Farm 1	flesh	5.28E-05 ± 3.41E-06	8.78E-05 ± 5.71E-06	4.81E-05 ± 2.44E-05	2.62E-05 ± 1.09E-05
	kidneys	2.05E-04 ± 1.61E-05	1.88E-04 ± 1.60E-05	5.35E-05 ± 1.33E-04	7.98E-05 ± 3.97E-05
	liver	1.79E-04 ± 1.06E-05	8.55E-05 ± 6.08E-06	1.14E-04 ± 4.92E-05	8.45E-05 ± 3.39E-05
	lungs	1.62E-04 ± 1.26E-05	1.44E-04 ± 1.15E-05	3.40E-05 ± 6.83E-05	4.29E-05 ± 3.11E-05
	trab. bone	3.78E-04 ± 3.71E-05	2.85E-04 ± 4.93E-05	2.46E-04 ± 6.82E-04	-3.34E-04 ± 2.24E-04
	cortical bone	1.49E-04 ± 3.37E-05	9.38E-05 ± 5.02E-05	-1.23E-04 ± 6.74E-04	-1.85E-04 ± 5.19E-04
Farm 2	flesh	1.17E-04 ± 1.59E-05	1.29E-04 ± 7.38E-06	1.88E-04 ± 4.23E-05	1.75E-04 ± 2.96E-05
	kidneys	2.49E-04 ± 3.59E-05	4.99E-05 ± 5.66E-06	NA	2.07E-04 ± 7.29E-05
	lungs	1.58E-04 ± 2.19E-05	1.12E-04 ± 7.42E-06	1.66E-04 ± 5.06E-05	2.02E-04 ± 3.48E-05
	trab. bone	5.86E-04 ± 8.66E-05	1.13E-04 ± 2.50E-05	NA	-9.05E-04 ± 4.34E-04
	cortical bone	4.87E-04 ± 7.63E-05	1.06E-04 ± 2.78E-05	1.22E-03 ± 1.01E-03	9.51E-04 ± 5.50E-04
Farm 10	flesh	2.38E-05 ± 1.47E-06	3.34E-05 ± 2.16E-06	4.79E-05 ± 1.41E-05	-1.71E-06 ± 9.40E-06
	kidneys	3.52E-05 ± 2.79E-06	2.53E-05 ± 3.32E-06	NA	4.27E-06 ± 1.97E-05
	trab. bone	3.02E-04 ± 4.50E-05	2.16E-04 ± 3.23E-05	NA	NA
	cortical bone	1.57E-04 ± 1.31E-05	9.97E-05 ± 2.29E-05	NA	1.72E-04 ± 1.97E-04

Animal Tissue to Soil Concentration Ratios (mBq per kg fresh sample/mBq per kg dry soil) for Pocos de Caldas Pigs

Location	Tissue type	Th-232 ± SD	U-238 ± SD	Ra-226 ± SD	Ra-228 ± SD	Th-230 ± SD
Farm 1	flesh	4.43E-05 ± 3.13E-06	3.86E-05 ± 3.43E-07	1.15E-04 ± 1.37E-05	5.45E-04 ± 1.56E-04	3.87E-05 ± 4.76E-06
	trab. bone	3.78E-04 ± 3.39E-05	1.55E-03 ± 1.06E-05	2.32E-03 ± 5.45E-04	7.26E-03 ± 5.09E-03	4.08E-04 ± 6.52E-05
	cortical bone	2.43E-04 ± 3.29E-05	1.79E-03 ± 1.44E-05	6.76E-03 ± 1.06E-03	1.33E-02 ± 1.25E-02	3.56E-04 ± 7.76E-05
Farm 2-a	flesh	2.17E-05 ± 2.08E-06	NA	NA	NA	2.55E-05 ± 2.31E-06
	bone	8.18E-05 ± 1.57E-05	7.80E-04 ± 1.94E-04	NA	NA	1.62E-04 ± 2.27E-05
Farm 2-b	flesh	4.06E-05 ± 3.68E-06	1.92E-05 ± 4.42E-06	3.57E-05 ± 4.41E-06	4.35E-04 ± 5.80E-05	1.93E-05 ± 1.98E-06
	trab. bone	1.46E-04 ± 1.76E-05	2.47E-04 ± 6.38E-05	1.64E-03 ± 1.37E-04	NA	8.67E-05 ± 1.50E-05
	cortical bone	7.99E-05 ± 1.17E-05	2.31E-04 ± 6.09E-05	1.92E-03 ± 3.64E-04	NA	5.84E-05 ± 9.90E-06
Farm 10	flesh	2.97E-05 ± 1.75E-06	1.21E-05 ± 1.30E-06	9.23E-05 ± 3.13E-05	3.25E-04 ± 4.89E-05	7.03E-06 ± 1.77E-06
	liver	4.16E-06 ± 7.55E-07	7.05E-06 ± 1.61E-06	NA	NA	1.76E-05 ± 2.02E-06
	lungs	2.45E-05 ± 2.08E-06	1.64E-05 ± 2.24E-06	NA	NA	1.55E-05 ± 2.00E-06
	trab. bone	4.59E-05 ± 9.93E-06	1.66E-04 ± 2.96E-05	9.83E-04 ± 2.12E-04	NA	3.10E-05 ± 1.17E-05
	cortical bone	2.59E-05 ± 7.28E-06	6.30E-04 ± 1.02E-04	3.23E-03 ± 8.90E-04	NA	3.42E-05 ± 1.40E-05

Animal Tissue to Soil Concentration Ratios (µg per kg fresh sample/µg per kg dry soil) for Pocos de Caldas Pigs

Location	Tissue type	La ± SD	Ce ± SD	Nd ± SD	Sm ± SD
Farm 1	flesh	5.58E-05 ± 4.10E-06	4.91E-05 ± 3.75E-06	5.30E-05 ± 4.89E-05	4.52E-05 ± 7.41E-06
	trab. bone	3.28E-04 ± 3.10E-05	6.58E-04 ± 5.56E-05	NA	3.31E-04 ± 1.86E-04
	cortical bone	2.96E-04 ± 2.27E-05	7.32E-04 ± 5.73E-05	-1.27E-04 ± -5.31E-04	-1.99E-04 ± 2.50E-04
Farm 2-a	flesh	4.03E-05 ± 5.82E-06	1.21E-05 ± 1.03E-06	5.91E-05 ± 3.57E-05	7.50E-05 ± 1.33E-05
	bone	4.74E-04 ± 8.57E-05	1.46E-04 ± 4.33E-05	7.44E-04 ± 1.24E-03	5.58E-04 ± 5.60E-04
Farm 2-b	flesh	5.35E-05 ± 7.70E-06	2.41E-05 ± 1.91E-06	4.64E-05 ± 4.18E-05	2.57E-05 ± 1.20E-05
	trab. bone	2.08E-04 ± 4.98E-05	7.53E-05 ± 2.28E-05	4.65E-04 ± 6.43E-04	5.67E-04 ± 4.82E-04
	cortical bone	1.84E-04 ± 3.16E-05	5.68E-05 ± 1.75E-05	7.43E-04 ± 5.82E-04	5.57E-04 ± 3.04E-04
Farm 10	flesh	1.57E-05 ± 9.20E-07	1.21E-05 ± 8.90E-07	2.11E-05 ± 6.08E-06	1.71E-05 ± 4.36E-06
	liver	5.78E-06 ± 1.16E-06	7.16E-07 ± 1.80E-06	7.34E-06 ± 1.70E-05	6.84E-06 ± 1.71E-05
	lungs	2.23E-05 ± 1.83E-06	1.42E-05 ± 2.11E-06	1.28E-05 ± 1.84E-05	3.16E-05 ± 2.57E-05
	trab. bone	1.98E-04 ± 1.92E-05	8.87E-05 ± 2.25E-05	NA	2.07E-04 ± 2.26E-04
	cortical bone	3.00E-05 ± 1.21E-05	1.69E-05 ± 2.29E-05	1.39E-04 ± 1.91E-04	-1.09E-04 ± 2.85E-04

Animal Tissue to Soil Concentration Ratios (mBq per kg fresh sample/mBq per kg dry soil) for Pocos de Caldas Chickens

Locatior	Tissue type	Th-232 ± SD	U-238 ± SD	Ra-226 ± SD	Ra-228 ± SD	Th-230 ± SD
Farm 1	flesh	1.21E-04 ± 7.78E-06	6.05E-05 ± 4.80E-07	3.88E-04 ± 4.59E-05	5.76E-04 ± 1.51E-04	6.65E-05 ± 8.39E-06
	bone	3.12E-04 ± 3.28E-05	2.22E-03 ± 1.22E-05	1.21E-01 ± 1.85E-02	1.63E-01 ± 8.92E-02	NA
Farm 2	flesh	1.94E-04 ± 1.58E-05	7.46E-05 ± 1.61E-05	2.86E-04 ± 2.08E-05	9.18E-04 ± 2.04E-04	7.02E-05 ± 6.02E-06
	bone	5.45E-04 ± 8.84E-05	1.13E-03 ± 2.67E-04	5.63E-02 ± 5.95E-03	6.69E-02 ± 1.48E-02	4.20E-04 ± 6.05E-05
Farm 10	flesh	5.65E-05 ± 3.45E-06	7.54E-05 ± 7.73E-06	6.77E-04 ± 4.49E-05	1.25E-03 ± 1.20E-04	6.15E-05 ± 4.07E-06
	bone	1.02E-04 ± 5.26E-05	1.35E-03 ± 1.71E-04	1.61E-01 ± 1.31E-02	1.67E-01 ± 2.63E-02	NA

Animal Tissue to Soil Concentration Ratios (µg per kg fresh sample/µg per kg dry soil) for Pocos de Caldas Chickens

Location	Tissue type	La ± SD	Ce ± SD	Nd ± SD	Sm ± SD
Farm 1	flesh	1.32E-04 ± 9.87E-06	8.71E-05 ± 6.91E-06	4.65E-05 ± 2.87E-05	6.31E-05 ± 1.27E-05
	bone	3.28E-04 ± 3.12E-05	4.18E-04 ± 4.35E-05	5.33E-04 ± 7.42E-04	NA
Farm 2	flesh	1.51E-04 ± 9.78E-06	6.91E-05 ± 5.36E-06	1.27E-04 ± 3.59E-05	1.36E-04 ± 2.59E-05
	bone	3.57E-04 ± 4.55E-05	1.62E-04 ± 3.05E-05	8.88E-04 ± 1.45E-03	5.51E-04 ± 4.04E-04
Farm 10	flesh	7.05E-05 ± 4.11E-06	4.80E-05 ± 3.31E-06	1.21E-04 ± 1.66E-05	1.13E-04 ± 1.64E-05
	bone	2.12E-04 ± 1.38E-05	2.58E-04 ± 2.39E-05	2.68E-04 ± 2.66E-04	3.62E-04 ± 1.42E-04

PART III

Physicochemical Studies of the Thorium, Rare Earth Element Ore Body at Morro do Ferro

Part III: Physicochemical Studies of the Thorium, Rare Earth Element Ore Body at Morro do Ferro

Abstract

This section summarizes our findings to date on the distribution and mobilization of Th-232, light rare earth elements (LREE), U-238 and Ra-228 in the MF basin. Estimates of first order, present day, mobilization rate constants resulting from ground water solubilization and seepage/stream transport are calculated using revised inventory estimates for the occurrence of these elements in the ore body and annual flux estimates for the transport of these elements away from the ore body.

New data are presented on uranium, thorium and actinium series isotopic disequilibrium measurements in cores, ground and surface waters. Preliminary measurements of core samples taken in the mineralized zone show a strong decline in the Th-230/U-234 ratios from the extremely high grade (5.7% Th and 13% LREE), hydrothermally altered and deeply weathered surface samples (ratios of 2.5 to 3.5), to samples at depth (ratio of 0.87), indicating loss of U in the oxidizing surface environment and possible accumulation at depth.

Using sequential extractants to investigate the partitioning of Th and LREE's among certain chemical phases in the ore (eg, exchangable, organic bound, carbonate bound, bound to Fe-Mn oxihydroxides, and matrix bound), preliminary data indicate that up to 50% of the Th and LREE's in some samples is associated with the reductant-soluble, Fe-Mn oxihydroxides. In general however, more than 50% of the total content of these elements was not solubilized with the extractant solutions used. Only minor percentages were leached from the remaining phase extractants.

Data is also presented in the Appendix to Part III which shows that Th concentrations in prefiltered percolation and ground waters is highly correlated with colloidal humic acid concentration, defined as that fraction of the dissolved organic carbon which passes the 0.45μ prefilter but is retained by a 1,000 molecular weight unit ultrafilter. Indirect evidence exists which implies that of the water samples analyzed herein, inorganic complexation of Th plays only a very minor role in Th

mobilization from the ore body.

I.Introduction to Part III

The final section of this report summarizes our findings on the distribution and mobilization of Th and REE's in the MF ore body, the association of these elements with different chemical seperates in ore, surface and ground water, and the results of uranium, thorium and actinium-series disequilibrium measurements in water and ore. The study was initiated because the near-surface, relatively undisturbed, Th-REE deposit at Morro do Ferro (MF) presents an unusual opportunity to gain information relevant to understanding some of the processes which may play a role in the far-field migration of long-lived transuranic elements of importance in high-level nuclear waste management. As described in detail by Krauskopf (1986), quadravalent Th is analogous in its geochemical behavior to Pu(IV), the oxidation state in which Pu exists under many chemical conditions, while the light, trivalent REE's, particularly Nd and also La, are good analogues for the trivalent transuranics Am and Cm.

A. Background

The geology of the MF and of the Pocos de Caldas plateau, which contains the MF near its center, has been previously described (Ellert, 1959, Frayha, 1962, Wedow, 1967, Bushee, 1971, Almeida, 1977 and Ulbrich, 1983) with the findings summarized by the IPT (1984) and by Barretto and Fugimori (1986). The Pocos de Caldas plateau, which is roughly circular and about 35 km in diameter, is believed to be a deeply eroded caldera. Age determinations by Bushee show that intrusion of molten rock took place over a long period: phonolites and tinguaites give ages between 75 and 87 million years, and foyaites 63 to 64 million years. Thus the body of alkalic igneous rocks was built up by piecemeal additions over some 20 million years towards the end of the Cretaceous. The underlying rock of the 140m high MF hill shows extensive alteration, due in part to weathering and in part to hydrothermal activity. Material fresh enough for identification is tinguaite (fine grained nepheline syenite), partly massive and partly brecciated. The only rock outcrops at MF are magnetite, which occurs as dykes (1-3m thick) running subparallel to the south face of the hill and as finely dispersed veinlets which are found throughout the hill.

Identification of the host minerals containing Th and REE's has traditionally been very difficult because of the extensive alteration and weathering producing finely dispersed grains within the potassic host rock. Barretto and Fugimori have reported that the primary radioactive, REE minerals formed at time of emplacement of the alkaline rock or brought in later during hydrothermal periods, include a Th-rich, REE-silicate, which is relatively more susceptible to the formation of secondary radioactive minerals, than other identified primary minerals which include cheralite, monazite, microlite (pyrochlore), and zircon, all of which are refractory. Secondary minerals which have been identified include thorbastnaesite, thorianite, and cerianite.

The great majority of solid material that has been examined from drillcores penetrating the upper 50m of the hill's south face (Fig. 1), which contains the bulk of high-grade ore (> 0.1% Th or REE's) is, with the exception of that material crossing magnetite layers, composed of silt to clay size particles. Recent analysis of silty-clay sized particles from borehole MF 10 (Fig. 2) which is located on the same horizon as core SR 5 (shown in Fig. 1) and intersects some of the richest ore, indicates that kaolinite, followed by illite/sericite and goethite are the most frequently occuring minerals found in the upper 20m (Peters and Weber, 1987). Considerable amounts of gibbsite were also reported to this depth and found to at least 54m, indicating weathering at least to this depth. Alternating white and red/brown clay layers were reported in this core with a high correlation between peaks in the gamma scintillation log and the darker material in the highly mineralized first 11 meters. The varying colors were attributed to the differing amounts of iron phases present (geothite, hematite and amorphous hydrous ferric oxides) and most notably, to the presence of Mn-oxides in the red-brown and brown layers. Since the occurrence of primary and secondary Th minerals was not notably different between layers of differing colors, these authors and others before them, have attributed a considerable fraction of the Th and REE content to amorphous complexes absorbed on the surface of Fe-Mn oxihydroxides as well as on clay mineral surfaces.

Whole-rock composition measurements of the high-grade Th-REE alteration

product (Miekeley et. al., 1982) show low amounts (in %) of SiO_2 (19), K_2O (2.1), Na_2O (0.06), MgO (0.21), P_2O_5 (0.65) and reduced iron (FeO = 0.6) indicating a high degree of leaching. Oxidation products Fe_2O_3 (22.4), Al_2O_3 (26.6) and low mobility elements (Th + Ti + REE oxides ≈ 12%) are enriched confirming the dominant oxidizing conditions and the subsequent enrichment of these immobile elements.

Rainfall on the P. C. plateau averages 170 cm y^{-1} with about 80% of it occurring during a four month wet season (Nov. - Feb.). As shown diagramatically in Figure 2, the groundwater level is a subdued replica of the surface topography, with recharge from precipitation and discharge into a network of seepages at or near the level of the stream. Within the weathered mantle, the system has been described as an open aquifer, although a second confined or semi-confined aquifer, has been identified in the fractured rock at depth (IPT, 1984). The association between the two is currently being determined. Based on measurements (Oct. 81 thru Jan. 82) conducted on nine shallow (from 30m to 60m below ground level) boreholes drilled in 1981 (Fig. 3), the highest point of the water table during this period, which reflected long-term, average rainfall rates, was about 75m below the summit of the hill, or about 75m above the hill's base (IPT, 1982). The water table may be lower by about 20m during the dry season (Holmes, 1987). Zones of highest recharge, located near wells 2, 5 and 6 on the southeastern flank, give hydraulic conductivities in the range of 6-30 cm hr^{-1}, while typical values lie in the range of 0.04-0.2 cm hr^{-1} (IPT, 1984). Recent estimates of ground water flux are on the order of 10^{-7} $m^3m^{-2}s^{-1}$ with typical residence times on the order of 1000's of days (Chapman, 1988). This flux estimate is in good agreement with data given in Eisenbud et. al. (1984) for baseflow discharge as measured at the South Stream flume during 1981-82 (Fig. 3) eg., 0.7 m^3 min^{-1}/(ore body area, 6.2 x 10^4 m^2 x 60) = 1.9 x $10^{-7}m^3m^{-2}s^{-1}$.

