INVESTIGATION OF RADIOLOGICAL CONTAMINATION OF SOIL SAMPLES

FROM IDAHO NATIONAL LABORATORY

By

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of ROSARA FAITH PAYNE find it satisfactory and recommend that it be accepted.

_____
Chair

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INVESTIGATION OF RADIOLOGICAL CONTAMINATION IN HISTORIC SOIL

FROM IDAHO NATIONAL LABORATORY

Abstract

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Anthropogenic radionuclides have been introduced into the environment through a variety of mechanisms ranging from nuclear weapons testing to satellite failures to leakage from waste disposal sites. In this study, ^{137}Cs, ^{241}Am and Pu isotopes were utilized to gain a better understanding of the contamination history of soils collected in 1972 near the Subsurface Disposal Area (SDA) at the Idaho National Laboratory. The atom and activity ratios of these isotopes have been well characterized for many environmental contamination events and can therefore be used as markers for identifying the processes from which the isotopes originated.

A suite of traditional and new radiochemical methodologies were modified to analyze small soil samples for the above mentioned isotopes. Activity detection and determination limits were calculated to evaluate the methods employed. Further investigation was done to couple fission track analysis (FTA) to laser ablation mass spectrometry (LAMS). The purpose of this study was to interrogate the soil aggregates that were associated with fissile material.

Two sampling locations were investigated and two depths at each of these locations. The total activity of the samples were higher in the surface soils and contained more ^{241}Am than could be accounted for by ingrowth from ^{241}Pu alone. This indicates that there must be an additional contamination source of ^{241}Am. The ^{137}Cs activity was slightly elevated over background levels in the surface soil and at background below that, indicating that the primary contamination pathway was on-site activities. Plutonium atom and activity ratios are radically different from expected fallout values and correlate well with the ratios expected for weapons grade Pu in a soil matrix. The Pu contamination most likely originated from waste generated by activities at Rocky Flats Site, CO which was buried at the SDA. The work on using FTA to located contaminated soil, prior to LAMS showed values for correlation coefficients between masses of greater that 0.6. This indicates that the soil was influenced by a flooding event which occurred in 1969.

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ACRONYMS

AEC – Atomic Energy Commission

ARS – Acute Radiation Syndrome

ANL-W – Argonne National Laboratory West

BOMARC – Boeing Michigan Aeronautical Research Center

DOE – Department of Energy

EBR-1 – Experimental Breeder Reactor 1

FSU – Former Soviet Union

FTA – Fission Track Analysis

HPGe – High Purity Germanium

IAEA – International Atomic Energy Agency

ICP – Inductively Coupled Plasma

ICPP – Idaho Chemical Processing Plant

INL – Idaho National Laboratory

LAMS – Laser Ablation Mass Spectrometry

LEPS – Low Energy Photon Spectrometry

LSC – Liquid Scintillation Counting

NRF – Naval Reactors Facility

NTS – Nevada Test Site

PIPS – Passive Ion Implanted Silicon

RFS – Rocky Flats Site

RWMC – Radioactive Waste Management Complex

RWMIS – Radioactive Waste Management Information System

SDA – Subsurface Disposal Area

SIMS – Secondary Ionization Mass Spectrometry

SNAP – Systems for Nuclear Auxiliary Power

TAN – Test Area North

TIMS – Thermal Ionization Mass Spectrometry

TRA – Test Reactor Area

WGP – Weapons Grade Plutonium

Dedication

This dissertation is dedicated to my boys;

Theo, Damian, and Gavyn and their daddy Tyson,

for the inspiration and joy they have brought me!!

CHAPTER ONE

INTRODUCTION

Introduction

Global fallout is the distribution of anthropogenic radioactivity as a result of nuclear weapons testing. The United States stopped atmospheric and above ground nuclear weapons testing in 1963. Despite this, fission products and actinides are still being introduced into the environment from storage of nuclear weapons, legacy waste, and waste from ongoing nuclear power production. The behavior of the actinides in the environment is dependant on their chemical and physical form, which can vary depending on the source. The oxidation state and complexation of the radionuclide will influence its environmental interactions. Different nuclear processes also result in products with varying isotopic and activity ratios, which can be used to elucidate the source of the waste. Identification of the processes that created the actinides and fission products is a first step to understanding their eventual behavior in the environment.

The goals of this work were to determine the total ^{241}Am, isotopic Pu and ^{137}Cs activities in soil collected from the Idaho National Laboratory, and to use this information to gain a better understanding of the source of the contamination. The development and adaptation of specific methods and techniques to accomplish these goals were required. The first approach was to examine the contamination source information by investigating actinide isotopic and activity

ratios. Differentiation between ^{241}Am present at the time of sampling and that

present due to ingrowth provides evidence of multiple contamination sources.

The second approach was to understand the composition of the soil aggregates

that contained fissile nuclides. This was done by locating soil particles which

contained fissile material by fission track analysis (FTA) and further interrogating

the soil particles with laser ablation mass spectrometry (LAMS). The information

gained from the research described here has suggested that additional

experimental investigations should be explored to obtain a better understanding

of the radiological soil contamination in these soils.

Background: history

In August 1939, Albert Einstein wrote a letter to the President, Franklin D.

Roosevelt, warning him of the possible implications of a uranium (U) chain

reaction which could produce large amounts of energy (DOE 1994). He

hypothesized that a single U bomb "potentially could destroy an entire seaport".

Einstein believed that the U.S. Government should support U research because

it was believed that German physicists were doing the same. Roosevelt initially

responded cautiously but by December 28, 1942 he had authorized construction

of full scale production facilities with an initial budget of $500 million (DOE 1994).

The atomic bomb project was run by the U.S. Army Corps of Engineers

that established the Manhattan Engineering District to manage the project under

the direction of General Leslie R. Groves. In 1946 the Atomic Energy Act

created the Atomic Energy Commission (AEC), which took over the Manhattan

Engineering District's growing scientific and industrial facilities which had spent approximately $2.2 billion by the end of the war (DOE 1994, DOE 1997, Lenhard, 2004). Reorganization occurred in 1974 with the establishment of two new agencies, the Nuclear Regulatory Commission and the Energy Research and Development Administration. By the 1970's the prolonged energy crisis showed the need for unified energy organization and planning. On October 1, 1977 the newly created Department of Energy (DOE) assumed the responsibilities of several agencies (DOE 1994, DOE 1997).

This department provided a basis for a comprehensive and balanced national energy plan. The DOE had many responsibilities including long-term, high-risk research and development of energy technology, federal power marketing, energy conservation, the nuclear weapons program, energy regulatory programs, and central energy data collection and analysis program (DOE 1994). Since its inception, DOE's focus has changed with the needs and priorities of the nation. In the 1980's nuclear weapons research and production took priority; however, with the end of the Cold War the focus was directed towards environmental clean-up, nonproliferation and stewardship of the nuclear stockpile (DOE 1997).

A portion of the efforts of DOE is currently dedicated to cleanup and closure of over 140 contaminated locations in the United States. These sites include the national laboratories that are part of the legacy of nuclear-weapons production during the Manhattan Project and the Cold War (DOE 1994, DOE 1997, Lenhard, 2004).

Anthropogenic radioactivity in the environment

In the past 50 years since nuclear weapons and power production began, the global and local environment has been contaminated with actinides as well as radioactive fission and activation products. At Present the DOE scientists are assessing the presence of contaminated environmental media or waste at approximately 9,900 sites across the United States (DOE 1997). Figure 1.1 shows the processes which have contributed to the environmental release of radionuclides over the last 50 years. The contaminated material consists of about 79,000,000 m^3 of solid material and 1,800 m^3 of contaminated water, greater than 90% of which is from weapons production (DOE 1997).

There are several pathways by which these radionuclides can come into contact with people as shown in Figure 1.2. Radionuclides behave differently in the human body and in the environment. They can cause damage in either location through their decay processes. The most important route for radionuclides into the body from contaminated soil is via the inhalation of small soil particles into the pulmonary region of the lung (EPRI 1981). The long half-lives, radiotoxicity and high alpha energies of Pu and Am isotopes cause concern where they are present in the environment and thus potentially transferable to the plant, animal and human populations.