Reliable hydrochemical data from ground and surface waters at the MF are unfortunately, still sparce. This is due in part, to the very dilute concentrations of major species, and in part, to questionable methods of sampling and analysis. We have however, attempted to summarize the data available as reported by several

investigators in Tables 1 and 2 for surface and ground water, respectively. The surface water data for the South Stream, which flows year-round and originates from a seepage point at the hill's base (Fig. 3), indicate acid, oxidizing waters which apparently, are extremely dilute with respect to inorganic ligands capable of complexing thorium (eg., SO_4^{-2}, F^- and PO_4^{-3}, see Figure 4). Based on Table 1 data and theoretical solubility curves for thorium (Fig. 4 and Krauskopf, 1986) at pH's typical of these waters (≈ 6), it became apparent that the concentration of Th typically observed in filtered (< 0.45μ) surface waters (0.05 μg/l or ppb, Eisenbud et. al., 1984) was much too high to be accounted for by inorganic complexation. This apparently also holds true for ground waters collected immediately below the mineralized zone (wells 10 and 11, Fig. 2 and Table 2, and other ground water sampling points) where Th concentrations have been reported to be two to 300 times that measured in surface stream waters (Lei, 1984, Miekeley et. al., 1985 and this volume). Consequently, attention has focused on Th complexation by naturally occurring, colloidal organic matter since this has been shown to occur in natural environments containing "dissolved" organic carbon at levels not unlike those seen in MF surface and ground waters (Wahlgren and Orlandini, 1982).

II. Distribution of Th, REE's Ra and U in MF Ore and Water

The longitudinal and transverse crossections of Th concentrations shown in Figure 1 were assembled from hundreds of scintillation and x-ray fluorescence (drillcores SR 2-9) measurements of solids from drillcores, surface trenches and exploratory adits penetrating the hill horizontally, that have been conducted over a 20 year period (1965-85). The XRF procedures used in our laboratory have been described in detail (Laurer et. al., 1982). That the trends shown for Th reasonably describe the light REE distribution in the mineralized region, is exemplified by the similarities in the concentration vs. depth profiles for Th and REE's shown in Figs. 5 and 6 which were obtained from XRF measurements of well cuttings from SR 5 and SR 8, respectively. We have focused on light REE's (La - Sm) purposefully because their

ionic radii more closely match that of the trivalent transuranics Am and Cm, and thus should approximate their chemical behavior more closely than the heavier REE's. That the light REE's are relatively enriched within the MF is illustrated in Figure 7, in which we show the percent abundance of the REE's which have been measured in samples from wells 8, 7 and 5. The combination of Ce + La + Nd is shown to account for 89% to 94% of the weight of the eight REE's included in the assay technique. Cerium enrichment in the near-surface samples taken from within the mineralized zone (well SR 5, Fig. 7) is striking. Based on100 XRF measurements of well cuttings from boreholes 5, 6, 7, 8 and 9, which lie in or border the mineralized zone, Ce has been shown to be more closely correlated with Th (R = 0.69) than with other light REE's (Lei et. al., 1986). These authors have stated that since Eh and pH conditons are suitable for Ce oxidation to the quadravalent state, it is perhaps this factor that results in Ce fractionation (greater retention) from other light REE's in the surface environs and provides for an observed distribution more closely resembling that of Th (IV).

The inventory of Th at the MF has been assessed at between 12,000 (Wedow, 1967) and 30,000 (Frayha, 1962) metric tons. The larger value has been adopted since this estimate includes samples taken to much greater depths (to 100m bgl or below ground level) than the Wedow estimate. Since the distribution of Th and REE concentrations within the 100 samples taken from boreholes 5-9 are best represented by lognormal plots (eg., Fig. 9), we have used the the ratio of the REE/Th geometric mean concentrations (x the Th inventory) to obtain the least biased estimator for calculating REE inventories. The geometric mean concentrations and the estimated REE inventories are given in Table 3 together with the median concentrations (for comparison) determined from 29 farm soil samples from the Pocos de Caldas plateau. The farm surface soil concentrations for all analytes are within a factor of two of their respective concentrations seen either in non-orebody well cuttings from the MF, or in samples taken from boreholes which penetrated well below the mineralized zone. Relative to Th and REE's, U is not enriched at the MF, with mean concentrations being only a factor of two greater than that determined in nearby surface soils. The geometric mean concentration in ore (34 ppm, N = 100), is however, 8 times that of the

"worldwide" median for salic rock (4 ppm, Clark et. al., 1966), while soil from the plateau is 8 times the worldwide soil average of 2 ppm (UNSCEAR, 1982). Based on U-series isotopic ratio data, we address the question in section III, of whether or not uranium previously existed at higher concentrations at the MF, such that the distribution observed now is a reflection of intense weathering and loss of U under oxidizing conditions.

A. Concentrations in water and mobilization rate estimates

Concentrations of Th, La, Ce and Ra-228 which have been measured in 20 liter evaporates of filtered (< 0.45μ) water collected from the South Stream flume (Fig. 3) during baseflow periods (average flowrate in the absence of precipitation = $54 m^3 hr^{-1}$) average (in $\mu g\ l^{-1}$) 0.053, 0.31, 0.81 and 1.7 ($pCi\ l^{-1}$), respectively (Table 4). Based on average "dissolved" concentrations and baseflow discharge (which accounts for about 85% of year-round discharge), annual baseflow transport estimates for these elements in "solution" (and,or as colloids) are presented (Table 4). Assuming that the quantities transported by the South Stream are derived from ground water solubilization of that fraction of the ore which has been in contact with ground water (eg., either saturated or subject to periodic water infiltration during annual wet seasons), first order, mobilization rate estimates (i.e., annual "dissolved" flux/inventory ratios) are calculated to fall in the range of (1-9) $x10^{-9}\ y^{-1}$ for Th and REE's and $10^{-7}\ y^{-1}$ for Ra-228. These estimates indicate that at the present time, the mean life of the Th-REE deposit, relative to ground water solubilization and stream transport, is of the order of 10^8 to 10^9 years. Order of magnitude estimates are given because of: uncertainties in the inventory estimates (perhaps a factor of 2); uncertainties that exist with respect to flow characteristics (porous, uniform flow throughout the ore body assumed in lieu of information on the magnitude of channeling, especially near dyke contacts); uncertainties due to contributions to the baseflow (and dissolved analyte concentrations) from non-orebody areas; and uncertainties in analyte solubilization from surface runoff during stormflow periods. Stream water sampled during stormflow periods (N = 20) have indicated "dissolved" Th concentrations to increase by a factor of four (Eisenbud et. al., 1984), which corresponds to a factor of two increase in the

mobilization rate considering the integrated volume of stormflow water that passes the flume during a typical flow year. The increased concentration is thought to result from higher quantites of colloidal material present during stormflow periods. Based on gross estimates of mean analyte concentrations in the mineralized zone and in non-orebody core samples taken upstream of the flume but within the drainage basin, and the relative proportions of rock volume in each zone, the relative contributions made by the orebody with respect to analyte concentrations in seepage water were estimated to lie in the range of 70 to 85% (Eisenbud et. al and Lei et. al.).

Overall transport of Th and REE's from the MF has been shown to be dominated by the erosion of particulate matter occurring during stormflow periods, such that mobilization rates calculated for this pathway are about three orders of magnitude greater than those calculated for the ground water solubilization-stream transport pathway (Lei, 1984, Eisenbud et. al. and Lei et. al.). This is certainly not surprizing considering the magnitude of suspended solids transported during a typical flow year (≈ 110 metric tons, Lei, 1984) and the relatively high values of the (particulate/dissolved) partition coefficients (K_d) which are shown in Table 5 and calculated from available data on filtered water samples in which both filtrates and filters were analyzed.

III. Natural Series Disequilibrium Measurements in Cores and Water

A. Cores

Three core samples from borehole MF 10 (Fig. 2) intersecting the surface mineralization (Nos. 10-1-1B and 10-3-1A) and nonmineralized, but hydrothermally altered/weathered rock from 55m bgl (No. 10-56-1A), were analyzed radiochemically for isotopes of Th, U and Pa (Pa-231) as well as for light REE's. The methods used for determination of these elements with the exception of protactinium, have been given in earlier Progress Reports (NYUMC, 1986) and publications (Linsalata et. al., 1986, and Linsalata et. al., 1987). As such, we only include the new method developed for protactinium (Fig. 10). All Th, U, Pa and LREE concentrations reported (± 1SD) are

based on complete sample dissolution followed by sequential chemical seperation and purification of the various fractions. Thorium, U and Pa isotopes are determined seperately by alpha spectrometry (detection limits associated with the entire prodecure for core samples are on the order of 0.1-0.5 dpm or 1.7-8.3 mBq per sample). Detection limits for water samples are about 5-10 times less than the range of values given for cores since they are processed seperately in a low background laboratory and counted using detectors reserved for low level samples. The light REE's, which are determined sequentially using an IL-200 inductively coupled plasma optical emission spectrometer (ICPOES), have detection limits on the order of 0.5-2.0 μg per sample. Conversion factors for the S. I. activity units used are 4.033×10^{-3} Bq/μg Th and 1.23×10^{-2} Bq/μg U.

Any discussion of natural series disequilibrium data revolves around the assumption that reduced U, i.e., U(IV) is, like Th(IV), chemically immobile relative to oxidized U, i.e. U(VI), which is considered relatively soluble. Since Th exists only in the quadravalent oxidation state, its solubility is unaffected by redox changes such that changes in redox environments ultimately contribute either to U loss from the solid phase (gain to the ground water) under oxidizing conditions, or gain to the solid phase (loss from solution due to precipitation and,or adsorption) under reducing conditions relative to Th. Considering U series isotopic activity ratios in rock, Th-230/U-234 ratios which significantly exceed the equilibrium value of unity are indicative of U loss while ratio values < 1 are indicative of U gain. Uranium isotopes are lost from the solid phase by bulk dissolution of the mineral, in which all U isotopes (U-238, 234 and 235) should be lost at equal rates, and, or by the preferential loss of U-234. This occurs either directly by recoil loss of U-234 during alpha particle decay, or indirectly by accelerated leaching of U-234 located within an alpha track (Fleischer, 1982a and 1982b). Thus when the rate of bulk dissolution is low, the effects of accelerated U-234 removal should be manifest as U-234/U-238 ratios < 1 in rock (and > 1 in ground water). Conversely, a high rate of bulk dissolution serves to occlude the effects of preferential U-234 removal, and 234/238 ratios tend towards unity in rock and water. In a manner similar to Th-230/U-234 systematics, Pa-231/U-235 ratios (actinium decay series) can

also be used to infer whether uranium is or has in the recent past (relative to the 32,760 year half life of Pa-231) been accumulated (Pa-231/U-235 < 1), or whether it has recently been removed (231/235 > 1) if it is assumed that Pa is relatively immobile (as we assume for Th).

Activity (Table 6) and mass (Table 8) concentration data indicate that sample 10-1-1B (analyzed in triplicate) taken at 0.5m bgl contains among the highest Th (5.6-5.8%) and REE (sum ≈ 13%) concentrations reported for the MF. Within two vertical meters of this sample, the LREE's drop by more than an order of magnitude (excluding Ce), Th and Ce by factors of 5 and 8, and U by only 30% from 50 to 36 ppm. Well below the mineralized zone, at 55m bgl, sample 10-56-1A (Table 8) indicates a further decline in Ce by a factor of two (to 3500 ppm), a striking 30 fold reduction in Th (to 370 ppm), no change in La or U, and a 2-3 fold increase in Nd, Pr and Sm relative to concentrations at 2.5m. That quite great fluctuations in Th as well as in absolute or chondrite-normalized REE concentrations exist in the upper orebody has now been shown in several profiles, however, previous samples have not shown concentration declines from surface to depth as precipitous as those reported in the top 2.5m of core MF 10. All of these samples are composed of extremely altered and weathered material, such that mineralogical distinctions between them have so far been limited to gross observations (eg. coloration, Table 6) with clay mineral determinations in progress at other laboratories.

As might be expected from the oxidizing conditions existing in the near surface environs, the first complete set of isotopic ratio results for MF ore (Table 7) indicate severe disequilibrium (loss of U) between Th-230 and its U-234 parent, with Th-230/U-234 ratios declining from 3.3 ± 0.8 (10-1-1B, N=3) at 0.5m bgl to 2.1 ± 0.6 (N=2) at 2.4m bgl, to 0.87 ± 0.07 at 55m bgl. The U-234/U-238 ratio in the upper most sample, 0.93 ± 0.07, is indicative of preferential U-234 loss, although this value and that obtained at 2.4m bgl (0.99 ± 0.10) have uncertainties large enough to encompass secular equilibrium between U isotopes, implying from this data that bulk dissolution of U is the dominant process. If this were in fact true, we would expect Pa-231/U-235 ratios to exceed unity, and this is clearly not the case based on the two values obtained

(0.96 and 0.94) in the two upper most samples. The Th-230/U-234 ratio of 0.87 ± 0.07 at 55m bgl, is indicative of recent (relative to the 75,200 year half life of Th-230) U accumulation at this depth. However, such accumulations are usually accompanied by U-234/U-238 ratios > 1, if it is assumed that this ratio in the precipitating ground water solutions was > 1. Since the U-234/U-238 ratio in rock at this depth is 0.93 ± 0.07, it may indicate that earlier uranium-bearing, precipitating ground water solutions did not contain 234/238 ratios much greater than 1.0 (implying bulk dissolution). The collection of additional data along the length of this core is clearly warrented to sort out the major mechanisms for U removal and to begin to assess the rates at which these processes have (are) occurred (ing).

B. Ground and Surface Water

Isotopic Th and U concentrations in recently collected (1987 dry season), filtered, surface (N=2) and ground water (N=2) samples taken well beneath the mineralized zone (well nos. 2 and 12 located near the hills' base, Figs. 1 and 2) are given in Table 9. Th-232 levels in surface waters (0.055 µg/l using 4.03 mBq/µg conversion) agree exactly with the earlier determined mean concentration (Table 4). It is notable that "dissolved" Th-230 activity concentrations equal (SW 05) or exceed (SW 04) those of Th-232 in surface water, since even at depth in core MF 10, Th-232/Th-230 activity ratios are about 5, and are between 2-3 in nearby farm soils (see Part II of this report). Whether or not this is caused by any preferential mobility of Th-230 (U series) relative to Th-232 (Th series) due to inclusion in different minerals, or siting at locations which are relatively more susceptible to leaching (eg., due to recoil or from precipitation / sorption of U-234) is unknown but worthy of future investigation. Surface water concentrations of U are between 0.18-0.26 µg/l (using 12.3 mBq/µg conversion) with U-234/U-238 ratios between 1.3 and 1.5.

Although wells 2 and 12 are only about 50m apart and penetrate similar upper horizons (to 20m), well 2 is shallow (20m cased with perforated PVC pipe) and is characterized by oxidizing water, while well 12 was mechanically packed off at 47m and thus represents water flowing between 47-71m bgl. No significant conductive zones are present and the hydraulic gradient is upward and vertical (Fig. 2). Based on

chemical measurements reported in Table 2, water at this depth is reducing. Uranium concentrations in these reducing waters are between 2-3 times lower than in oxidizing water sampled in well 2 or in the surface streams perhaps indicating loss due to precipitation of U(IV). Although absolute U concentrations appear to be different in the two wells, U-234/U-238 ratios are similar (1.22 and 1.25) but differ from that in the South Stream (1.50) perhaps indicating two compartment flow characteristics, with the second compartment having higher U-234/U-238 ratios. Although Th-232 concentrations appear to be notably less in well 2 (0.04 μg/l) than in well 12 (0.17), additional data on Th-232 concentrations in well 2 water (see Appendix 1 of this section) collected earlier, indicate a range between < detectable limits (about 0.002μg/l for a 40 liter sample, 95% C. I.) to 0.31 μg/l. Variability in ground water concentrations of Th is shown in that appendix to be associated with fluctuations in colloidal organic carbon concentrations (where COC is that fraction of the organic C having equivalent molecular weights > 1000 units).

IV. Speciation of Th and REE's in MF Ore

Based on the methods of Tessier et. al. (1979), partitioning of Th and REE's among five operationally-defined geochemical phases was addressed as follows. The method has previously been used for heavy trace metals (Tessier et. al.) and radionuclides (Cooper et. al. 1981) in various matricies.

I. Exchangeable fraction: 1M $MgCl_2$ at pH 7.0; 1g + 8ml at ambient temp. for 6 hours with continuous mixing.

II. Carbonate bound: 1M sodium acetate at pH 7.0; 1g + 8ml at ambient temp. for 6 hours with continuous mixing.

III. Fe-Mn oxide bound: 0.04M $NH_2OH{\cdot}HCl$ in 25% acetic acid; 1g + 20 ml at 96°C for 5 hours with occasional mixing.

IV. Organic bound: residue from (III) + 3ml 0.02M HNO_3 + 5ml 30% H_2O_2 at pH 2; 85°C for 2 hours with occasional mixing. After cooling; 5ml 3.2M ammonium acetate in

20% HNO_3, dilution to 20ml, continuous mixing for 0.5 hours.

V. Residual phase (after the sequential removal of phases I-IV): complete digestion with 5:1 HF-$HClO_4$.

Since the quantitation of Th and REE's was by XRF, the measurements had to be made with the solid phase remaining after each treatment, with the percentages of elements extracted determined by difference. Results from several different bulk samples including high-level ore from well 5, the adit (gallery, Fig. 2) and a surface trench, and lower-level material from well 7, South Stream sediments and a swampy region, are given in Figure 11. With the exception of sample muck taken from the swamp, Th, Ce and La were predominantely extracted from the reductant solublilized iron and manganese oxide fraction (III) as follows: 16 to 43% of the total in samples from the ore body; 17 to 36% from the adit; 26 to 50% from the trench; and relatively smaller and more variable percentages from non-ore body samples eg., gully, sediment bed and swamp. In general, the percentages of these elements extracted with hydroxylamine hydrochloride/acetic acid (reductant soluble) are greater in the higher concentration, ore body material. For the great majority of the samples analyzed by this technique, more than 50% of the Th, Ce and La remained in the residue, that is, was unavailable using these extractants. Removal from other geochemical phases was relatively minor compared to that available in the reductant soluble phase. It must be stressed however, that quantitative values assigned to the percentages extracted from the remaining phases have a relatively large error associated with the measurement technique used. For most of the samples analyzed, Th and the light REE's are shown to be distributed similarly among the phases extracted. In the single sample analyzed from the swamp, Th was only leached from the organic phase, with more than 80% remaining in the matrix (residual phase). The organic phase also contained significant portions of the Ce and La which were removable.

Although these results indicate the importance of Th and REE association with Fe-Mn oxides, the procedure used lacks specificity, since it does not distinguish between amorphous Fe and Mn oxides and crystalline iron minerals. Accordingly, an

alternative method was chosen (AAEC, 1983). This procedure seperates five geochemical fractions as follows:

A. Soluble salts and exchangeable ions: unbuffered 0.1M NH_4Cl (2g + 80 ml) at ambient temp. for 24 hours with continuous mixing.

B. Amorphous minerals and ferrihydrite: residue from (A) is extracted with Tamm's acid oxalate (2g + 80ml) at ambient temp. in the dark for 4 hours.

C. Crystalline iron minerals: residue from (B) is extracted twice, for 0.5 hours each, at 80°C, with citrate-dithionate-bicarbonate solution using continuous mixing.

D. Residual amorphous inorganic materials, aluminous interlayers, allophane and imogolite: the residue from (C) is shaken with 5% Na_2CO_3 (2g + 80ml) solution at ambient temp. for 16 hours.

E. Resistant minerals including clays, quartz anatase and zircon: residue from (D) is digested with a mixture of HNO_3, HF and $HClO_4$. Residual insolubles are fused with sodium peroxide.

Two aliquots from each extract were processed: one for Ra-228 (eventual determination by beta-gamma coincidence counting), the second for Th and REE's (coprecipitated with $FeOH_3$ and counted using XRF).

Preliminary results obtained with a sample of MF surface soil are given in Figure 12. The majority of the Mn (about 70%) was dissolved by Tamm's acid oxalate whereas most of the Fe was removed by citrate- dithionate-bicarbonate (CDB solution for crystalline Fe minerals), and much less by Tamm's reagent. Final results for Th partitioning are not available but there is qualitative indication that it follows the Fe distribution.

X-ray diffraction analysis was used to investigate the effect of Tamm's (B) and CDB (C) reagents in the extraction of crystalline Fe. Neither of the two reagents seemed to extract a significant fraction of the crystalline Fe present in the original sample and magnetite was still identified in the final residue. It is thought that organic matter may interfere in the seperation and thus an additional extraction, prior to (B)

may be necessary to remove organics.

Radium-228 was extracted in all phases except D (residual amorphous minerals), but was mostly associated with iron oxides (B+C). However, more than 40% of the Ra-228 in the sample remained associated with the final residue.

Clearly, the work reported here represents just a beginning in quantifying the speciation of analogue elements in the MF environment. Our preliminary data indicate the importance of Fe-Mn oxihydroxides in sequestering a large fraction of the Th, Ra and REE's present in the ore body. Additional speciation work on ore material which has been mineralogically characterized is needed together with more precise analytical measurements of the extractant solutions.

REFERENCES (including those cited in Appendix 1 to Part III)

Almeida, E.B. 1977. Geology of the Bauxite Deposits of the Poços de Caldas District, State of Minas Gerais, Brazil. Ph.D. Dissertation, Stanford University, Stanford, CA.

Australian Atomic Energy Commission. 1983. Radionuclide migration around uranium ore bodies - analogue of radioactive waste repositories. Annual Report, AAEC, Canberra, A.C.T.

Barretto, P.M.C. and Fujimori, K. 1986. Natural analogue studies: Geology and mineralogy of Morro do Ferro, Brazil. Chem. Geol. 55(No. 3/4): 297-312.

Bushee, J.M. 1971. Geochronological and Petrographic Studies of Alkaline Rocks from Southern Brazil. Ph.D. Dissertation, University of California, Berkeley, CA, 145 pp.

Campos, M.J., Penna Franca, E., Lobão, N., Trindade, H., and Sachett, I. 1986. Migration of radium from the thorium ore deposit of Morro do Ferro, Poços de Caldas, Brazil. J. Environ. Radiat. 3: 145-161.

Chapman, N. 1988. Personal communication.

Clark, S.P., Jr., Peterman, Z.E., and Heier, K.S. 1966. Abundances of uranium, thorium and potassium. In: Handbook of Physical Constants, Rev. Ed. (Sydney P. Clark, Jr., ed.). Geological Society of America Memoir 97. Geological Society of America, Inc., New York, NY. p. 521.

Cooper, M.B., Stanney, K.A., and Williams, G.A. 1981. Investigation of the speciation of radionuclides. Australian Radiation Laboratory, Report TR 039. Yallambie Victoria.

Eisenbud, M., Lei, W., Ballad, R., Krauskopf, K., Penna Franca, E., Cullen, T.L., and Freeborn, P. 1982. Mobility of thorium from the Morro do Ferro. In: Environmental Migration of Long-Lived Radionuclides. International Atomic Energy Agency. IAEA-SM-257/49. Vienna. pp. 739-755.

Eisenbud, M., Krauskopf, K., Penna Franca, E., Lei, W., Ballad, R., Linsalata, P., and Fujimori, K. 1984. Natural analogues for the transuranic actinide elements. Environ. Geol. Water Sci. 6 (1): 1-9.

Ellert, R. 1959. Contribuicão a geologia do macico alcalino de Poços de Caldas: Fac. Filos. Cienc. Letras de Universidade São Paulo, Bol. No. 237, Geologia No. 28, pp. 5-64.

Fleischer, R.L. 1982a. Alpha-recoil damage and solution effects in minerals: Uranium isotope disequilibrium and radon release. Geochim. Cosmochim. Acta 46: 2191-2201.

Fleischer, R.L. 1982b. Nature of alpha-recoil damage: Evidence from preferential solution effects. Nucl. Tracks 6: 35-42.

Frayha, R. 1962. Uranio e torio no planalta de Poços de Caldas, Nat. Dept. of Mineral Production. Bull. 116. 75 pp.

Holmes, D.A. 1987. Hydrogeology of the Poços de Caldas Area: End of Year Report. In: Poços de Caldas Project Progress Report, Appendix 6 (March-May, 1987). Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden.

IPT (Instituto de Pesquisas Tecnologicas do Estado de São Paulo). 1982. Estudos para a Caracterizacão do Comportamento do Lencol Freatico na Area do Morro do Ferro - Poços de Caldas, MG. Relatoria No. 16, 423. 16 pp.

IPT (Instituto de Pesquisas Tecnologicas do Estado de São Paulo). 1984. Revision of the Bibliography of Morro do Ferro, Poços de Caldas, MG. Cidade Universitaria 05508 S. Paulo, 5p.

Kamath, P.R., Khan, A.A., Rao, S.R., Pillai, T.N.V., Borkar, M.L., and Ganapathy, S. 1964. Environmental natural radioactivity measurements at Trombay Establishment. In: The Natural Radiation Environment. The University of Chicago Press, Chicago, IL. pp. 957-978.

Krauskopf, K.B. 1986. Thorium and rare earth metals as analogs for actinide elements. Chem. Geol. 55(No. 3/4): 323-335.

Langmuir, D. and Herman, J.S. 1980. The mobility of thorium in natural waters at low temperatures. Geochim. Cosmochim. Acta 44: 1753-1766.

Laurer, G.L., Furfaro, J., Carlos, M., Lei, W., Ballad, R., and Kneip, T.J. 1982. Energy dispersive analysis of actinides, lanthanides, and other elements in soil and sediment samples, In: Advances in X-ray Analysis, Vol. 25. (J.C. Russ, C.S. Barrett, P.K. Predecki and D.E. Leyden, eds.). Plenum Publishing, New York, NY. pp. 201-208.

Lei, W. 1984. Thorium Mobilization in a Terrestrial Environment. Ph.D. Dissertation, New York University, New York, NY. 414 pp.

Lei, W., Linsalata, P., Penna Franca, E., and Eisenbud, M. 1986. Distribution and mobilization of cerium, lanthanum and neodymium in the Morro do Ferro Basin, Brazil. Chem. Geol. 55(No. 3/4): 313-322.

Linsalata, P., Morse, R.S., and Ford, H. 1986. Sequential determination of environmental levels of isotopic Th, U and the light rare earth elements within the terrestrial food chain by induced coupled plasma (ICP) and alpha spectrometry. In: Thirty-Second Annual Conference on Bioassay, Analytical and Environmental Radiochemistry. (October 21-23, 1986; Gaithersburg, MD). Abstract.

Medeiros, J.A. 1982. Written Communication. Catholic University of Rio de Janeiro, RJ, Brazil.

Miekeley, N., Vale, M.G.R., Tavares, T.M., and Lei, W. 1982. Some aspects of the influence of surface and ground water chemistry on the mobility of thorium in the "Morro do Ferro" environment. In: Scientific

Basis for Nuclear Waste Management V. (W. Lutze, ed.). North-Holland/Elsevier Science Publishing Co., New York, NY. pp. 725-733.

Miekeley, N., Dotto, R.M., Kuchler, I.L., and Linsalata, P. 1985. The importance of organic compounds on the mobilization and bioassimilation of thorium in the Morro do Ferro Environment. In: Scientific Basis for Nuclear Waste Management VIII, Materials Research Society Symposia Proceedings, Vol. 44. Materials Research Society, Pittsburgh, PA. pp. 591-597.

Miyake, Y., Sugimura, Y., and Tsubota, H. 1964. Content of uranium, radium, and thorium in river waters in Japan. In: The Natural Radiation Environment. The University of Chicago Press, Chicago. pp. 219-225.

Moore, W.S. and Sackett, W.M. 1964. Uranium and thorium series inequilibrium in sea water. J. Geophys. Res. 69: 5401-5405.

New York University Medical Center. 1986. Studies of Transport Pathways of Th, U, Rare Earths, Ra-228 and Ra-226 from Soil to Plants and Farm Animals. Annual Progress Report to DOE/OHER, Feb., 1986. 120 pp.

Peters, J. and Waber, N. 1987. Mineralogy-geochemistry of the Osamu Utsumi mine and Morro do Ferro sites, Poços de Caldas. In: Poços de Caldas Project Progress Report, Appendix 2 (March-May, 1987). Swedish Nuclear Fuel and Waste Management Co., Stockholm, Sweden.

Somayajulu, B.L.K. and Goldberg, E.D. 1966. Thorium and uranium isotopes in seawater and sediments. Earth Planet. Sci. Lett. 1: 102-106.

Tessier, A., Campbell, P.G.C., and Bisson, M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. Anal. Chem. 51: 844-851.

Thurber, D. 1955. The concentrations of some natural radioelements in the waters of the Great Basin. Bull. Vulcanol. 28: 195-201.

Ulbrich, M.N.C. 1983. Aspectos Mineralogicos e Petrologicas de Nefelina Sienitas do Maciço Alcalino de Poços de Caldas, MG-SP. Ph.D. Dissertation, Univ. São Paulo, São Paulo, Brazil.

United Nations Scientific Committee on the Effects of Atomic Radiation. 1982. Ionizing Radiation: Sources and Biological Effects. United Nations, New York, NY. 772 pp.

Wahlgren, M.A. and Orlandini, K.A. 1982. Comparison of the geochemical behavior of plutonium, thorium and uranium in selected North American lakes. In: Proc. Symp. Migration in the Terrestrial Environment of Long-Lived Radionuclides from the Nuclear Fuel Cycle. IAEA-SM-257. Knoxville, TN, July 23-31, 1981. pp. 757-774.

Wedow, H. 1967. The Morro do Ferro thorium and rare-earth deposit, Poços de Caldas District, Brazil. U.S. Geological Survey Bull. 1185-D. 35 pp.

Williams, R.L. and Sill, C.W. 1974. Simple method for the preparation, storage and use of chromous chloride solutions. Anal. Chem. 46: 791-794.

TABLE 1

Morro do Ferro Surface Water Chemistry*

Species	Mean Concentration (mg/ℓ)±SD	N
K^+	2.8±0.2†	5
Na^+	0.2±0.01†	5
Mg^{+2}	0.07±0.02	6
Ca^{+2}	0.34±0.07†	6
Mn^{+2-+5}	0.22±0.01	6
Fe^{+2}	0.09±0.11	6
Si	4.3±0.9	5
HCO_3^-	4.5±0.7	3
SO_4^{-2}	17	2
F^-	0.11±0.01†	3
Cl^-	<0.16†	3
PO_4^{-3}	<0.04	3
NO_3^-	0.77±0.32	3
SiO_2	11.8±1.6	3
Conductivity (μmho/cm)	13	39
Alkalinity	9	39
Hardness	4	39
pH	6.2±0.6	39
Eh (mv)	490±70	39
DOC	(1-3)**	5
DO	8.4	5
Suspended solids	4.4	59

* Based on samples collected in the South Stream (1981-1982) during baseflow periods. Data from Lei (1984) unless otherwise noted.

† Medeiros (1982).

** Miekeley et al. (1985).

TABLE 2

Morro do Ferro Ground Water Chemistry[1]

Concentration (ppm)

	Well 12 (n=3)	Wells 10 & 11 (n=2)
K^+	10-18	0.14-0.24
Na^+	0.5-1.3	0.09-0.18
Fe^{+2}	0.8-3.0	0.19-0.55
Fe (total)	1.3-3.1	0.24-0.58
HCO_3^-	30-39	12-27
$CO_3^=$	ND	ND
$SO_4^=$	13-17	8-11
F^-	6-9	0.06-0.07
pH (field)	5.7-6.2	4.6-5.2
Eh (field) mV	57-154	210-285
T (°C)	21-25	22
DO	1-1.7	3.9-6.4

[1] Preliminary unpublished data for samples taken 12/87-1/88 (see Fig. 2 for sample location and depths).

TABLE 3

Estimated Inventories of Analogue Elements Within the MF Ore Body and in Surface Farm Soils of the Poços de Caldas Plateau

Element	Geom. Mean Ore Conc. ($\mu g \cdot g^{-1}$)	Ore Body Inventory (tonnes)	Median Soil Conc. ($\mu g \cdot g^{-1}$)
Th-232	2,668	30,000	93
U-238	34	400	15
La	2,945	33,000	213
Ce	4,329	49,000	799
Nd	1,480	17,000	68
Ra-228	291 ($pCi \cdot g^{-1}$)	3,000 (Ci)	8 ($pCi \cdot g^{-1}$)

TABLE 4

Concentrations of Th, La, Ce and Ra-228 in the South Stream

Baseflow and Estimates of Solution Phase Mobilization

Element	Mean Concentration (μg/ℓ±SEM)	(N)	Annual Transport (tonnes·y^{-1})	Estimated Inventory (tonnes)	Mobilization Rate[4] (y^{-1})
Th	0.053±0.013	(55)	2.5×10^{-5}	30,000[1]	10^{-9}
La	0.31±0.04	(17)	1.5×10^{-4}	33,000[2]	10^{-9}
Ce	0.81±0.09	(17)	3.8×10^{-4}	49,000[2]	10^{-9}
Ra-228 (pCi/ℓ)[3]	1.7±0.1	(13)	8.1×10^{-4} (Ci y^{-1})	3.3×10^{3} (Ci)	10^{-7}

1 Frayha (1962).

2 REE inventories based on the geometric mean of the ratios to Th and the Th inventory.

3 Campos et al. (1986).

4 Order of magnitude estimates.

TABLE 5

Estimates of K_d's in Surface and Ground Water from the Morro do Ferro

Element	$K_d \times 10^6$ Surface Water	Ground Water
Th	2.3	var., f (DOC > 1000 MWE)
La	1.8	?
Ce	1.7	?
U	1.0	0.7
Ra-228	0.17	0.03
Ra-226	0.08	0.03

Table 6

Radionuclide Concentrations in Core Samples from Borehole MF 10

			Concentration (Bq/g dry ± SD)					
Sample No.	Description	Depth (m bgl)	Th-232	Th-230	Th-228	U-234	U-238	Pa-231
10-1-1B-a	red-brown clay, magnetite	0.42-0.5	160±10	2.2±0.3	167±11	0.57±0.03	0.61±0.03	NA
-b	"	"	234±5	2.1±0.3	236±5	NA	NA	0.027±0.002
-c	"	"	226±3	1.4±0.2	219±3	NA	NA	NA
10-3-1A	bright red + white clay	2.35-2.40	47±3	1.1±0.2	50±3	0.43±0.03	0.44±0.03	NA
-b	"	"	47±1	0.72±0.07	51±1	NA	NA	0.019±0.001
10-56-1A	brown + white clay	55.2-55.25	1.5±0.1	0.33±0.02	1.5±0.1	0.38±0.02	0.41±0.02	NA

Table 7

Isotopic Ratios in Core Samples from Borehole MF 10

	Ratio ± SD			
Sample No.	U234/U238	Th230/U234	Th228/Th232	Pa231/U235*
10-1-1B-a	0.93±0.07	3.86±0.56	1.01±0.09	0.96±0.09
-b	NA	3.68±0.53	1.04±0.03	NA
-c	NA	2.39±0.36	0.97±0.02	NA
10-3-1A	0.99±0.10	2.56±0.50	1.06±0.09	0.94±0.08
-b	NA	1.67±0.20	1.10±0.02	NA
10-56-1A	0.93±0.07	0.87±0.07	1.00±0.09	NA

*U-235 estimated as 0.046(U-238 activity).