Figure 1.1
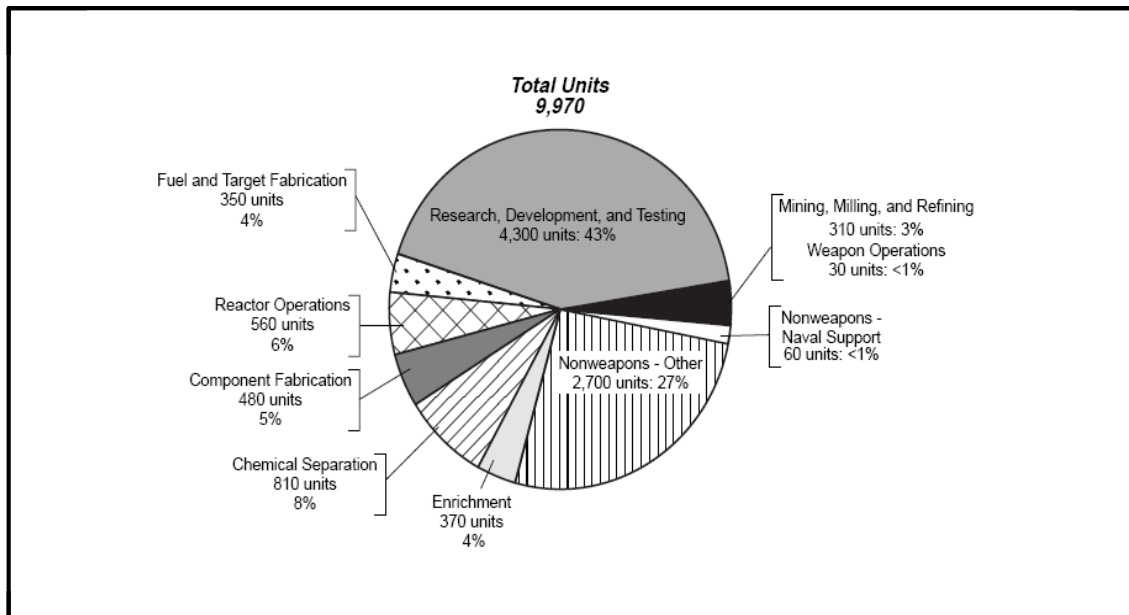
Figure 1.1: Processes which contributed to actinide, activation and fission product environmental release and the relative number of events from 9,970 sites. (DOE 1997)

Figure 1.2
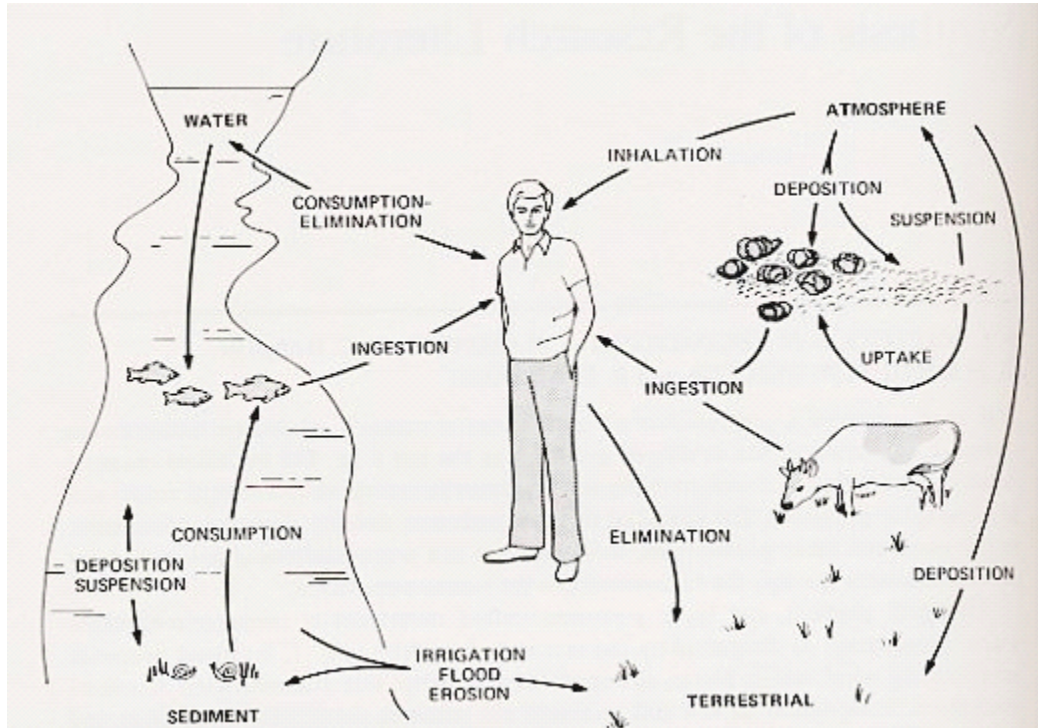
Figure 1.2: Pathways of transuranic elements to man from aquatic, atmosphere and terrestrial components. (DOE 1980)

Weapons detonation

July 16, 1945 marked the beginning of anthropogenic environmental contamination with the detonation of the first nuclear weapon in Nevada (DOE 1980). Between 1945 and 1962 the U.S. performed 210 atmospheric nuclear tests (DOE 1997). Debris from testing had been transferred into the troposphere and stratosphere depending on the yield of the test. In the high neutron flux of a nuclear testing event, transuranic elements, fission products, and activation products are formed. Detonation of thermonuclear (fusion) devices such as "Mike" in 1952 in the Enewekak Atoll, produced transuranic elements with masses up to 255 (DOE 1980). Table 1.1 shows the relative abundance of heavy elements formed during the "Mike" test and in worldwide fallout.

Stratospheric debris generally has an 11-12 month residence time before returning to the earth's surface (EPRI 1981, DOE 1980). This long residence time allows for global rather than local distribution of the nuclear debris. It has been estimated that 5 x 10^{19} Bq (>2,200 kg) of $^{239+240}$Pu has entered the atmosphere through nuclear testing (EPRI 1981, DOE 1980). In 1963 the U.S., United Kingdom and the former Soviet Union signed a nuclear weapons test ban which prohibited testing nuclear devices above ground. Since 1963 the radioactivity entering the stratosphere has primarily been from Chinese and French nuclear testing (DOE 1980).

Between 1956 and 1992 the United States has conducted 828 underground nuclear tests (Kersting et al., 1999). As with atmospheric testing, underground testing also produced transuranic elements, fission products and

Table 1.1

Mass no.	Isobar	Mike[a]	Fallout[a]	Mike[b]	Fallout[b]
239	Plutonium	1.0	1.0	1.0	1.0
240	Plutonium	0.363	0.18	1.35	0.669
241	Plutonium	0.039	0.013	63	21
242	Plutonium	1.9×10^{-2}	0.004	1.2×10^{-3}	2.53×10^{-4}
243	Americium	2.1×10^{-3}		6.9×10^{-3}	
244	Plutonium	1.2×10^{-3}		3.5×10^{-7}	
245	Curium	1.2×10^{-4}		3.6×10^{-4}	
246	Curium	4.8×10^{-5}		2.4×10^{-4}	
247	Curium	3.9×10^{-6}		6.2×10^{-9}	
248	Curium	1.2×10^{-6}		8.4×10^{-8}	
249	Berkelium	1.1×10^{-7}		3.2×10^{-3}	
250	Curium	$\sim 3 \times 10^{-8}$		$\sim 6.5 \times 10^{-8}$	
251	Californium	$\sim 1.4 \times 10^{-8}$		$\sim 3.8 \times 10^{-7}$	
252	Californium	1.0×10^{-9}		9.3×10^{-6}	
253	Californium	5.0×10^{-10}		2.5×10^{-4}	
254	Californium	5.0×10^{-11}		7.4×10^{-6}	
255	Einsteinium	4.0×10^{-11}		9.1×10^{-6}	

Table 1.1: Relative abundances of heavy elements produced during the Mike test compared with that measured in worldwide fallout (mass abundance at time = 0). (DOE 1980)

a. relative atom abundance

b. relative activity abundance

activation products. The high temperatures experienced ($>10^6$ K) vaporize and melt the surrounding rock. Although many of the radionuclides produced are incorporated into the glass melt, it has been shown that some of the radionuclides can form colloids. These colloids can transport the radionuclides over distances greater than 1 km providing an additional mechanism for soil contamination (Kersting et al., 1999).

SNAP-9A

One of the industrial uses of nuclear technology was the development of power sources for the space program, Systems for Nuclear Auxiliary Power (SNAP). In total, the space program has launched 3.5×10^{16} Bq of ^{238}Pu. Forty percent of this is in long term orbit around the earth, 24% is on the lunar surface, 9% is on the surface of Mars, 17% has been used in deep space exploration, and 10% was involved in 3 in-flight vehicle aborts, which did not result in nuclear accidents (DOE 1980).