Table 8

REE, Th and U Concentrations in Core Sections from Borehole MF 10*

	Concentration (µg/g dry ± SD)						
Sample No.	Ce	La	Nd	Pr	Sm	Th	U
10-1-1B-a	59,524±1,291	41,170±885	23,624±526	5,772±270	3,110±70	39,700±2,481	50±4
-b	52,289±1,593	42,139±1,281	23,229±694	6,810±282	3,031±98	58,196±1,172	NA
-c	54,682±1,624	44,005±1,291	24,772±744	6,800±269	3,019±92	56,058±827	NA
10-3-1A	7,545±153	3,151±62	637±42	159±7	100±22	11,663±744	36±2
-b	6,545±196	3,246±98	827±322	238±11	100±6	11,540±174	NA
10-56-1A	3,515±90	3,430±86	1,915±47	466±24	255±7	372±25	33±2

*See Table 6 and Fig. 2 for sample depths and core location.
REE's determined by ICPOES, Th and U by alpha spectrometry.

Table 9

Isotopic Th and U Concentrations in Surface and Ground Waters from the MF*

		Concentration (mBq/l ± SD)					
Sample No.	Type	Th-232	Th-230	Th-228@	U-238	U-234	U234/U238
SW 04	surf. water S. Stream	0.249±0.025	0.749±0.068	≈2.3±0.2	3.20±0.16	4.79±0.23	1.50±0.05
SW 05	surf. water N. Stream	0.198±0.026	0.198±0.026	≈2.4±0.2	2.24±0.12	2.99±0.15	1.34±0.05
GW 18	ground water MF 12	0.688±0.088	0.310±0.043	≈15.4±1.8	1.47±0.08	1.80±0.09	1.22±0.05
GW 26	ground water MF 2	0.168±0.023	0.141±0.027	≈20.2±1.7	3.60±0.17	4.55±0.21	1.25±0.04

*40 liter samples (< 0.45μ). Chemical dissolution and alpha spectrometry used.
@Approximate values given since results are not corrected for ingrowth following Ra-228 decay.

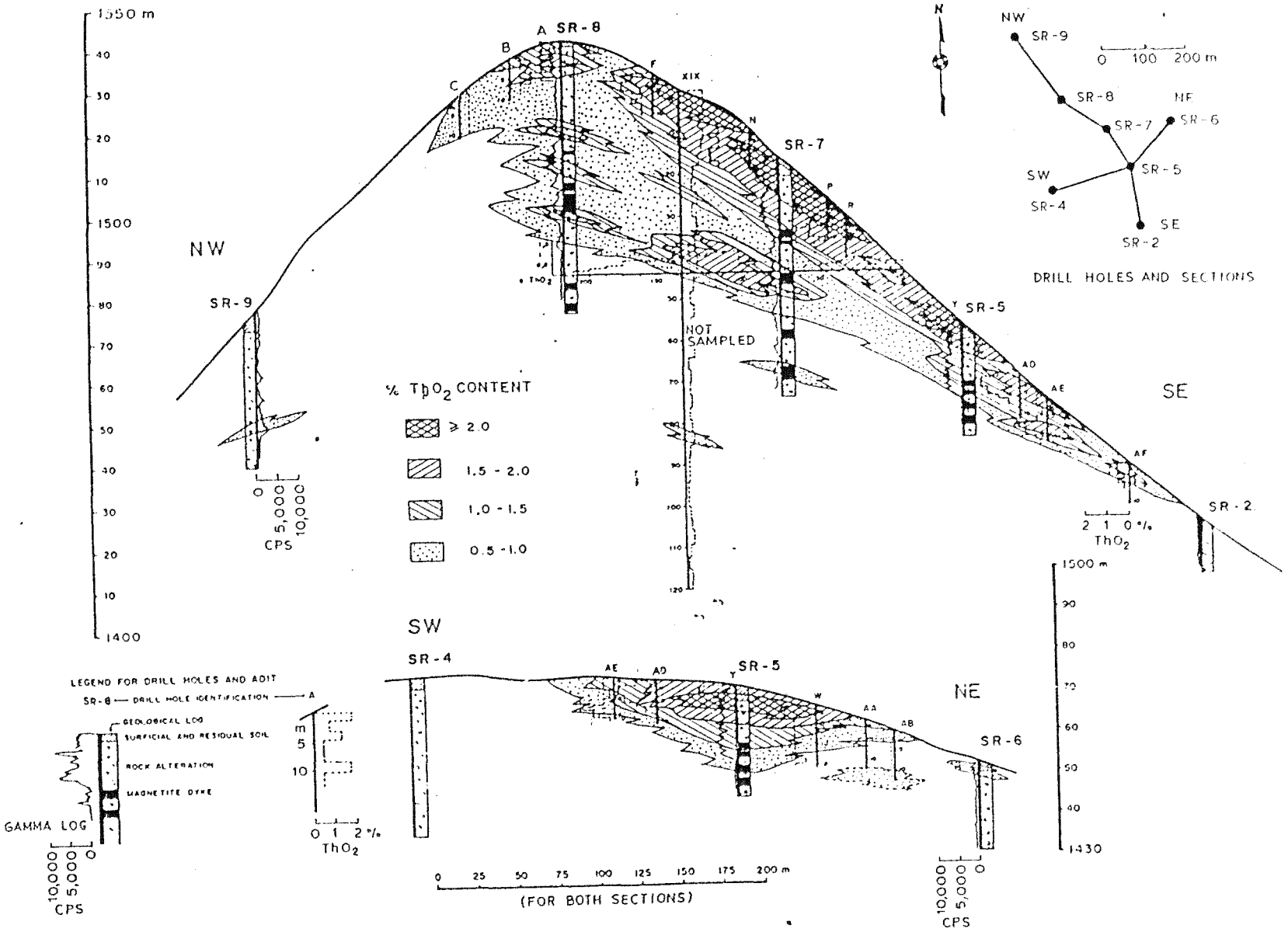


Fig. 1. Longitudinal and transverse cross-sections of the Th-REE-rich ore body. This interpretation, based on existing data, should be considered preliminary until better geological information is obtained (from Barretto and Fujimori, 1986).

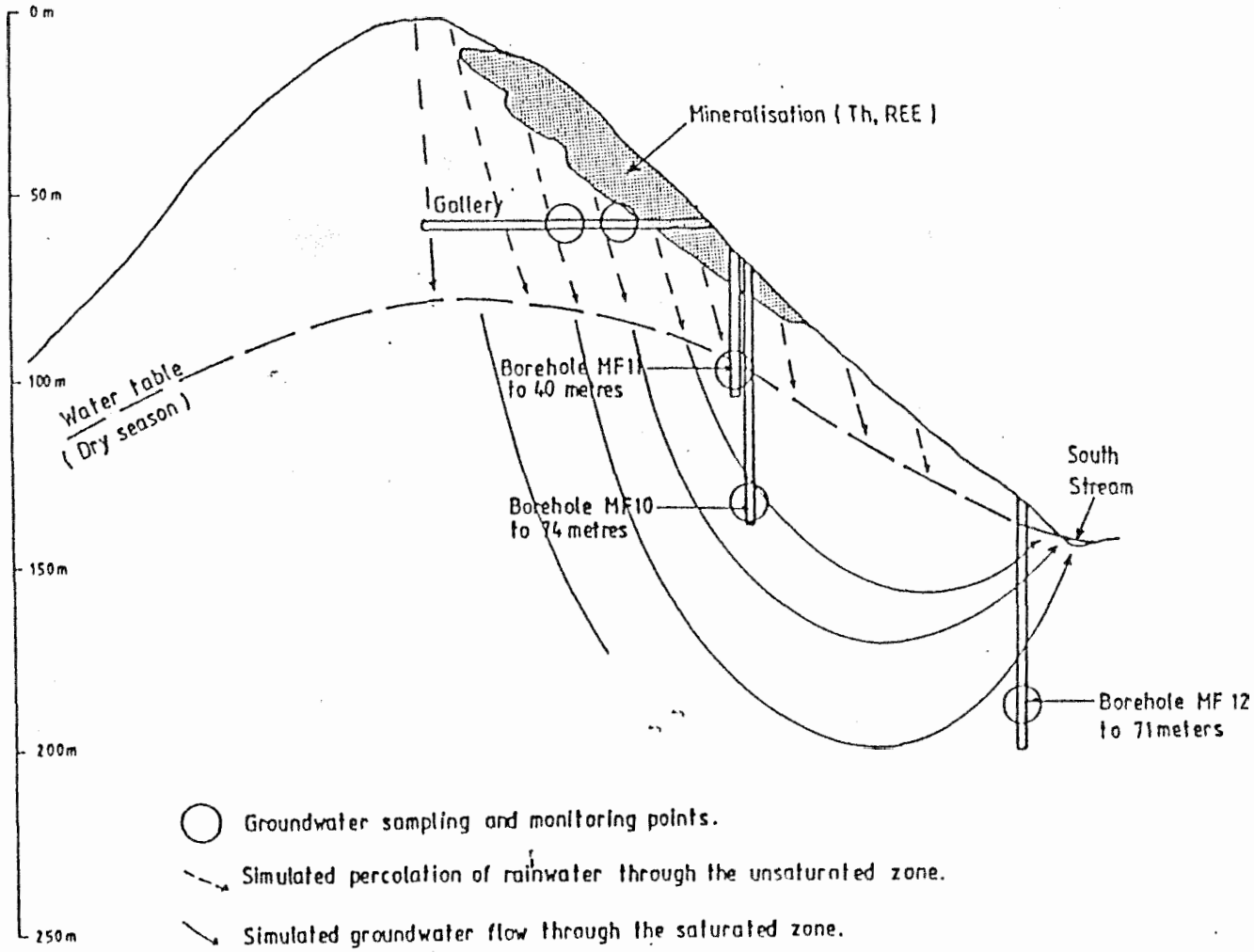

0 m
50 m
100 m
150 m
200 m
250 m
Mineralisation (Th, REE)
Gallery
Water table
(Dry season)
Borehole MF11
to 40 metres
Borehole MF10
to 74 metres
South
Stream
Borehole MF 12
to 71meters
Groundwater sampling and monitoring points.
Simulated percolation of rainwater through the unsaturated zone.
Simulated groundwater flow through the saturated zone.

Figure 2.

FIGURE 3

Areal View of the MF and Drainage Basin

(showing approximate location of the ore body)

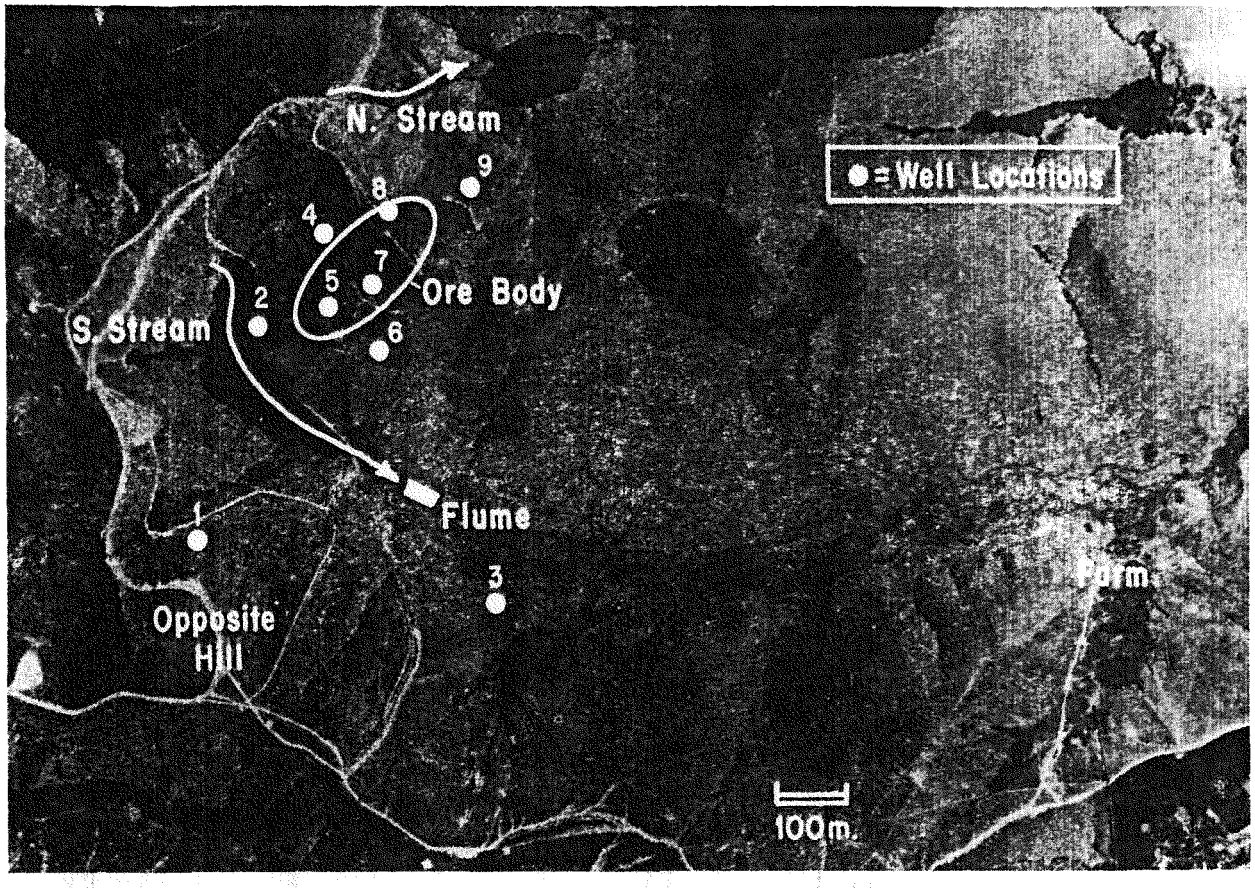
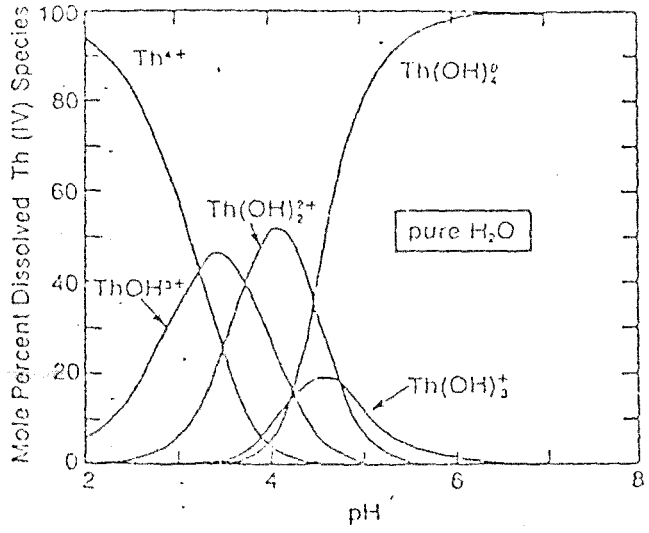
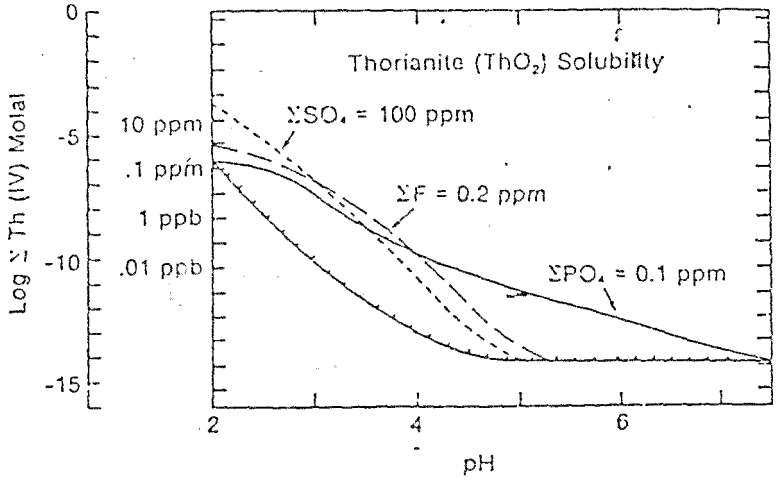


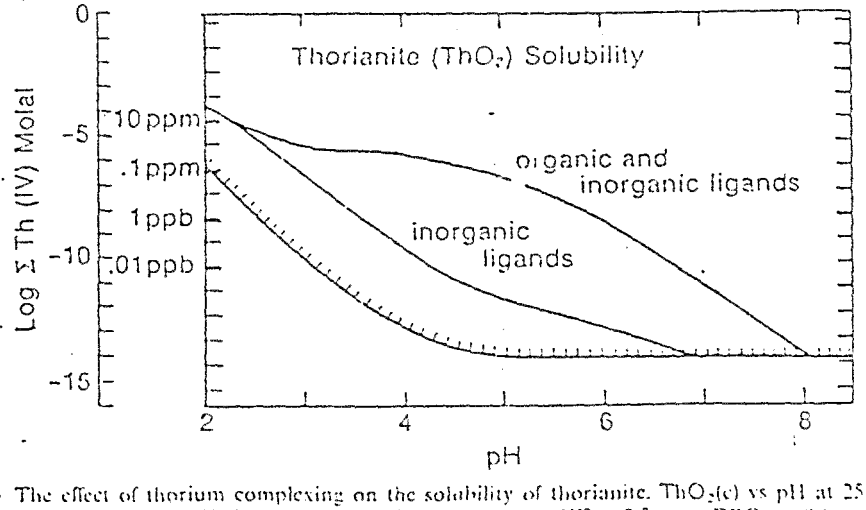
Fig. 4. Theoretical solubility curves for thorium (from Langmuir and Herman, 1980).



A — Distribution of thorium-hydroxy complexes vs pH at 25°C with ΣTh = 0.01 ppb in pure water.



B — The effect of thorium-sulfate, fluoride and phosphate complexing on the solubility of thorianite, $ThO_2(c)$, as a function of pH at 25°C. The cross-hatched curve denotes the solubility of thorianite in pure water. The curves indicating thorianite solubility as affected by complexing have been constructed assuming each ligand present in the absence of the others.



C — The effect of thorium complexing on the solubility of thorianite, $ThO_2(c)$ vs pH at 25°C in a solution of ΣCl = 10 ppm, ΣNO_3 = 2.5 ppm, ΣSO_4 = 100 ppm, ΣF = 0.3 ppm, ΣPO_4 = 0.1 ppm, Σoxalate = 1 ppm, Σcitrate = 0.1 ppm and ΣEDTA = 0.1 ppm.

FIGURE 5

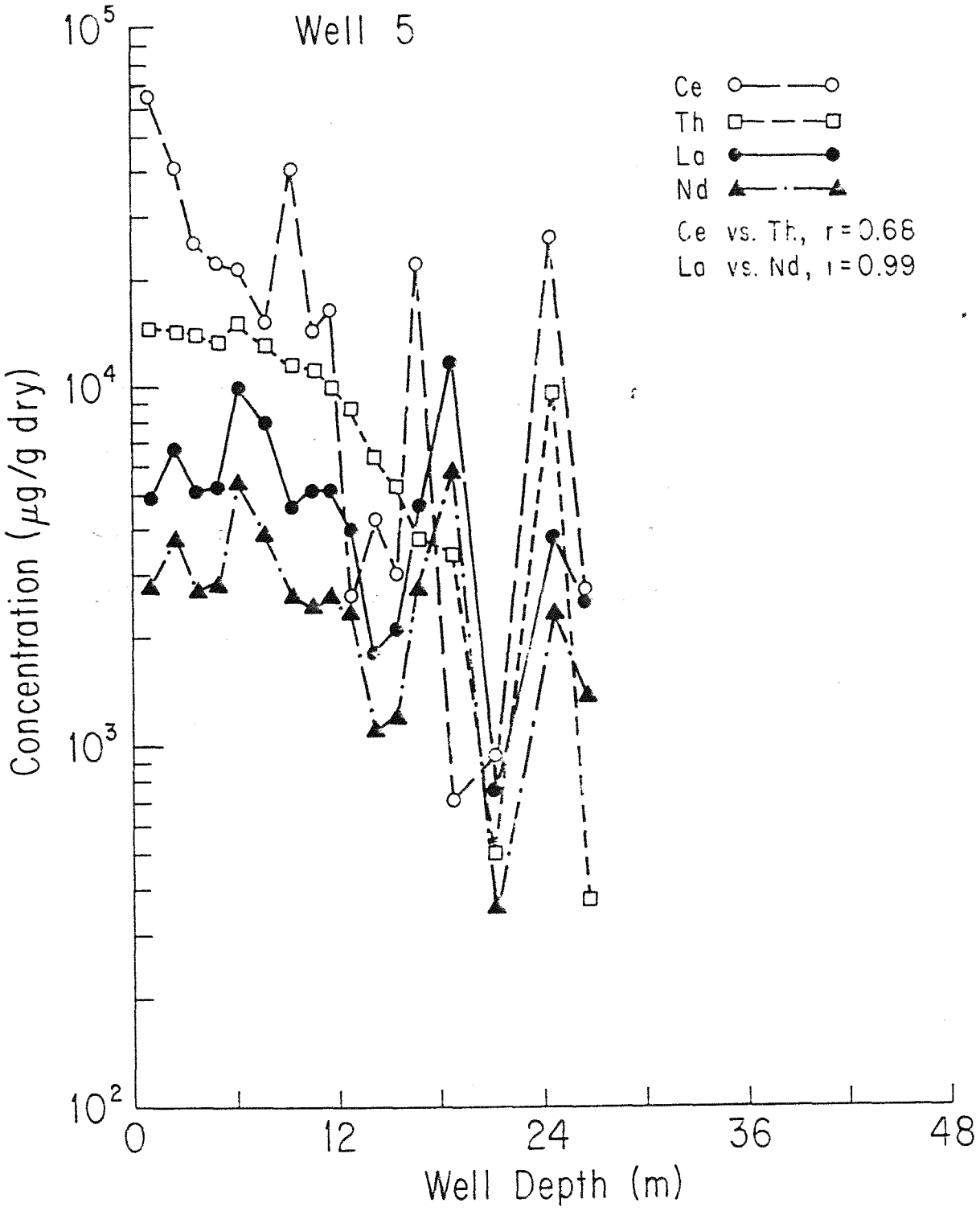

Well 5
Ce
Th
La
Nd
Ce vs. Th, r = 0.66
La vs. Nd, r = 0.99
Concentration (μg/g dry)
10^5
10^4
10^3
10^2
0
12
24
36
48
Well Depth (m)

FIGURE 6

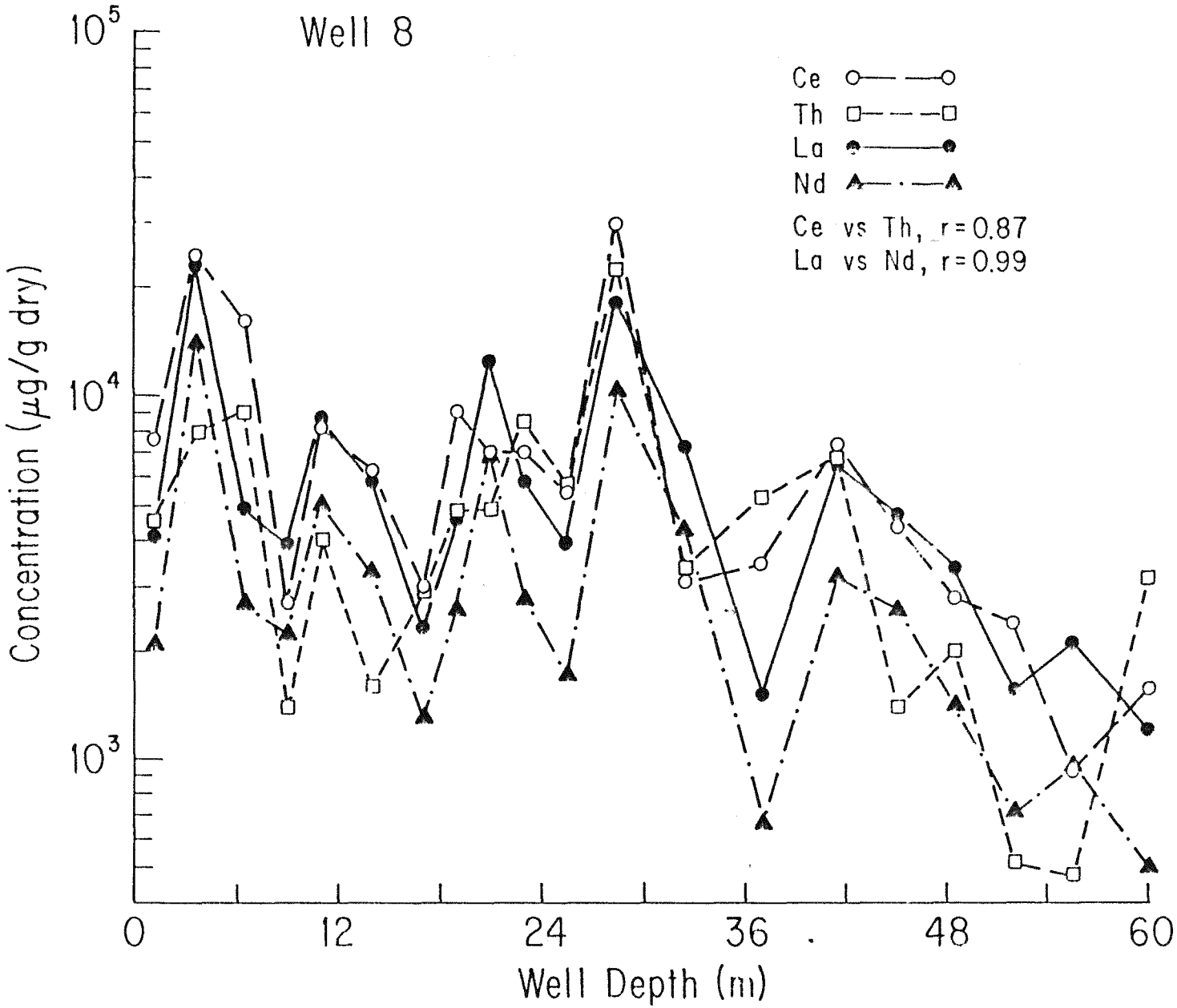

Well 8
Ce
Th
La
Nd
Ce vs Th, r=0.87
La vs Nd, r=0.99
Concentration (μg/g dry)
10^5
10^4
10^3
0
12
24
36
48
60
Well Depth (m)

FIGURE 7

Rare Earth Element Distributions in Morro do Ferro Well Spoils and Other Minerals

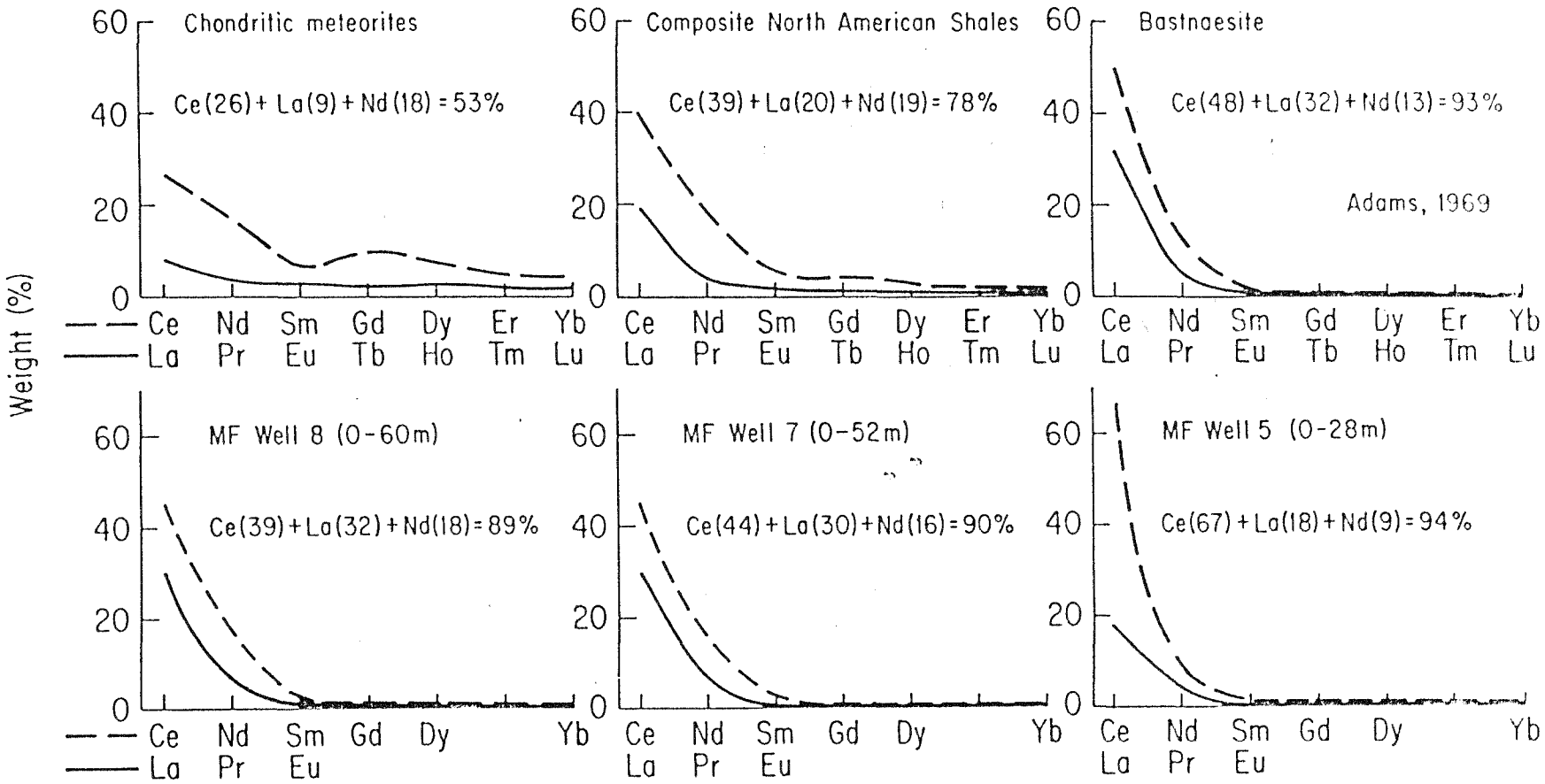


FIGURE 8

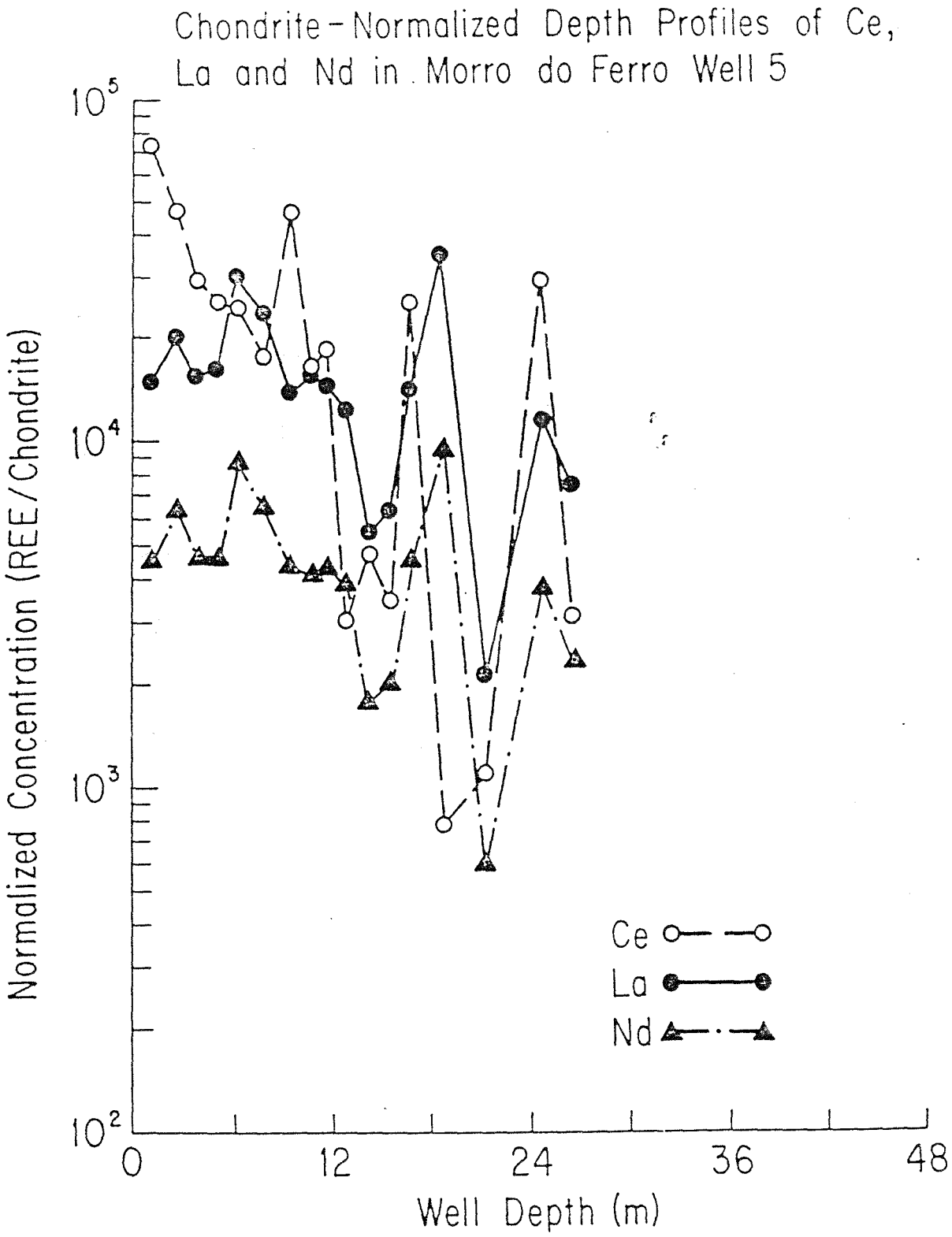

Chondrite-Normalized Depth Profiles of Ce, La and Nd in Morro do Ferro Well 5
Normalized Concentration (REE/Chondrite)
10^5
10^4
10^3
10^2
0
12
24
36
48
Well Depth (m)
Ce
La
Nd