In April of 1964 a navigational satellite failed to reach orbit. This satellite was powered by a nuclear device (SNAP-9A). It was carrying approximately 6.3×10^{14} Bq (1 kg) of ^{238}Pu that incinerated upon atmospheric reentry (EPRI 1981). Due to the high altitude of the satellite, the residence time for the debris was about 2 years with the peak deposition occurring during 1969 (DOE 1980). While fallout from weapons testing is greatest in the northern hemisphere temperate regions, the deposition pattern of the SNAP-9A accident is entirely different. Most (73%) of the SNAP-9A ^{238}Pu was deposited in the southern hemisphere

(DOE 1980). This significantly affects the $^{238}Pu/^{239+240}Pu$ activity ratio at different latitudes as seen in Table 1.2.

Accidental releases

The nuclear industry has experienced several accidents which have also contributed to the anthropogenic contamination of the environment. Plutonium fires occurred in 1957 and 1969 at the Rocky Flats Site (RFS) in Colorado which released Pu in the form of aerosols. These events and a Pu waste leak at RFS are discussed in detail later. The United States also experienced a fire at Boeing Michigan Aeronautical Research Center (BOMARC) in 1960. A Pu missile warhead was burned and melted in Missile Shelter 204. The fire burned for 30 minutes before efforts to distinguish the fire were initiated. The building was badly damaged and it has been reported that flames reached between 20-75 ft high. It is thought that up to 100 g of Pu could have been aerosolized and dispersed into the atmosphere through the smoke and the winds (2-8 knots) (LA 1996). On March 28, 1979 the power reactor, Three Mile Island Unit 2 in Pennsylvania, experienced a core meltdown. The release of radiological material was minimal from this event, although it had significant impacts on the confidence of the general public in the nuclear industry (U.S. Nuclear Regulatory Commission).

There have been two documented accidents involving aircrafts carrying nuclear weapons. The first occurred in January 1966 with a midair collision between a B-52 bomber and a refueling tanker. Four nuclear weapons were involved. Two were recovered intact and the chemical explosive components of

Table 1.2

Hemisphere	Latitude	$^{239+240}Pu$ (MBq)	Weapons ^{238}Pu (MBq)	SNAP-9A ^{238}Pu (MBq)	$\dfrac{^{238}Pu}{^{239+240}Pu}$
Northern	90-80	(3.70 ± 1.48)	(0.07 ± 0.04)	(<0.04)	0.020
	80-70	13.32 ± 1.85	0.33 ± 0.04	<0.04	0.025
	70-60	59.20 ± 37.00	1.41 ± 0.93	0.96 ± 0.56	0.040
	60-50	48.10 ± 7.40	1.15 ± 0.15	0.48 ± 0.15	0.034
	50-40	81.40 ± 18.50	1.96 ± 0.41	0.96 ± 0.41	0.036
	40-30	66.60 ± 22.20	1.55 ± 0.52	0.93 ± 0.56	0.037
	30-20	35.52 ± 2.59	0.85 ± 0.07	0.41 ± 0.15	0.035
	20-10	8.88 ± 3.70	0.22 ± 0.07	0.11 ± 0.07	0.038
	10-0	4.81 ± 2.22	0.11 ± 0.04	<0.04	0.023
Southern	0-10	11.10 ± 7.40	0.26 ± 0.19	0.37 ± 0.26	0.057
	10-20	6.66 ± 1.85	0.15 ± 0.04	1.33 ± 0.78	0.222
	20-30	14.43 ± 5.92	0.33 ± 0.15	2.59 ± 1.55	0.203
	30-40	14.80 ± 4.44	0.33 ± 0.11	2.26 ± 0.74	0.175
	40-50	12.95 ± 7.77	0.30 ± 0.19	2.55 ± 1.41	0.220
	50-60	(7.40 ± 3.33)	(0.19 ± 0.07)	(1.63 ± 0.85)	0.245
	60-70	(3.70 ± 1.48)	(0.07 ± 0.04)	(0.81 ± 0.44)	0.240
	70-80	(1.11 ± 0.37)	(0.04 ± 0.04)	(0.30 ± 0.19)	0.300
	80-90	(0.37 ± 0.15)	(<0.04)	(0.15 ± 0.07)	0.400
Activity deposited through 1971 (TBq)					
Northern		9472 ± 1221	226 ± 30	115 ± 30	0.036
Southern		2553 ± 518	59 ± 11	400 ± 78	0.180
Global		12025 ± 1332	285 ± 33	514 ± 81	0.066

Table 1.2: Average latitudinal distributions of cumulative $^{239+240}$Pu and ^{238}Pu fallout (MBq). Results in parentheses were derived by extrapolation; error terms are standard deviations. See report for more detail. (adapted from DOE 1980)

the other two detonated on impact, dispersing Pu and U over a 5 km^2 area near

Palomares, Spain. It is estimated that 0.1 TBq of residual $^{239+240}$Pu has not been

recovered from the detonation (Mitchell et al., 1997). Most of the activity is still

contained in the top 5 cm of soil although cultivation has caused deeper

penetration (Rubio Montero and Martin Sanchez, 2001). In 1968 a B-52 bomber

crashed 11 km from the Thule Air Base in Greenland. The chemical explosive

components of all four weapons detonated resulting in the dispersion of kilogram

quantities of Pu-oxide (8.8 TBq), of which only 85-90% was recovered during

cleanup (Eriksson, M. et al., 2004; Mitchell et al., 1997).

The former Soviet Union (FSU) has experienced several accidental and

intentional radiological releases to the environment. The most recognized

occurred on April 28, 1986 when unauthorized experiments were being run at the

Unit 4 reactor at the Chernobyl Atomic Power Plant. Detectable radioactivity

from this event has been spread throughout the northern hemisphere. By May 6,

both India and the US had detected the event, suggesting that large scale mixing

and dispersion had occurred (Mould, 2000). Of the 444 workers present when

the accident occurred, 300 were admitted to the hospital, 203 of which were

diagnosed with acute radiation syndrome (ARS). Twenty-eight workers and

firemen died within the first three months of the accident and by 1995 an

additional 14 of those originally diagnosed with ARS, had died (Mould, 2000).

Approximately 8.7 x 10^{13} Bq of $^{239+240}$Pu were released and a total surface area

of 146, 300 km^2 have been contaminated (Mould, 2000; Muramatsu et al., 2000).

A 30 km zone around the facility has been permanently abandoned and a total of

greater than 150,000 people were evacuated over four monitoring zones (Mould, 2000). Since the accident, the results of the associated soil and water contamination from many locations and countries have been extensively studied by researchers (e.g. Bunzel et al., 1992; Carbol et al., 2003; Cooper et al., 2000; Ketterer et al., 2004; Muramatsu et al., 2000; Robertson et al., 1992).

Additional intentional and unintentional FSU radiological releases have contributed to radiological environmental contamination. The Mayak Production Association was the site of the first Pu production U-graphite moderated reactor in the FSU. Between 1949-1956, 76×10^6 m^3 (1×10^{17} Bq) of liquid radioactive waste was intentionally dumped into the Techa-Iset-Tobol river system causing the contamination of the water, riverbed sediments, soil of the Techa flood lands and the adjoining bodies of water (Mould, 2000). Lake Karachai was used for radioactive waste disposal after large scale dumping into the Techa River had ended. Approximately 4.4×10^{18} Bq of radioactivity are currently contained in the lake. Although these two contamination sources were intentional they also led to unintentional contamination. In 1967, heavy winds carried 2.2×10^{13} Bq of radioactive particles in the form of dust from the shoreline of the lake. This activity has been measured up to 75 km away (Mould, 2000).

Waste disposal

Nuclear weapons and power production programs have produced vast quantities of radioactive waste. Waste has been stored in a variety of ways both above ground and in the subsurface (DOE 1997). Table 1.3 shows some of the methods of storage employed and the number of these sites which the DOE is

Table 1.3

Category	Subcategory	Number of Contaminated Sites
Above Ground	Storage yards and pads	594
	Debris piles	143
	Muck piles	17
	Scrap yards	49
	TOTAL	803
Surface/Subsurface	Miscellaneous	932
	Landfills	304
	Silos	5
	Trenches/Outfalls	508
	Pits	218
	Burn Pits	126
	Ditches	78
	Fire training areas	8
	Wells	78
	TOTAL	2257
Tanks	Above ground storage tanks	356
	Underground storage tanks	606
	Septic tanks	250
	TOTAL	1212
Liquid surface impoundments	Lagoons	53
	Holding ponds	109
	Settling basins	105
	Seepage & separation basins	73
	Leach fields	132
	Sumps	210
	Evaporation ponds/pits	82
	TOTAL	764

Table 1.3: Types of surface and subsurface disposal and the number of sites. (adapted from DOE 1997)

currently monitoring (DOE 1997). These storage facilities have been responsible

for some of the environmental contamination. Above ground and underground

storage tanks have leaked and subsurface disposal locations have been plagued

by flooding and waste container degradation.