FIGURE 9

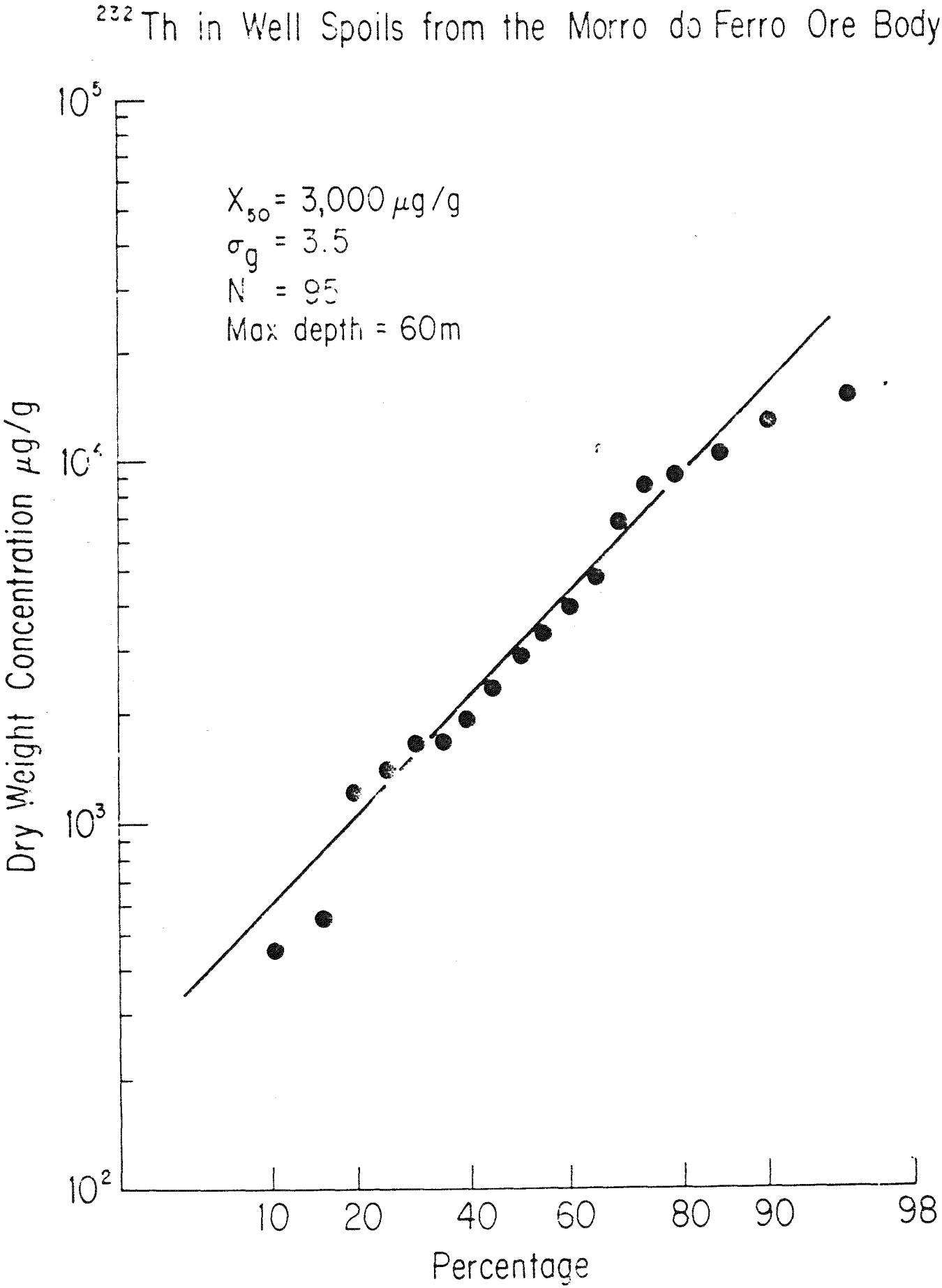
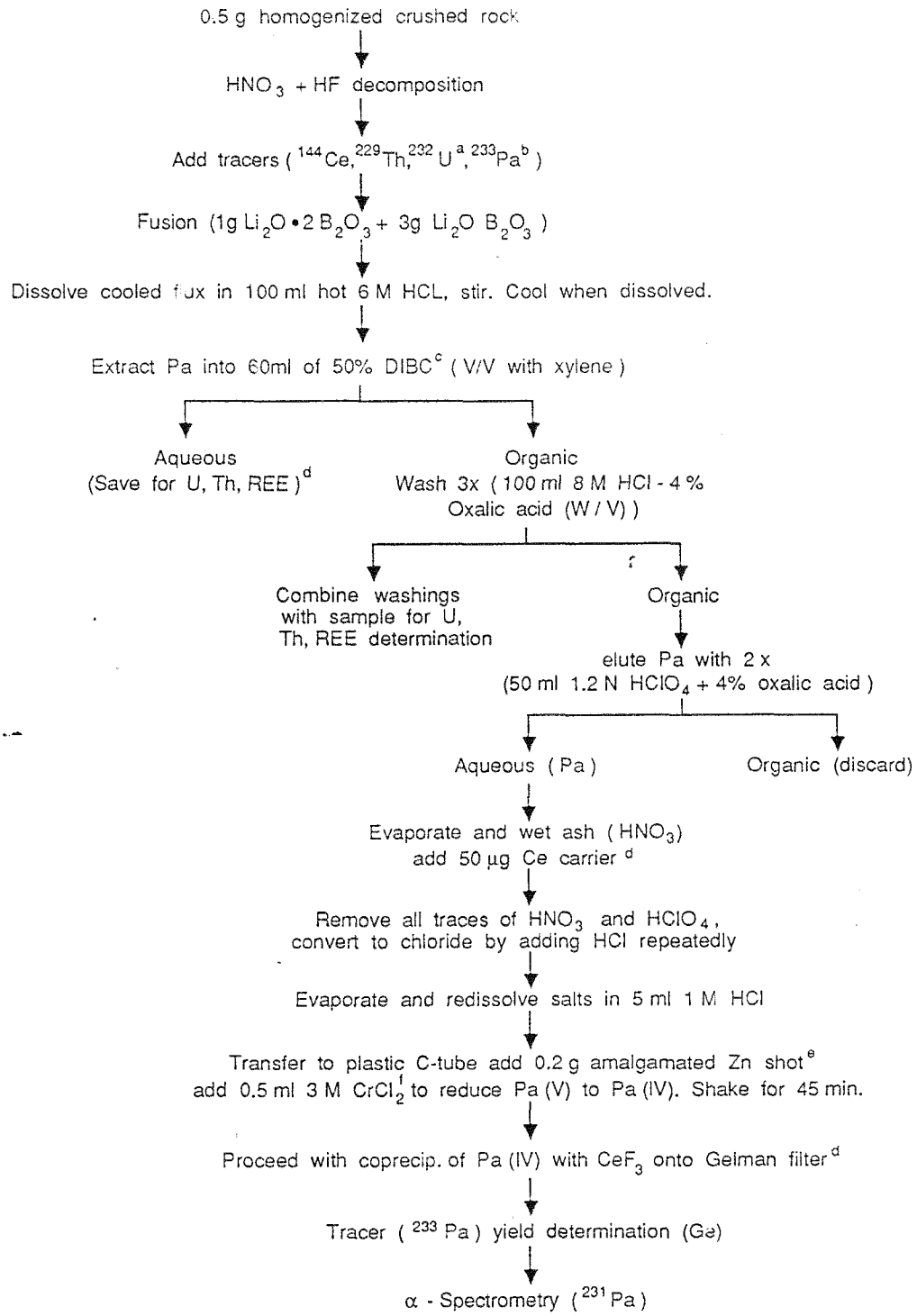

^{232}Th in Well Spoils from the Morro do Ferro Ore Body
X_{50} = 3,000 μg/g
σ_g = 3.5
N = 95
Max depth = 60m
Dry Weight Concentration μg/g
10^5
10^4
10^3
10^2
10
20
40
60
80
90
98
Percentage

FIGURE 10

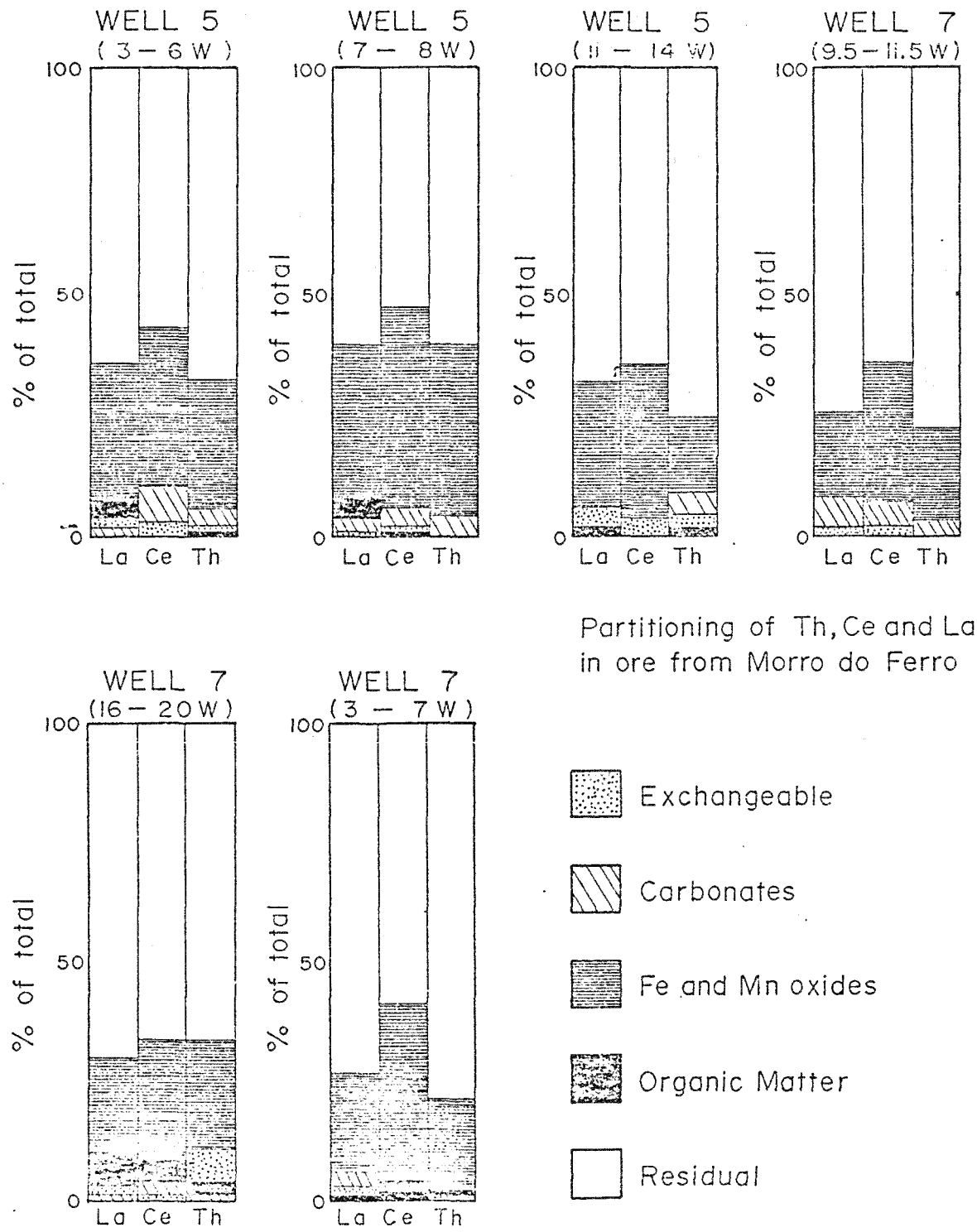
PRELIMINARY FLOWSHEET FOR Pa-231 DETERMINATION SEQUENTIALLY WITH Th, U AND REE's IN CORE SAMPLES



[a] Self cleaning ^{232}U tracer is used (ie., no ^{228}Th present).
[b] Protactinium - 233 tracer prepared and purified from it's ^{237}Np parent using a procedure similar to that shown.
[c] Diisobutylcarbinol (DIBC).
[d] Sequential determinations of U, Th and REE previously reported in NYUMC (1986).

[e] The amalgamated Zn serves to keep the Cr reduced and present a surface for the spontaneous deposition of ^{210}Po, which can cause spectral interference with ^{231}Pa.
[f] Preparation of the chromous chloride reductant after Williams and Sill (1974).

FIGURE 11



Partitioning of Th, Ce and La in ore from Morro do Ferro

FIGURE 11 (Cont'd)

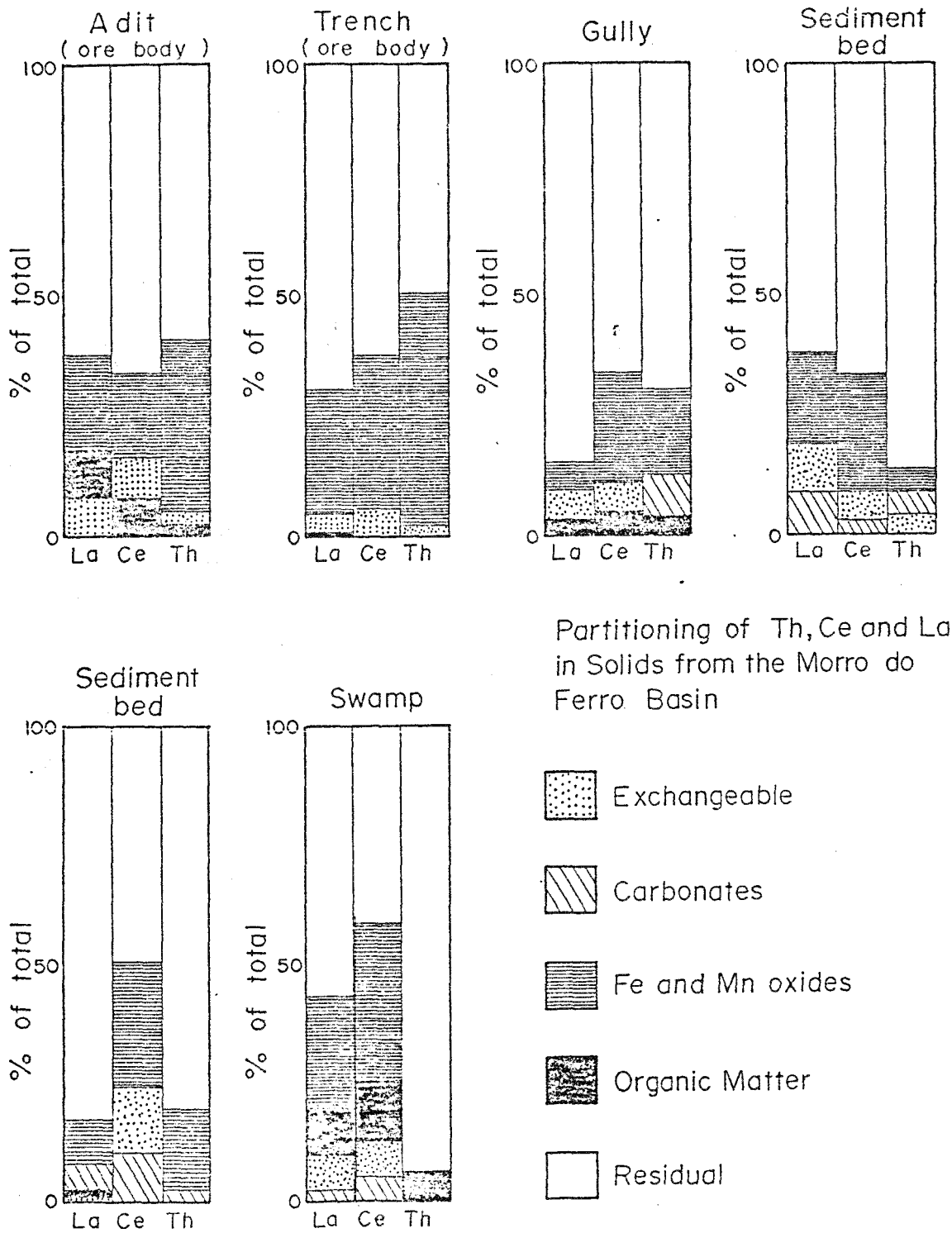
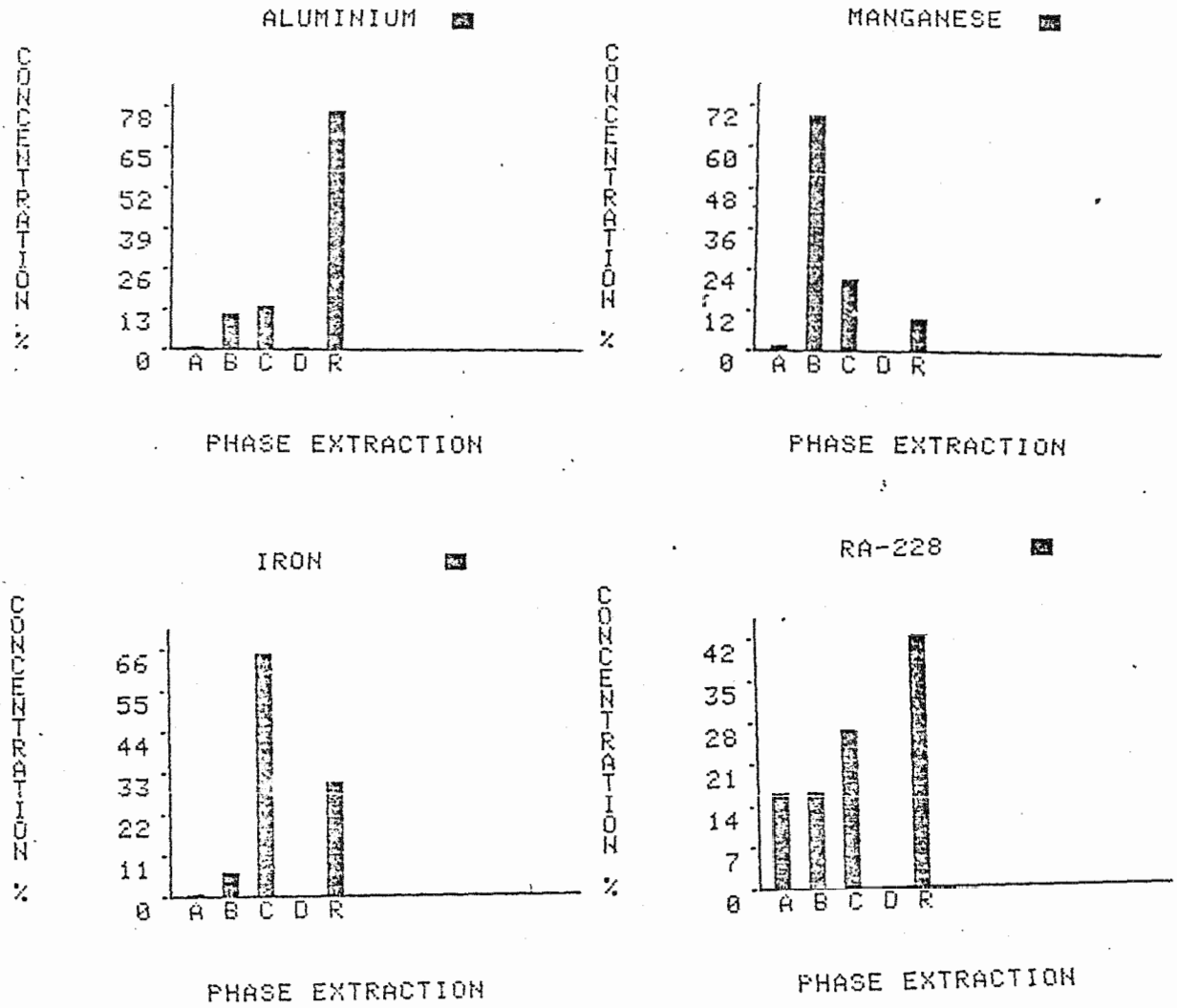


FIGURE 12



METALS EXTRACTED FROM ONE ORE BODY SURFACE SOIL

METAL	TOTAL CONCENTRATION ($mg\ g^{-1}$)	METAL EXTRACTED ($\mu g\ g^{-1}$)	(%)
Al	125.1	30.4	24
Mn	3.6	3.3	91
Fe	181.6	127.3	70

Appendix 1 to Part III: The Importance of Organic Compounds on the Mobilization of Thorium in the Morro do Ferro

N. Miekeley, I. L. Kuechler and R. M. Dotto, Department of Chemistry, Catholic University of Rio de Janeiro, RJ, Brazil

P. Linsalata, New York University Medical Center (editor)

Abstract

The potential use of Th as a natural analogue for Pu(IV) has focused new interest on the aquatic chemistry of this element. Utilizing a Th/REE deposit at Morro do Ferro as a model for a breached actinide repository exposed to supergeneous conditions, the influence of organic complexation on the mobility of Th and REE's in this environment is being studied.