Production of ^{137}Cs, ^{241}Am and Pu isotopes

Uranium (U) is a naturally occurring radioactive element that consists on

average of 99.2745% ^{238}U, 0.720% ^{235}U, and 0.0055% ^{234}U. The isotope ^{235}U is

fissile and thus can be considered directly relevant to nuclear weapons and

power technology. It has a high (585 barn) thermal neutron capture cross

section allowing it to fission upon bombardment with thermalized neutrons (Chart

of Nuclides, 1996). Fission is defined as the splitting of a nucleus into at least

two nuclei accompanied by the release of neutrons and a relatively large amount

of energy. More specifically the energy released is ~200 MeV per event and an

average of 2.5 neutrons are released, allowing the possibility of sustaining a

nuclear chain reaction (Choppin and Rydberg, 1980). An asymmetric split of the

fissile nucleus forms the resultant nuclei. Figure 1.3 shows the percentage of

fission events that results in a product of mass A (Ehmann and Vance, 1991).   It

can be seen that mass 137 and specifically ^{137}Cs is a major fission product. It is

expected that ^{137}Cs will be found when fission events have occurred (e.g. the

detonation of a nuclear weapon). To facilitate a U fission chain reaction the

material must be enriched in the fissile isotope ^{235}U.

Figure 1.3
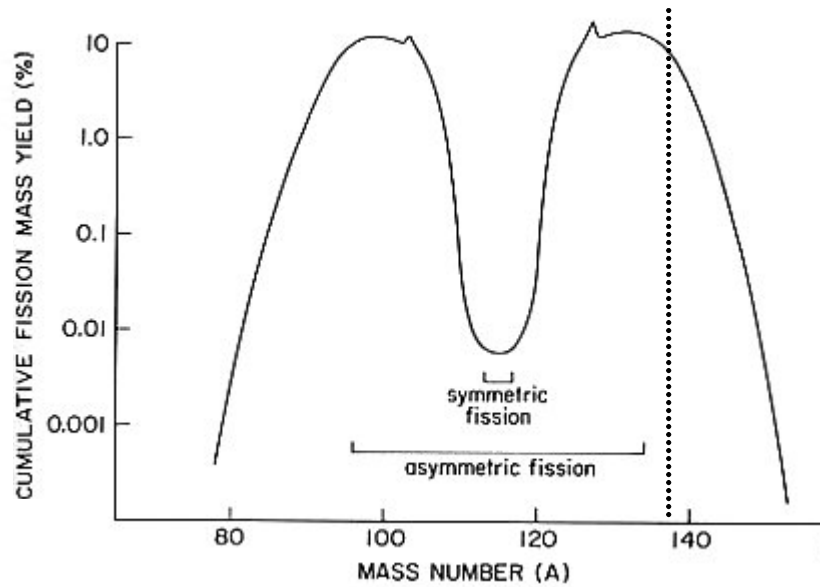
Figure 1.3: Fission mass yield curve for the low-energy neutron-induced fission of a heavy mass nuclide. The dashed line is at mass 137 showing the yield of ^{137}Cs during fission. (Ehmann and Vance, 1991)

The enriched material will contain varying amounts of ^{238}U and ^{235}U depending on the application. Under high neutron fluxes, many nuclear reactions are possible (Choppin and Rydberg, 1980). Figure 1.4 shows the relevant nuclear reactions for the work described in this dissertation. Due to the methods of production, the relative abundances of Am and Pu isotopes are considerably different depending on the nuclear processes or technologies that generated them. It is evident that the amount of the resultant ^{241}Am and Pu isotopes present can be an indicator of the process that was responsible for its production. In this way activity and isotopic ratios can provide insight into the source from which it came. The behavior of the actinides in the environment can also be dependaent on the source of the contamination (DOE 1980). The source will dictate the chemical form and speciation of the isotopes, which affects its reactivity and chemistry.

Relevant actinide chemistry

In order to determine activity ratios, it is necessary to determine the amount of each isotope present. To complete such an analysis the chemical and radioactive properties of the isotopes can be exploited. Table 1.4 shows that most of the actinides can exist in several different oxidation states (Choppin and Rydberg, 1980). The chemical properties of each actinide are different for the different oxidation states; however, to a first approximation in the same oxidation state their chemical properties are quite similar (Choppin and Rydberg, 1980). This provides the basis for separation based on ion exchange chromatography, where the differences in chemical properties and oxidation states of the actinides

Figure 1.4
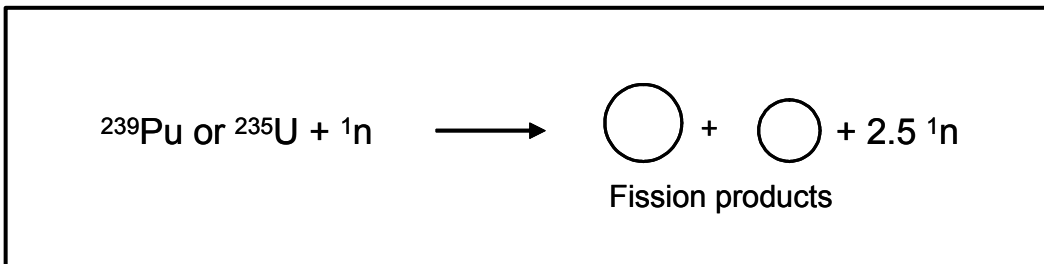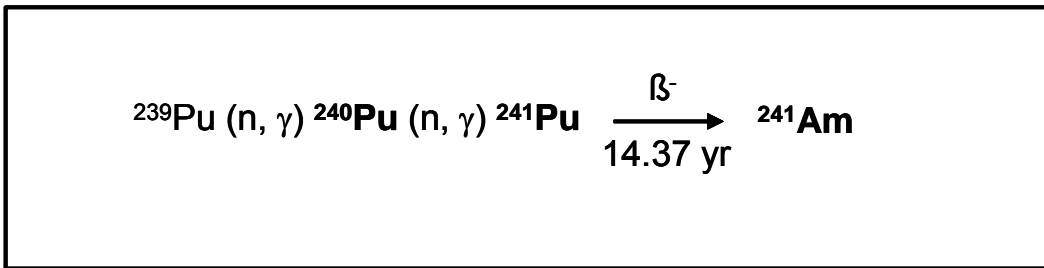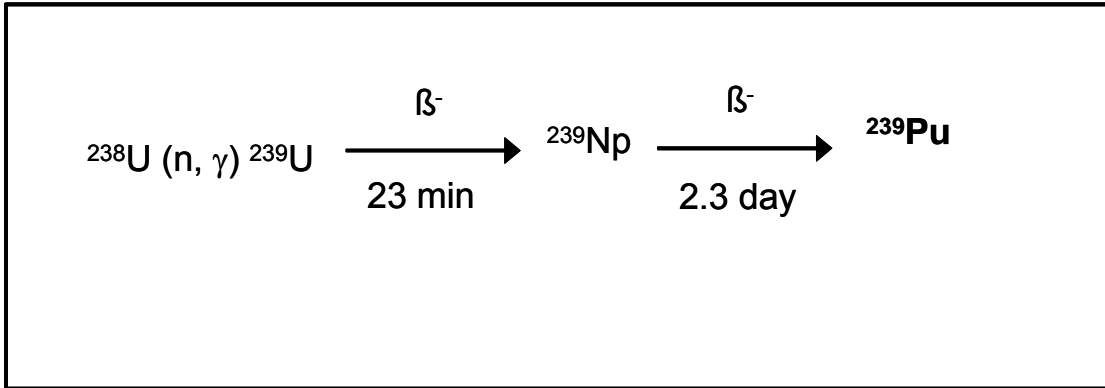
Figure 1.4: Production of ^{241}Am and Pu isotopes and fission products in a neutron flux.

Table 1.4
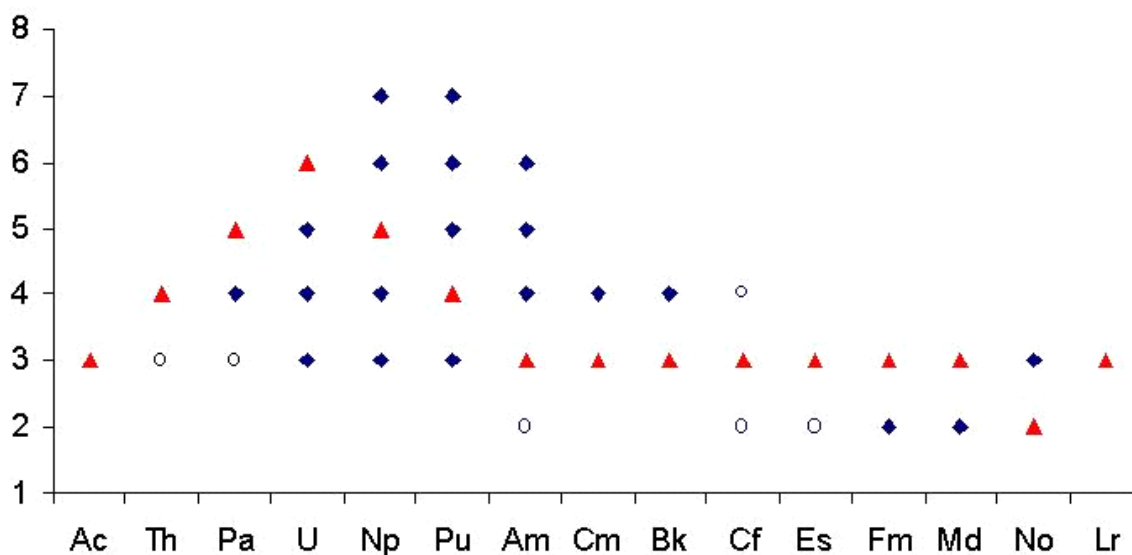
Table 1.4: Possible oxidation states of the actinides. The triangles depict the most stable oxidation state. Diamonds represent other oxidation states. Open circles denote oxidation states only observed in solids or of transient stability. (adapted from Kaltsoyannis and Scott, 1999)

can be manipulated to provide separation of the actinides from each other (Choppin and Nash, 1995; Choppin, 2005; Korkisch, 1989; Silva and Nitsche, 1995).

In many cases, each isotope of an element behaves identically both chemically and physically. The use of radiotracers is an example of this property. In the work described in this dissertation, ^{242}Pu was used as a tracer for the Pu isotopes. It has been assumed that the native ^{242}Pu was negligible (10^5 atoms/g). A known activity or number of atoms of ^{242}Pu is added to each sample. The determination of ^{242}Pu with the other Pu isotopes allowed the determination of the chemical yield of the experimental techniques and therefore the accurate determination of the activities present in each sample.

All isotopes of Pu and ^{241}Am decay by alpha emission except ^{241}Pu, which decays by beta emission as seen in Table 1.5. Alpha particles are characterized by having discrete energies typically in the 5 MeV range. Unlike alpha decay, beta decay processes do not have discrete energies. The decay energies span the range of 0 to some maximum energy, E_{max}, which is unique to each isotope. This imposes several difficulties in quantifying beta emitters. In the case of ^{241}Pu this maximum energy is 20.7 keV.

Rocky Flats Plant/Site

The Rocky Flats Plant now called Rocky Flats Site (RFS) was a Department of Energy (DOE) facility established in 1952 in Golden, Colorado.   It is situated on a 384 acre area within a 6,550 acre buffer zone (DOE 1995). This

Table 1.5

Mass no.	Isobar	Decay type	Energy (keV)	$t_{1/2}$ (yr.)
137	Cesium	γ	661.7	3.01×10^1
238	Plutonium	α	5,499	8.77×10^1
239	Plutonium	α	5,156	2.41×10^4
240	Plutonium	α	5,168	6.56×10^3
241	Plutonium	β^-	20.8	1.44×10^1
241	Americium	α	5,486	4.33×10^2
242	Plutonium	α	4,901	3.75×10^5

Table 1.5: Decay information on Cs, Pu and Am isotopes (Chart of the Nuclides, 1996).

facility housed specialized machine shops, used to process nuclear material (weapons-grade Pu) into finished components for hydrogen bombs (DOE 1995; INEL 1995). Plutonium purification and ^{241}Am recovery and purification were also conducted onsite (INEL 1995). Most of the waste generated at RFS was shipped to the Idaho National Laboratory (INL) for disposal.

There have been three major releases of weapons grade plutonium at RFS, two fires and leakage of Pu containing cutting oil. The first fire occurred in 1957 and the second in 1969 (Hulse et al., 1999; DOE 1995). The fire in 1957 resulted when alpha phase Pu spontaneously ignited while being stored in a dry glove box. The Plexiglas used for the glove box was flammable contributing to the spread of the fire. Minutes after the building fire was extinguished, the exhaust system exploded. Unburned, combustible gases had entered the exhaust system and ignited the flammable filters. Observers reported seeing a dark smoke plume that was 80-100 ft high billow from the exhaust stack (DOE 1995). The second fire occurred when Pu scraps ignited in a glove box that was filled with oily rags. The fire spread rapidly through the glove box and ventilation system and eventually ignited a Pu briquette. The building suffered extensive damage. However, the largest environmental contamination event at RFS was through release of cutting oil which contained Pu (Hulse et al., 1999; Krey, 1976). The 903 pad was a cement slab which housed 5,000 steel barrels filled with Pu contaminated waste oil and solvents (Margulies et al., 2004). As the drums began to corrode between 20 and 200 g of $^{239+240}$Pu is thought to have been

introduced into the surrounding soil (Margulies et al., 2004). Wind storms in 1968 and 1969 redistributed the soil both on and off-site.

Extensive studies have been performed on soil collected onsite to elucidate the extent of contamination from the original events and the resultant redistribution (Krey, 1976; HASL 1970; Litaor et al., 1998; Litaor et al. 1994; Hulse et al., 1999). These studies work under the assumption that the Pu introduced into the soil was weapons grade Pu. In this case it is reasonable to assume that negligible ^{241}Am was present at the time of the original contamination event. All ^{241}Am activity detected in the soils has therefore grown from β decay of ^{241}Pu. The large body of work on these soils provides a reference point of expected Pu and ^{241}Am isotopic and activity ratios for weapons grade Pu.

Idaho National Laboratory

The INL is a DOE facility that was established in 1949 as the National Reactor Testing Station (Lenhard et al., 2004). It is located in eastern Idaho at an elevation of 4900 ft and covers an area of 2350 km^2 (Figure 1.5). The first on-site nuclear reactor, Experimental Breeder Reactor-1 (EBR-1), became operational in 1951. EBR-1 is known as the world's first reactor to supply electricity from nuclear energy. To date, 52 reactors have been operated at INL (Lenhard et al., 2004). The function of INL expanded and eventually encompassed several facilities/areas. The onsite operations which contributed radiological contamination to the local environment were Test Area North (TAN),

Figure 1.5
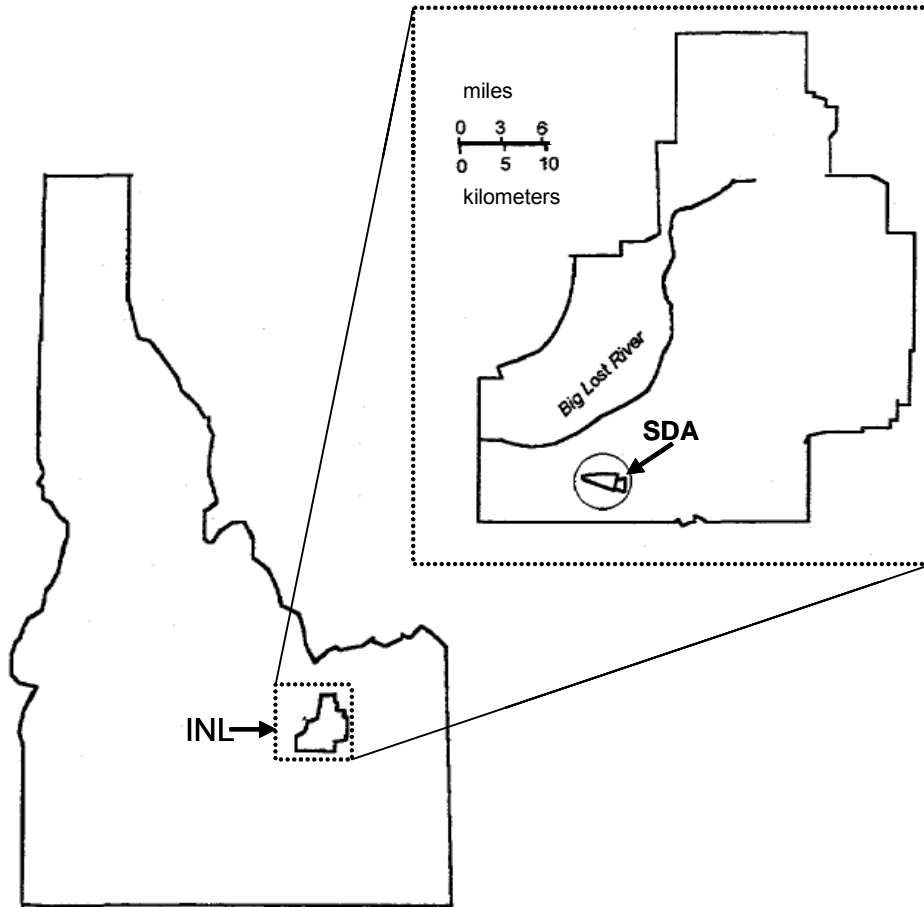
Figure 1.5: Location of Idaho National Laboratory (INL) and the Subsurface Disposal area within INL. (adapted from EML 1998)

Test Reactor Area (TRA), Idaho Chemical Processing Plant (ICPP), Naval Reactors Facility (NRF), Argonne National Laboratory West (ANL-W) and the Subsurface Disposal Area (SDA) (INEL 1995). The largest contributors to contamination at the site are the SDA and ICPP.