Surface and ground water samples were analyzed for isotopic Th by alpha spectrometry, and for dissolved organic carbon (DOC). Th and DOC concentrations are in the range of 0.1 - 18 μg/l and 0.8 - 40 mg/l, respectively. Highest Th concentrations are measured in waters with high DOC content. Ultrafiltration experiments with membranes (300,000, 10,000 and 1,000 molecular weight cut-off limits) show that Th is predominantly concentrated in the high molecular weight fractions, mainly on colloidal humic, and to a lesser extent, fulvic acids. However, molecular weight distribution patterns of Th indicate variations with water type and with time of collection (seasonal). Chemical composition and IR spectra of humic acids seperated from water, confirm the soil origin of these compounds.

Measurements on the distribution coefficient of Th between water (< 0.45 μ) and suspended particulate matter (> 0.45μ) indicate the K_d to be inversely proportional to DOC concentrations. Results obtained to date give evidence that formation of humic colloids is an important factor in the migration behavior of Th in the terrestrial environment.

A. Methods

Water from various sampling points including the shallow boreholes SR 2, 5 and 6 (see Fig. 1, Part III), standing water from a surface trench, and water which had percolated thru the mineralized zone and collected from the ceiling of the gallery (see Fig. 2, Part III) was analyzed for Th (alpha spec.) and DOC (Beckman 915 total organic carbon analyzer). The sampling and radiochemical procedures used are given in Figures 1 and 2, respectively. The aqueous phase which contains trivalent REE's were stored for future analyses after solvent extraction of Th by TOPO. Aqueous phases from ultrafiltration experiments (using Amicon Diaflow membranes) were also stored for future analyses of Mn and Fe to obtain information concerning the participation of these elements on colloidal transport of Th and REE's via adsorption on hydrous oxides.

B. Results and Discussion

Th and DOC concentrations in filtered water from the various sampling points are given in Table 1. Compared with Th concentrations reported in the literature from natural environments (Table 2), Th concentrations at the MF appear to be the highest reported and can be explained only by effective complexing of this element. According to Langmuir and Herman (1980) minor amounts of organic complexors can increase Th solubility by orders of magnitude above pure inorganic solubility (Fig. 3). For instance, assuming the solubility product of $Th(OH)_4$ in pure water to be $10^{-44.7}$ (Krauskopf, 1986), one would expect the concentration of Th^{+4} to be on the order of 5 x 10^{-5} ppb at typical MF water pH of 6 which is three orders of magnitude less than that measured in MF surface waters.

Tentatively, we tried to correlate Th concentrations in water with total DOC (Fig. 4), based on the observations that high Th concentrations coincided in some samples with high DOC. As can be seen in Figure 4, a modest correlation coefficient (R = 0.82) was obtained. The hypotheses to be tested were that solubility of Th is also influenced by inorganic complexation (eg., with F^-, HPO_4^{-2} and,or SO_4^{-2}), or that some fraction of the total DOC is more closely associated with Th. To test these hypotheses and to get

some insight into the nature of the organo-Th complexes, membrane filtration experiments were performed as outlined in Figure 1. As can be seen in Figure 5, nearly all of the Th is found in molecular weight fractions above 1,000 units, which would exclude complexation of Th by inorganic ligands since such complexes would be expected to pass the 1,000 unit membrane. Acidification of the molecular weight fractions above 10,000 units resulted in precipitation of humic acids, which coprecipitated about 70% of the Th. The flocculated humic acids were analyzed by infra red spectroscopy and chemical analysis (C, N, O) with results indicating the soil origin of these compounds.

Although individual patterns of DOC and Th fractionation differ among the various samples reported in Figure 5, the general trend of Th association with colloidal humic acids persists. Also observed in many of the samples is that the greatest portion of the DOC (and not the Th) is associated with the lowest molecular weight fraction obtained, i.e., < 1,000 units (Fig. 5). Although not confirmed, this fraction is probably composed largely of low molecular weight fulvic acids. Based on these results, we have plotted in Figure 6 the Th concentration as a function of DOC concentration in the > 1,000 molecular weight unit fraction. The correlation coefficient is subsequently improved from 0.82 to 0.97.

The influence of organic complexation on adsorption/desorption equilibria of Th was examined in field samples by analyzing Th in both the suspended solids retained on the 0.45μ prefilter and the sample filtrate which was also assayed for DOC (total). Using x-ray diffraction spectroscopy, the paticulate matter was found to consist mainly of illite, kaolinite, and gibbsite, with minor amounts of goethite. A bulk K_d term was calculated as μg Th g^{-1} (solid)/μg Th ml^{-1} (filtrate) and expressed as a function of the DOC filtrate concentration (Fig. 7). Although there is considerable variability in the data (probably a result of using total DOC instead of DOC > 1,000 molecular weight units), it is clear that at higher DOC levels, Th is either effectively complexed such that it is unavailable for sorption onto suspended particulates, or Th is desorbed from the particulate phase. In either case, the K_d term is lower by about two orders of magnitude

as the DOC increases from 1-2 ppm to 30-40 ppm.

Although this work represents preliminary findings, the association between DOC and Th is not unlike that observed for fallout Pu and DOC as measured in river and lake waters by Nelson et. al. (1985, Fig. 7). Although certainly not conclusive in itself, the similar trends seen between Pu and Th K_d's in natural waters containing DOC in the range of 1-40 ppm, supports the theory that in environments where Pu is expected to exist in the quadravalent oxidation state, its chemical behavior should be similar to that of quadravalent Th, such that under these conditions, Th may serve as an analogue for predicting Pu behavior.

TABLE 1

Th-232 and DOC-Concentrations in Morro do Ferro Waters

Sample No.	Collection Date	Location	Th-232 (μg/ℓ)	DOC (mg C/ℓ)	pH
GW-188	08/22/84	PZ-2	0.31	3.2	7.1
GW-190	08/22/84	PZ-6	<LLD	2.5	
GW-191	08/28/84	PZ-5	0.58	2.5	
GW-192	09/11/84	PZ-5	<LLD	1.4	
GW-193	09/11/84	PZ-6	0.15	1.9	
GW-194	09/12/84	PZ-2	0.22	2.6	
SW-448	09/11/84	Trench	12.5	8.2	
GW-196	10/25/84	PZ-6	3.34	1.8	
GW-197	10/25/84	PZ-2	0.27	2.0	4.7
GW-469	10/25/84	Trench	0.17	6.1	5.1
SW-485	12/11/84	Trench	5.26	6.0	4.2
SW-486	12/11/84	Gallery	<LLD	1.8	
GW-205	01/10/85	PZ-5	0.06	1.9	4.3
GW-207	01/14/85	PZ-2	0.11	0.8	4.3
GA-5	01/10/85	Gallery	0.13	3.8	3.4
GW-208	03/14/85	PZ-6	0.22	1.1	6.3
GW-209	03/14/85	PZ-5	<LLD	2.2	5.8
SW-509	03/14/85	Gallery	<LLD	1.6	4.8
SW-510	04/04/85	Gallery	<LLD	1.5	5.2
GW-210	04/04/85	PZ-5	<LLD	1.9	5.2
GW-211	04/04/85	PZ-2	<LLD	1.1	5.9
GW-213	05/08/85	PZ-2	0.71	1.7	5.1
GW-215	05/08/85	PZ-5	0.94	1.5	5.9
GW-216	06/07/85	PZ-2	0.14	1.0	5.7
GW-218	06/07/85	PZ-6	0.11	1.5	5.9
GA-1	10/82	Gallery	17.4	11.7	5.8
GA-2	10/82	Gallery	13.7	12.6	5.8
GA-3	10/82	Gallery	15.7	10.0	5.8

TABLE 2

Summary of Data on Th-232 Concentrations in Natural Waters (SW = surface water, GW = ground water)

Water Type	Concentration (μg/ℓ)	Pretreatment	Authors
Atlantic Ocean (SW)	0.00064	centrifuged	Moore and Sackett (1964)
Pacific Ocean (SW)	0.00033	unfiltered	Somayajulo and Goldberg (1966)
SW from Nonradio-active areas in India	1.1-2.7	filtered	Kamath et al. (1964)
near U-mining	1.9-5.4	<10 μm	
River Waters in Japan	0.0087-0.045	< 5 μm	Miyake et al. (1964)
SW from Lakes and Rivers (USA)	0.08-0.4		Thurber (1965)
GW from a Granitic Area (USA)	0.2-0.9		Dementyev (1965)
SW and GW from the Morro do Ferro Site	0.02-17	<0.45 μm	Eisenbud et al. (1982) Miekeley et al. (1982, 1984)

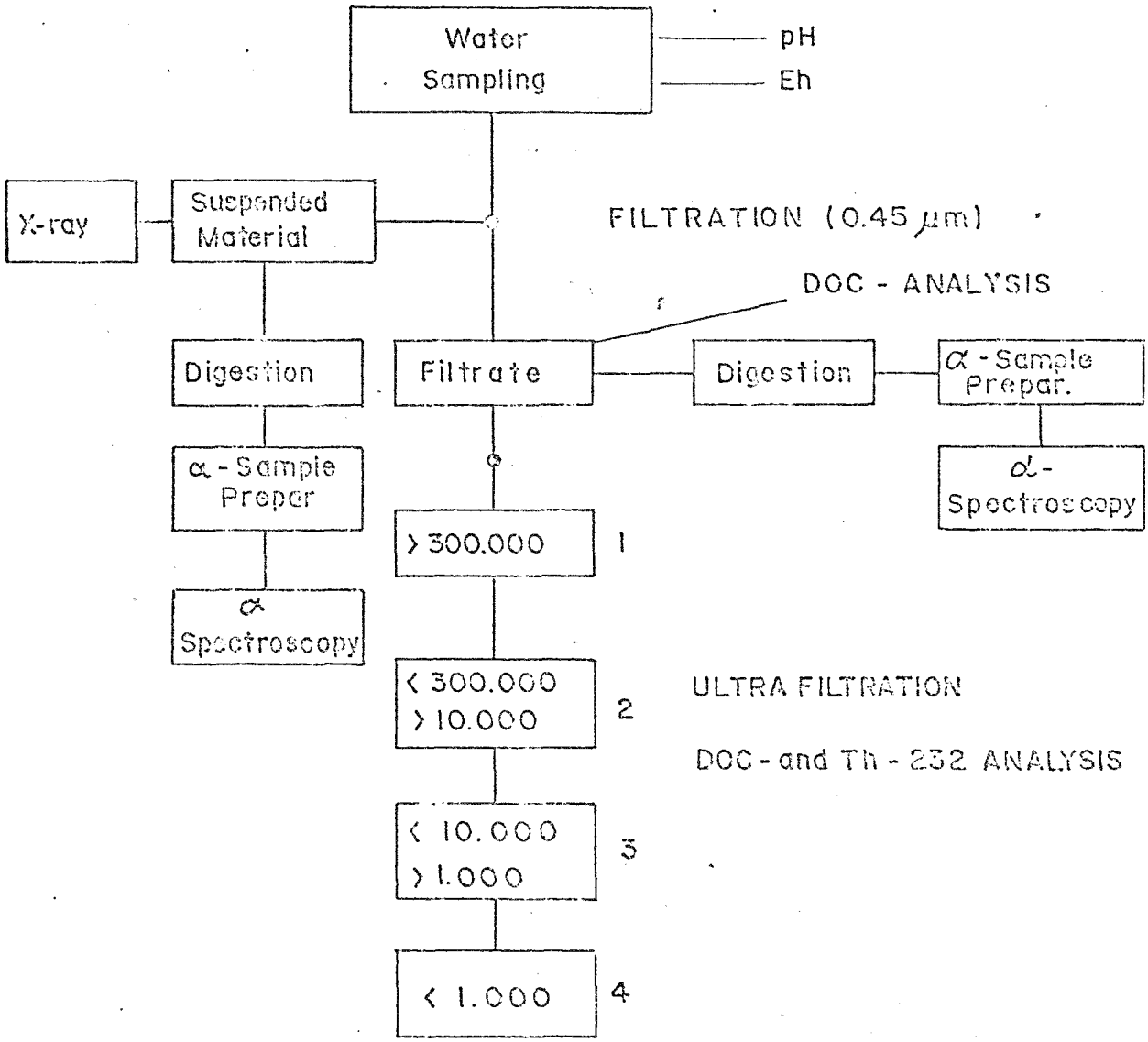


FIGURE 1 : Analytical Procedures for Water and Sediment Analysis.

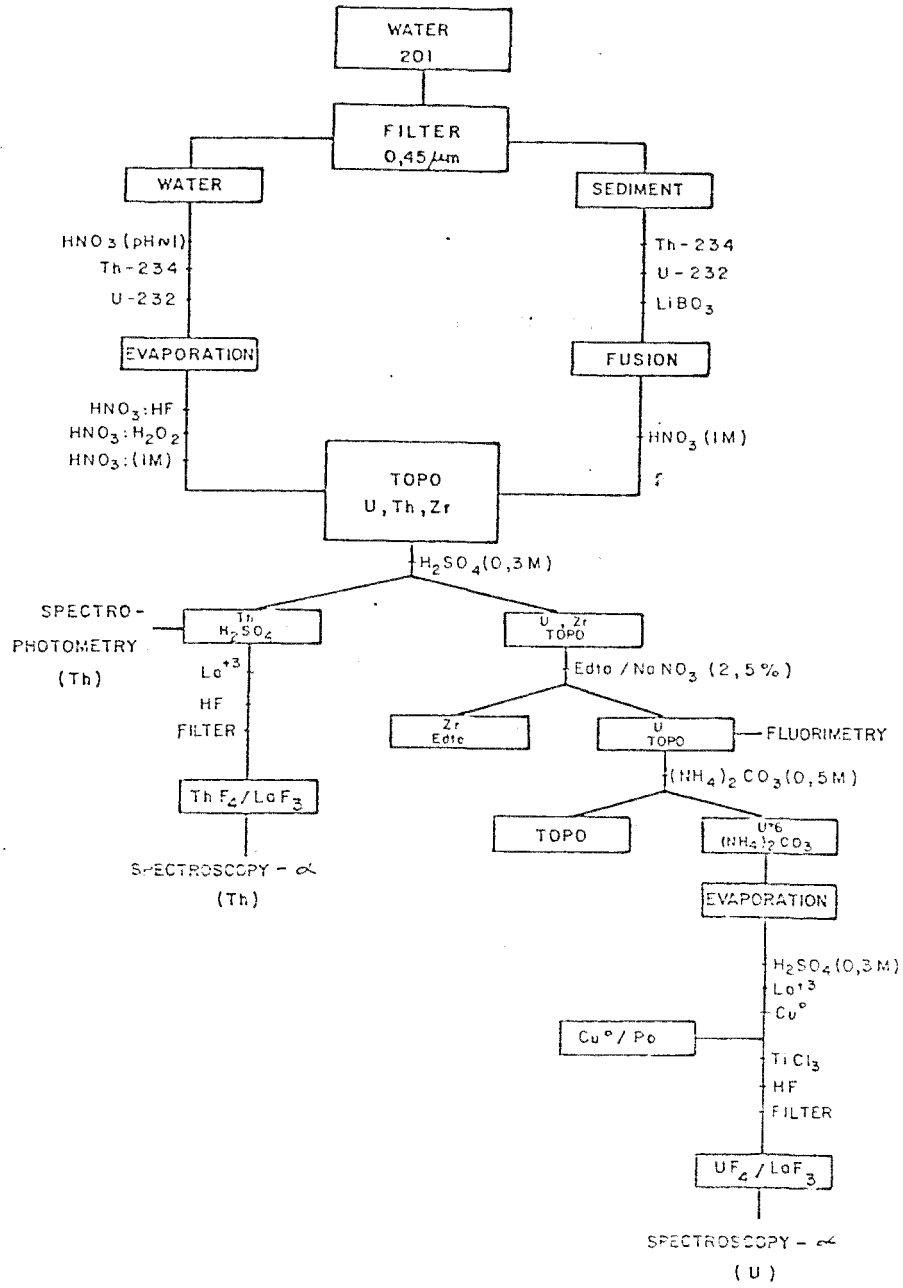


FIGURE 2 : Analytical Procedures for Th-isotopic Analysis by α- Spectroscopy.

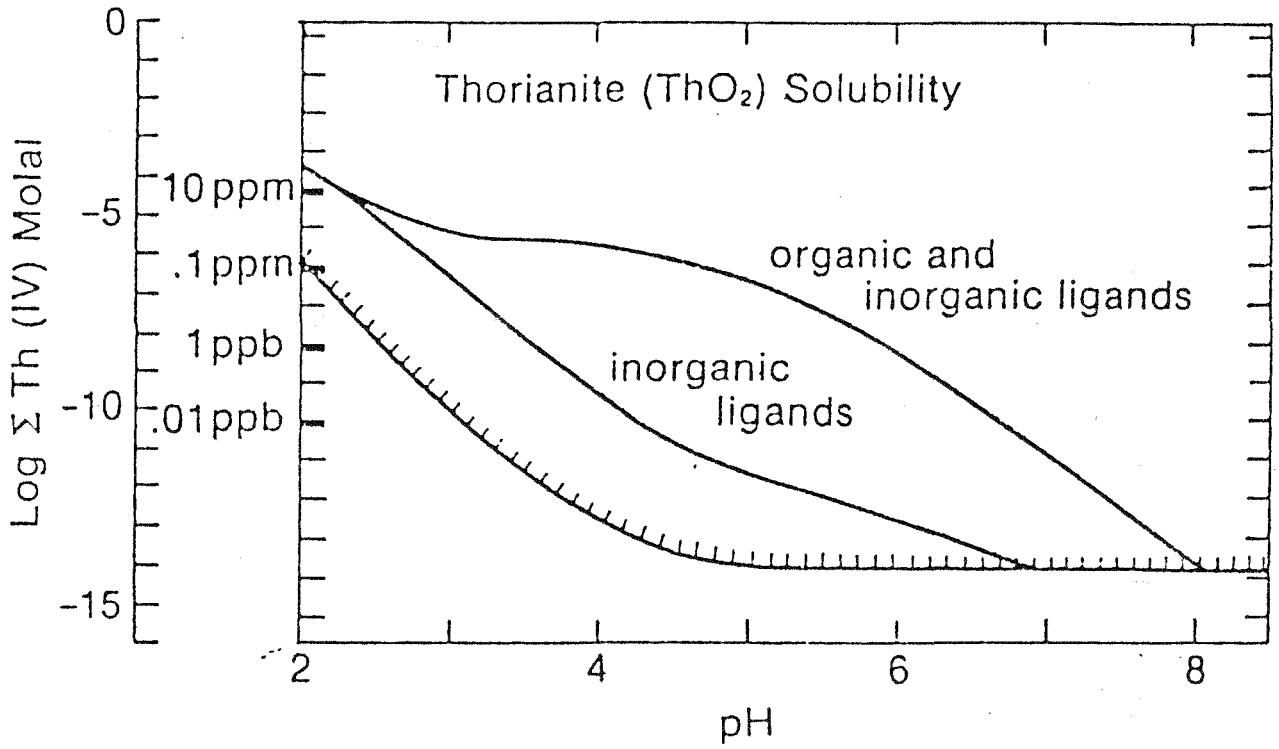


FIGURE 3 : The Effect of Th-Complexing on the Solubility of Thorianite (Langmuir and Herman, Geochim. Cosmochim.Acta 44, 1753-66,1980) ThO2 vs. pH at 25 C in a solution of Cl=10ppm, NO3=2.5ppm, SO4=100ppm, F=0.3ppm, PO4=0.1ppm oxalate=1ppm, citrate=0.1ppm and EDTA=0.1ppm.

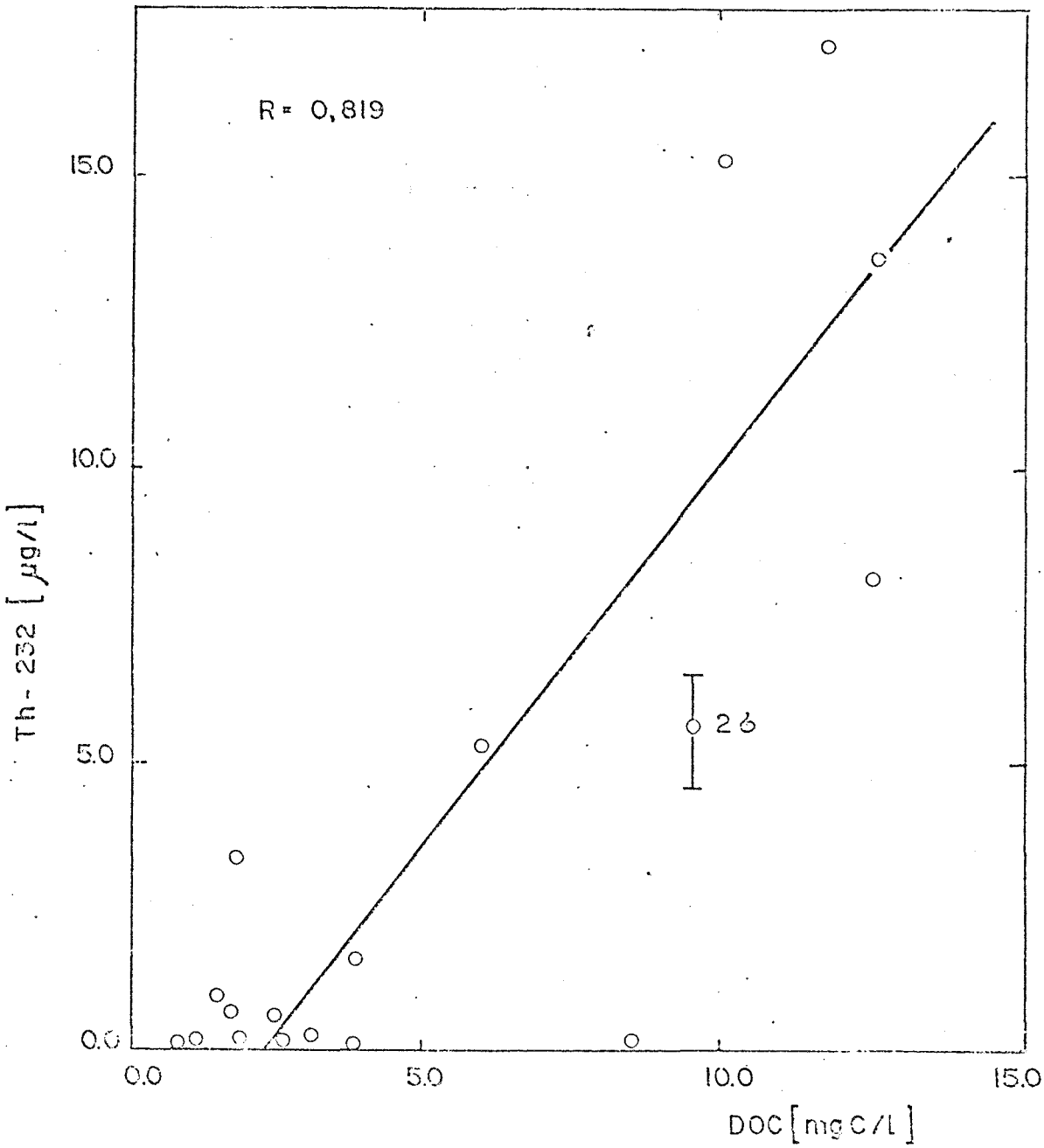


FIGURE 4 : Correlation Graph : Th-232 vs. DOC in Morro do Ferro Water.

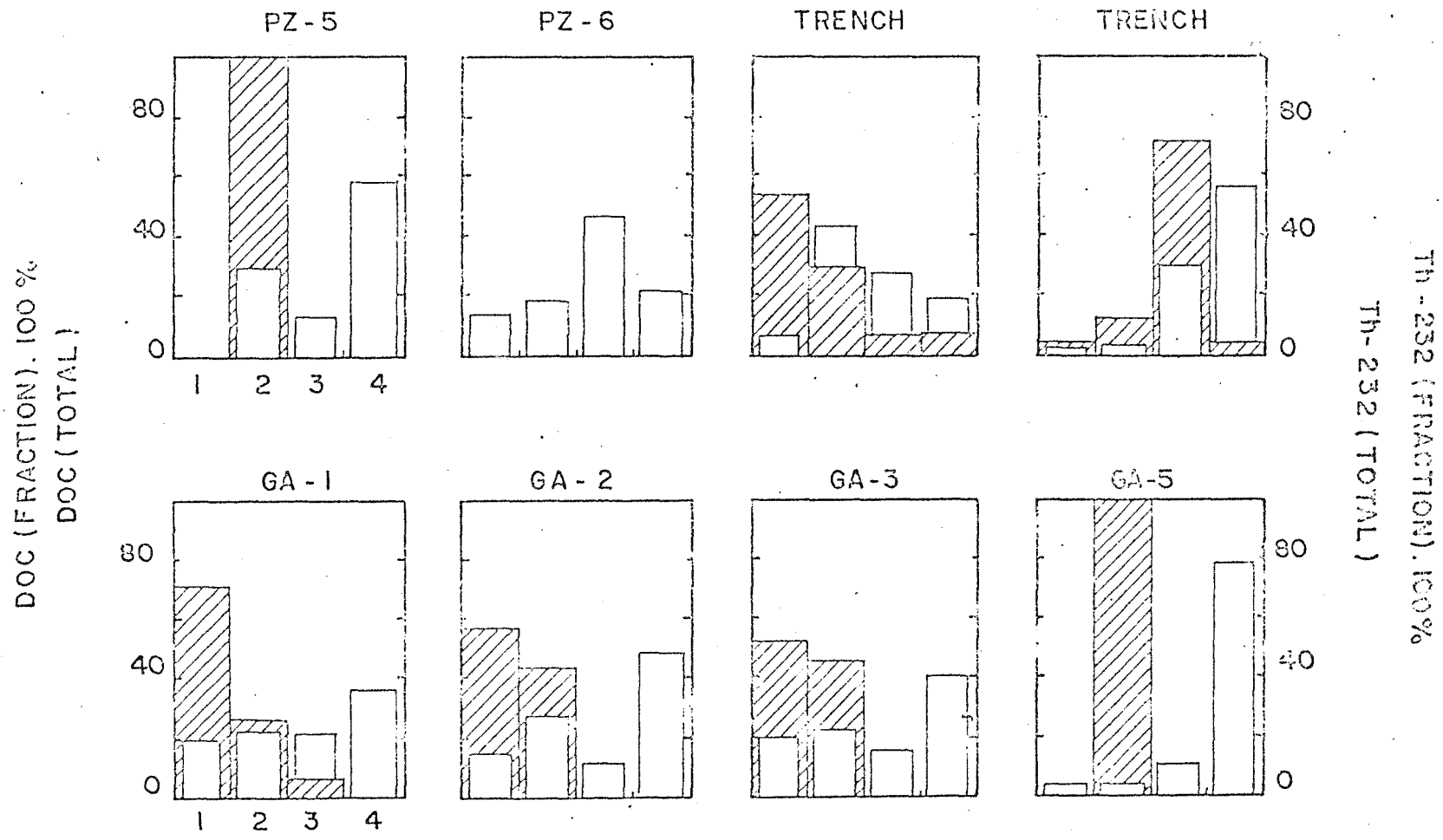


FIGURE 5 : Distribution Patterns of DOC and Th-232 in different Molecular Weight Fractions (1: >300,000, 2: between 300,000 and 10,000, 3: between 10,000 and 1,000, 4: <1,000) —shadowed areas: Th-distribution, unshadowed areas: DOC-distribution.

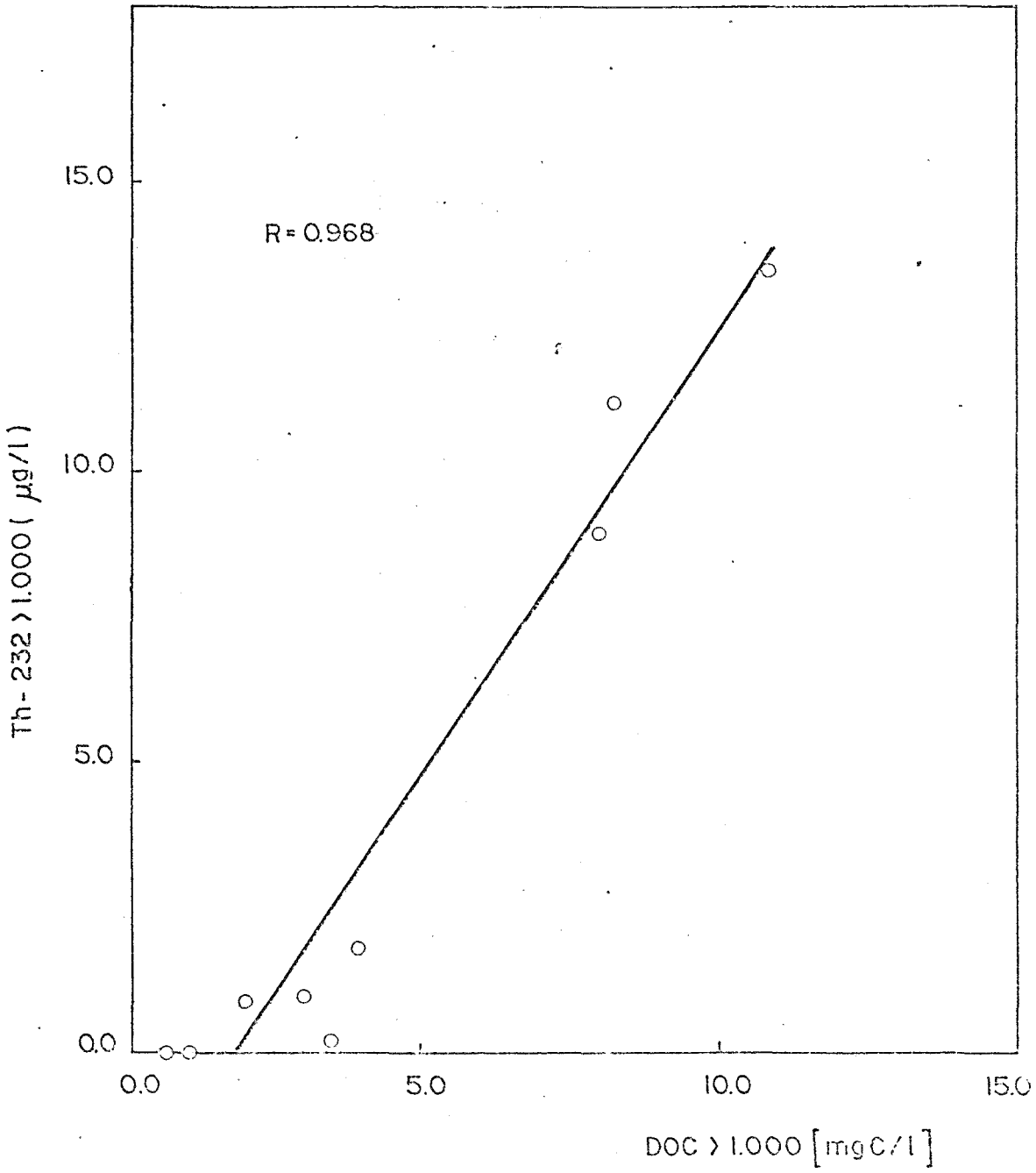


FIGURE 6 : Correlation Graph : Th-232 vs. DOC (>1.000 MW-units.

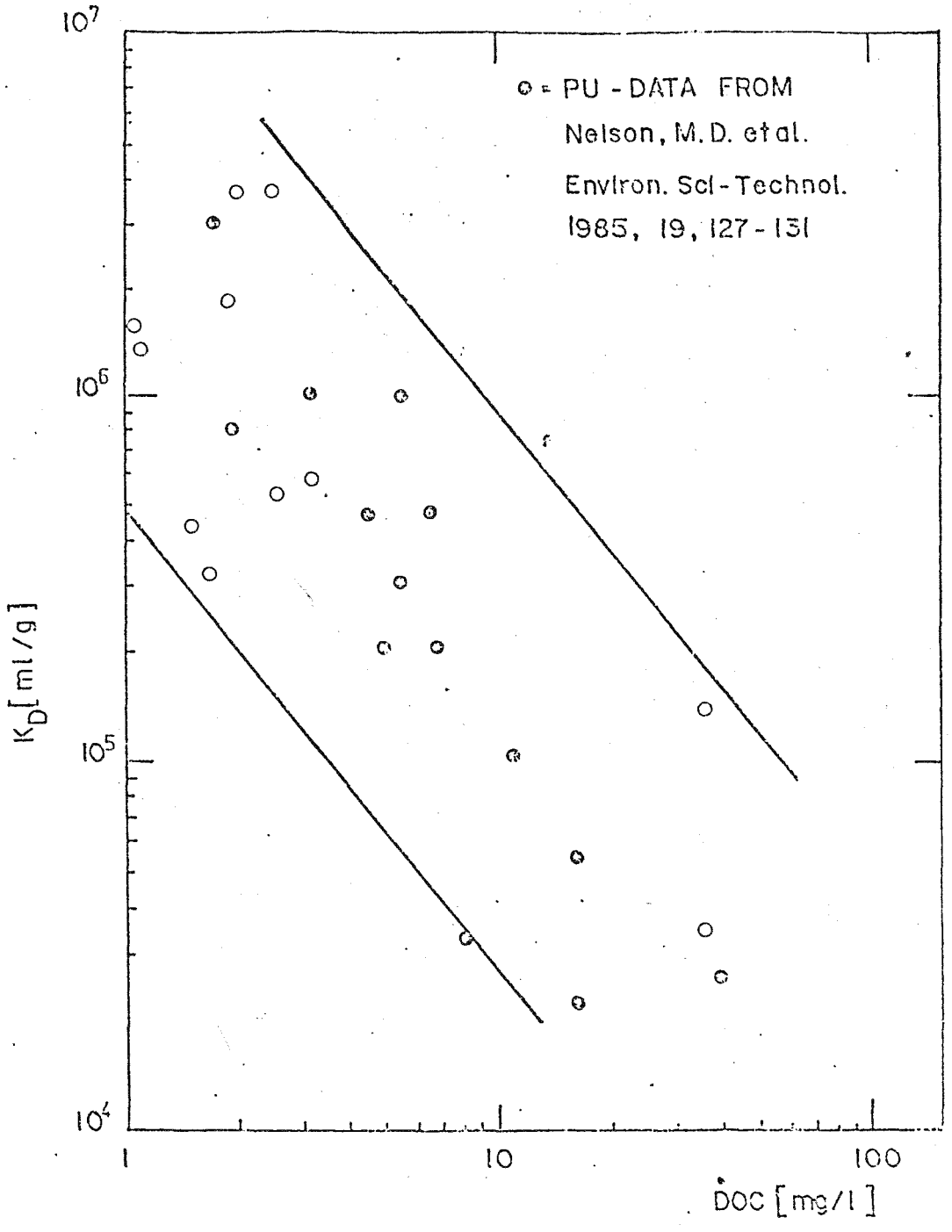


FIGURE 7 : Distribution Coefficients of Th-232 as Function of DOC in Morro do Ferro Waters, including Data for Plutonium.