Test Area North

The TAN was designed and constructed in the 1950's to support the Aircraft Nuclear Propulsion Program. The mission of this program was to test and develop the idea of a nuclear powered aircraft. Over its nine year operational history three full scale nuclear engines were tested. The facility primarily supported onsite activities. A few exceptions include, testing on reactor cores from Systems for Nuclear Auxiliary Power (SNAP) and research and development of material from the Three Mile Island-2 reactor (INEL 1995).

Test Reactor Area

In addition to test reactors and their support facilities, 13 other facilities have been or are being operated in the TRA. A few of the other facilities include hot cells, radiation measurements, physical and radiochemical laboratories, advanced and engineering test reactor critical, metallurgical laboratory and maintenance shops among others (INEL 1995).

The primary purpose of a test reactor is to explore the chemical, physical and nuclear properties of materials that have been subjected to high neutron and gamma fields. All of the reactors utilized highly enriched uranium fuels with water for cooling and neutron moderation. The used reactor cores were stored in canals for a cooling period and then sent to ICPP for ^{235}U recovery (INEL 1995).

Idaho Chemical Processing Plant

The ICPP began operation in 1953 with the mission of reprocessing test reactor and military fuel to recover ^{235}U. More than 31,000 kg of ^{235}U were recovered between 1953 and 1988 (Lenhard et al., 2004). Other radioactive elements were recovered for private industry and nuclear facilities (Lenhard et al., 2004). Monitoring of stack releases began in 1974 and were recorded by the INL Radioactive Waste Management Information System (RWMIS) (EML 1998). A majority of the airborne releases (Pu, Np, Cs) occurred before this time, specifically between 1957-1965 (EML 1998). Before that time stack effluents were recorded as total or unidentified alpha. Most of the radioactive waste produced by the ICPP is still stored at that facility, although throughout its history waste has also been sent to the SDA (INEL 1995).

Naval Reactors Facility

The NRF was established in 1950 to construct the prototype power plant for the US Navy's first nuclear powered submarine (INEL 1995). It was also the site of testing propulsion plant designs and training navy personnel. Irradiated Navy fuels were examined at a building within this facility. Much of the fuel was then transferred to the ICPP (INEL 1995). Other than fuel, the primary facility waste generated was low level waste (INEL 1995).

Argonne National Laboratory West

The ANL-W consisted of seven major complexes. The objectives of this facility were to increase reactor safety, reduce radioactive waste, and improve reactor fuel efficiency (INEL 1995). This was accomplished by research and

development of liquid metal-cooled reactors and advanced nuclear power plant technology. Onsite fuel recycling process called pyroprocessing was also housed at ANL-W.

Subsurface Disposal Area

In the early history of national laboratories, each facility independently decided how to dispose of their radioactive waste. At INL, a landfill was chosen at an area that only received an average of 20 cm of precipitation per year. In 1952, a 13 acre site was established, initially called the burial grounds, and now called the SDA, which was later expanded to 97 acres (Lenhard et al., 2004). It is located in the southwestern portion of INL. There are 5-7 m of sediment above fractured basalt which is >175 m above the Snake River Aquifer (Lenhard et al., 2004).

Unlined, shallow pits and trenches were used to bury low level mixed and transuranic waste until 1970 (INEEL 1997). The transuranic waste was contained in steel drums and wooden boxes or crates. This waste was primarily segregated into pits that averaged 30 m wide and 4 m deep. When the pits were filled, they were leveled to grade with approximately 1 m of soil (Markham et al., 1978). Although segregation was attempted, transuranic and activation and fission products were often buried together. It is estimated that between 1952 and 1983 approximately 4.4×10^{17} Bq of mixed waste were buried at the SDA (INEL 1995). Over 230 different processes have been identified as sources of radioactivity buried at the SDA from the onsite facilities discussed and other government and commercial generators (INEL 1995). Table 1.6 shows the

Table 1.6

Radionuclide	Activity (GBq)
^{241}Am	5.5×10^6
^{137}Cs	2.6×10^7
^{238}Pu	9.3×10^4
^{239}Pu	2.4×10^6
^{240}Pu	5.6×10^5
^{241}Pu	1.5×10^7
^{242}Pu	3.7

Table 1.6: Activity (GBq) of ^{137}Cs, ^{241}Am and Pu isotopes for disposal in the Subsurface Disposal Area from all generators. Best estimate at time of disposal. (adapted from INEL 1995)

estimated activities of Pu isotopes, [241]Am and ^{137}Cs buried between 1952 and 1983 (INEL 1995).

The SDA lies in a shallow valley and despite the low annual rainfall, it has experienced several floods due to snow melt and rain. The two floods relevant to this study occurred in February 1962 and January 1969 (Markham et al., 1978). During 1969, Pit 9, located in the northeastern corner of the SDA, was uncovered when it flooded. Pit 9 (40 m x 125 m) was larger than the average pit, 40 m x 125 m, covering approximately 1 acre of surface area. Waste was deposited in Pit 9 from November 1967 to June 1969 and consisted primarily of mixed waste from RFS (INEL 1995b). Approximately 3×10^3 m^3 of transuranic mixed waste from RFS and 1×10^3 m^3 of low level and mixed waste from INL was buried at Pit 9 which consisted of 1×10^5 L of organics (over 30% of the organic inventory at the SDA) and 30 kg of transuranic radionuclides (between 3% and 4% of the total transuranic inventory at the SDA) (INEL 1995b).

The contents of the SDA are not known with certainty, although significant effort has been put forth to estimate the contents (INEL 1995). Records of shipments received before 1960 only contained entries from RFS and these records were primarily qualitative. Descriptions such as "plant waste" and "unidentified β-γ or α" or indications of only one radionuclide, fission product, or activation product when many must have been present, were common. Alternatively, elemental information with no indication of which particular radionuclide was also recorded. The chemical and physical forms of the waste were also not specified (INEL 1995).

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Soils used

In the early 1970's, soil was collected from over 70 locations surrounding the SDA (Markham et al., 1978). Samples were collected at a depth of 0-4 cm at all but 4 locations and at a depth of 4-8 cm at 22 locations. At each sampling station, five sample cores (10 cm diameter x 4 cm depth) were obtained, one from each corner plus the center of a 1 m x 1 m square area. The composite samples were oven dried, mixed thoroughly, ground and screened through a 0.5 mm mesh. Each sample was then analyzed for ^{241}Am, ^{238}Pu and $^{239+240}$Pu by alpha spectrometry. Isopleths were observed with the highest activities being at the 0-4 cm depth centered around the northeastern corner near Pit 9 (Figure 1.6). The maximum activities were 1.9 Bq/g for ^{241}Am, 1.4 Bq/g for $^{239+240}$Pu and 0.03 Bq/g for ^{238}Pu (Markham et al., 1978). After analysis, the soils were packaged for storage. Our laboratory acquired these soils in 2003. The samples were chosen for this study based on the knowledge that they contained higher activities than other samples. Locations 1 and 2 are north and east of the northeast corner of the SDA. At these two locations both the 0-4 cm and 4-8 cm depths were analyzed by gamma, alpha and mass spectrometry and liquid scintillation counting.

Fission track analysis

The high thermal neutron cross sections (585 b, 750 b) of ^{235}U and ^{239}Pu, make them appropriate for nuclear power and weapons also make them prime candidates for fission track analysis (FTA). When a fission event occurs,

Figure 1.6
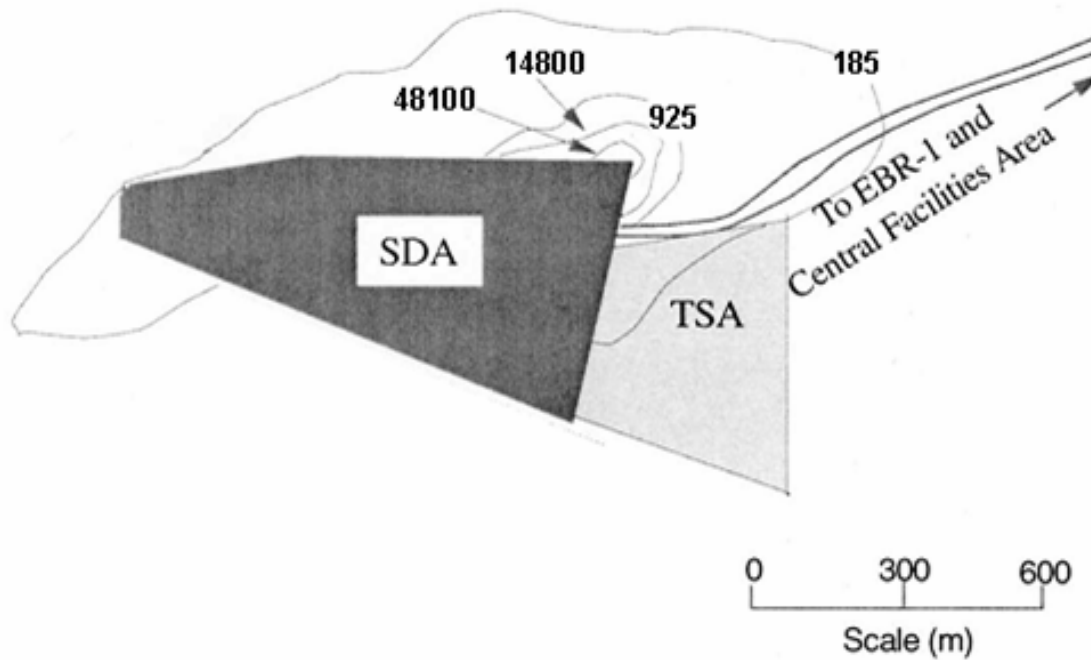
Figure 1.6: Principle aerial extent to which $^{239+240}$Pu moved beyond the perimeter of the SDA by 1974. Isopleth units: Bq/m^2. (adapted from Markham et al., 1978 and EML 1998)

the fission products have sufficient energy and velocity to cause damage to an insulating material. This damage is called a track and has a radius typically less than 50 Å upon formation (Fleischer et al., 1975). Tracks are chemically reactive centers of strain that are made by the displacement of atoms (Fleischer et al., 1975). These tracks can then be enlarged to be visible under an optical microscope by chemical etching. The material itself can be etched to determine age, because ^{238}U decays at a predictable rate by spontaneous fission 5×10^{-5} % of the time or fission can be induced under a neutron flux to determine combined ^{235}U and ^{239}Pu concentrations. The induced ^{235}U and ^{239}Pu tracks are indistinguishable in FTA; therefore, further analysis must be done to distinguish between the two. One of the advantages of neutron induced FTA is the ability to visualize the distribution of the ^{235}U and ^{239}Pu within the sample.

Several sample preparation methods have been employed for FTA. In particular, epoxy has been used to mount tissue and bone (Priest et al., 1992; Gore and Jenner, 1980; Morris and Bachelor, 1988) and mineral grains and artifacts (Zielinski and Budahn, 1998; Amaral et al., 1997; Bellot-Gurlet et al., 1999). Soil cores have also been impregnated with epoxy and subsequently processed into 15 μm thin sections (Povetko and Higley, 2001).

Quantitative determination of ^{235}U and ^{239}Pu has been done on soils prepared in many ways other than the epoxy mounts mentioned. A common method is to pulverize the sample and sieve it (100 mesh) and press it into a pellet with no binder (Qureshin et al., 2001; Moharram et al., 2002; Singh et al., 1988). In another method, pellets have been mixed with a binding agent, methyl

cellulose, in a 1:2 ratio (Jojo et al., 1993; Shin and Park, 1989; Jojo et al., 1995; Azam and Prasad, 1989). Methyl cellulose has also been used to create a ring around the pellet, which helped maintain its shape (Fisher, 1970). Other work has indicated success by making packets out of detector material and placing the sample powder into the packet (Guzel et al., 1997). Soils have been sprinkled on tape which is then directly adhered to the detector (Loyland-Ashbury et al., 2001; Kurosaki et al., 2002). In a move away from maintaining original structure and integrity, soils have also been suspended and dried onto filters which are then irradiated (Yumi et al., 1991).

Relative location of fissile material

In many cases it is informative to be able to understand the location of the fission events within the sample. People interested in tissue samples have come up with some novel ways to accomplish this task. In one study, flesh was mounted on the detector and then exposed to a ^{238}Pu source (Gore and Jenner, 1980). The alpha particles were stopped by the solid tissue and where the alphas penetrated the tissue, damage occurred to the detector. This damage led to an image of the tissue on the detector. Induced alpha particles have also been used for lung matter investigated by FTA. In this case the lung was saturated with boron before irradiation (Morris and Batchelor, 1988). The boron underwent an n, α reaction to ^{7}Li. This alpha damage again served as an indicator of tissue structure relative to fissile nuclides.

Pin pricks with diameters approximately 100 μm have been made in the grain mount and detector as a reference point. Reference holes at each corner

of the sample have also been used with a diameter of 0.8 mm (Povetko and

Higley, 2001).   A new method has been described and called the repositioning

method (Jonckheere et al., 2003). In this method the detector was repositioned,

track side down, on the grain mount after etching. It was manipulated into the

exact position in which it was irradiated by cotton tipped sticks. Fossil tracks in

the sample from spontaneous fission of ^{238}U and induced fission tracks are then

examined under a microscope by adjusting the focus to different heights.

FTA coupled with other techniques

The relative locations of fissile nuclides within the material examined can

provide useful information on their distribution and inclusion. In some cases this

is not sufficient information and the identity of the particles (^{235}U or ^{239}Pu) is

desired. Swipe tests are an example in which information on individual particles

is important to the task at hand. The International Atomic Energy Agency (IAEA)

has sponsored a large amount of work with FTA coupled with secondary

ionization mass spectrometry (SIMS) and thermal ionization mass spectrometry

(TIMS) to obtain isotopic information on individual particles (Stetzer, 2003;

Donohue, 1998; Donohue, 2002; Betti et al.,1999; Tamborini et al., 1998;

Tamborini and Betti, 2000; Veniamonov, 2000; Torok et al., 2004). For SIMS

work on swipes, the particles were removed from the swipe in an ultrasonic bath

of heptane. The particle suspension was then dried on a polished graphite

planchet. FTA/TIMS have been combined successfully by IAEA. First the

particles were extracted from the swipes then they were embedded into a

collodion film that was irradiated. Fission tracks and alpha tracks were identified.

The particles were then cut out of the collodion and loaded onto a filament for further analysis by TIMS (Stetzer et al., 2004; Donohue, 1998; Betti et al., 1999). The FTA/TIMS has also been successful for identifying air particulates (Esaka et al., 2004).

Recently FTA/SIMS has been used on particles extracted from swipe samples with ethanol (Stetzer et al., 2004). The suspension was centrifuged several times to ensure that the particles were all at the bottom of the tube. Then 1 mL was pipetted from the bottom of the vessel and deposited onto a graphite planchet. A sandwich assembly was made with a detector which was then irradiated and subsequently analyzed by SIMS. These methods for combining FTA with SIMS for particle analysis are both time consuming and labor intensive.

Laser ablation mass spectrometry

Lasers can be used as a method of introducing a solid sample into a mass spectrometer. This technique is called laser ablation mass spectrometry (LAMS). A few of the major advantages of the technique are that nearly 80% of the elements on the periodic table may be analyzed for and analyses can be performed to determine spatial heterogeneity and bulk determinations. Other advantages are that any type of solid sample can be used, there are no sample size limitations and there are many sample preparation options (Russo et al., 2002; Hattendorf et al., 2003).

A high powered laser pulse is focused at the surface of a solid material which removes material to a depth of 0.02-5 μm (Russo et al., 2002; Hattendorf

et al., 2003). The material after ablation is swept into an inductively coupled plasma (ICP) by a helium gas stream where the sample is atomized and ionized prior to introduction into a mass spectrometer for detection.

In general, the primary goal of LAMS is quantitative determination of elemental concentrations, although there are several challenges in achieving this goal. Elemental fractionation occurs when the recorded ion signals do not represent the sample composition, i.e. the stoichiometry of the sample and the aerosol are not identical. This can occur during the ablation, aerosol transport, or the atomization and ionization processes (Hattendorf et al., 2003). Fractionation is primarily due to thermal mechanisms which influence the behavior of atoms depending on their elemental identity (Russo et al., 2002). Using shorter wavelengths for the laser seems to decrease the effects of fractionation. Another challenge of LAMS is the lack of availability of matrix matched standards. Therefore, external calibration is often used. Glass, ceramic, cement, and metals constitute the available certified reference materials for LAMS (Russo et al., 2002). Many laboratories prepare their own matrix-matched standards by mixing known amounts of the analyte with the appropriate matrix (Russo et al., 2002). Liquid solutions have also shown success as a calibration method (Russo et al., 2002; Bi et al., 2000). In order to achieve quantification, it is also necessary to explicitly know the volume of sample transported to the plasma. This is further complicated by the observation that similar materials often exhibit different ablation rates (Hattendorf et al., 2003). The use of an internal standard such as the minor isotope of a major element, has improved this drawback although it

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requires accurate knowledge of the concentration of that element in the matrix

and assumes spatial homogeneity (Baker et al., 1999; Gastel et al., 1997; Bi et

al., 2000).

Analysis of soils with LAMS

While ideally suited for micro-local sampling of uniform samples such as

those encountered in geological applications, with minimal sample preparation,

LA can accommodate powders and other unconsolidated materials (Seltzer,

2003; Scholze et al., 1994, Baker et al., 1999; Song et al. 2001; Lee et al., 2003).

Direct methods of analysis are advantageous because they eliminate time

consuming sample preparation and the risk of contamination from chemical

reagents used in digestions (Baker et al., 1999). Usually the soil is made into a

pellet before analysis. This can be done directly on ground and homogenized

soil (Schloze et al., 1994; Baker et al., 1999) or by employing a binding agent

(Lee et al., 2003, Seltzer et al., 2003). Fused borate soil samples have been

analyzed directly with LAMS providing a mechanism for improved matrix

matching (Guo and Lichte, 1995). Another method for analysis of soils was to

pack the soil into a capillary column, which was then mounted on a ring electrode

(Song et al., 2001). The laser was then focused onto the target surface and the

ablated ions were then introduced into an ion trap without the use of ion optics or

acceleration devices providing an increased sensitivity.

Analysis of actinides by LAMS

The actinides have been extensively examined using LAMS. The most

typical application for the determination of U is for dating purposes. Age has

been determined for geologic samples such as zircons (Tiepolo et al., 2003) and minerals (Hasebe et al., 2003; Poitrasson et al., 2000). Determination of Th, U and Np in nuclear wasteforms such as nuclear ceramics (Poitrasson et al., 2000) and concrete (Gastel et al., 1997) has also been accomplished using LAMS. The behavior of impurities within Pu immobilized in glass and ceramics is also of interest. The impurities were prepared with CeO_2 to simulate PuO_2 (Borisov et al., 2001). This study provided confidence that information about oxide blending and re-blending requirements for Pu ceramification could be determined using LAMS. Examination of plant surfaces with LAMS has elucidated the leachability of deposited U from long-term contamination events (Punshone et al., 2004). Similarly, soils contaminated with U have been investigated to differentiate between depleted, anthropogenic and natural U (Seltzer, 2003). Plutonium in soils and sediments has been detected at pg/g concentrations, although precision is limited due to the spatially inhomogeneous nature of Pu in soil (Boulyga et al., 2001).

Missing Pieces

Environmental radiological contamination is a worldwide concern due to possible negative health implications. To formulate predictions regarding the possibility of human contact with radionuclides requires an understanding of how radionuclides interact with the groundwater and soil. Depending on the source of the radionuclide, it may not be in chemical equilibrium with the environment even after many years. This will influence projections of the migration and therefore

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the possible remediation decision. Determining the source of the contamination is a critical first step toward understanding the environmental interactions.

Many experimental studies have reported characterization of actinides in soil and sediment matricies. These studies have focused on both global fallout and localized specific contamination events. Typically these analyses have utilized large sample sizes (10-1000 g) due to the low levels of environmental contamination and the expected inhomogeneity of actinide distribution in the soil. The ability to quantitatively analyze small samples is important in cases where sample quantity is limited.

Radiologically contaminated soils are primarily analyzed for Pu isotopes in conjunction with other actinides (Am, Np) or fission products (^{137}Cs). Soils are less frequently analyzed for all three: Pu isotopes, other actinides, and fission products. Additionally, there is a strong focus on determination of Pu alpha activities which neglects the determination of [241]Pu in soils except in rare cases (Lee et al., 2003; Lee et al., 2005; Paatero and Jaakkola, 1994; Yu et al., 1992; Moreno et al. 1998; Bokowski, 1974). As described earlier, [241]Pu is difficult to quantify because it decays by a low energy beta and has a short half life (14.35 y) but it provides critical information about the interpretation of [241]Am activity data. Near the time of deposition [241]Pu often accounts for the largest fraction of the transuranic activity and is the only transuranic isotope emitting beta particles in low level waste. [241]Am is more radiotoxic and has a longer half-life than its parent [241]Pu, therefore evaluating ingrowth is important.

Analysis of soils contaminated by nuclear processes focuses on the detection of radioactive species. Actinides and fission products are associated with discrete soil particles and do not distribute themselves equally throughout the bulk soil. Evaluation of soil particles containing actinides and fission products can lead to a better understanding the interactions that are associated with actinide and fission product contamination.

The work detailed in the subsequent chapters addressed the above issues and attempted specifically to:

- develop an analysis method that sequentially determined ^{241}Am, ^{238}Pu, $^{239+240}$Pu and ^{241}Pu on small soil samples.

- determine the activity of ^{241}Am, which is present in the samples from the time of sampling versus that which has grown in from the decay of ^{241}Pu.

- determine Pu atom concentrations and investigate isotopic and atom ratios to understand the source of both the Pu and ^{241}Am and elucidate the mechanism of transport into soil.

- explore ^{137}Cs activity to provide additional insight into the soil contamination history.

- develop a method which will identify soil particles that contain fissile material.

- show the utility of analyzing the previously identified soil particles using mass spectrometry.

Specific aims

Idaho National Laboratory soils were analyzed for ^{241}Am, ^{137}Cs and Pu isotopes to achieve a more detailed understanding of their contamination. Building on established radiochemical methodologies, a procedure to sequentially analyze ^{241}Am, $^{239+240}$Pu, and ^{241}Pu has been developed to gain a better understanding of the contamination in the INL soils. Investigation into the composition of soil particles which contain fissile nuclides was accomplished using a combined FTA and LAMS technique. The objectives of the research were addressed by work which is divided into the following chapters.

Chapter 2 is a manuscript written in the format required by the *Journal of Radioanalytical and Nuclear Chemistry*, and has been submitted for publication. This chapter describes the development of radiochemical methodologies to investigate Pu and ^{241}Am contamination. The ^{241}Am was determined prior to soil dissolution using the 59.5 keV gamma emission by HPGe gamma spectrometry. The soils were then completely dissolved using a fusion method, which was followed by anion exchange to separate the Pu fraction from the matrix. The Pu fraction was used to prepare an electrodeposited sample for determination of ^{238}Pu and $^{239+240}$Pu by alpha spectrometry. Lastly, ^{241}Pu was determined using liquid scintillation counting (LSC). The ^{241}Pu β activity was discriminated from any Pu α activity using energy resolution. In this dissertation, the methods used will be described, along with estimates of limits of detection and other statistical considerations.

Chapter 3 is a manuscript written in the format required by *Environmental Science and Technology*. The Pu isotopic atom concentrations were determined using sector field ICPMS. Isotopic and activity ratios for Pu isotopes and [241]Am were investigated in conjunction with ^{137}Cs activity determined by HPGe gamma spectrometry. These ratios were explored to elucidate the source of the contamination in the soils. This study demonstrates that the Pu, [241]Am and ^{137}Cs are derived from different sources.

Chapter 4 is a manuscript written in the format required by *Radiochimica Acta*. The feasibility of locating contaminated soil aggregates using a novel FTA preparation technique and coupling it to LAMS was investigated. The FTA preparation method was developed with assistance from S. Cornelius of the Geoanalyical laboratory at WSU. Charles Knaack assisted with the development of the LAMS technique and use of the LAMS instrument.

Chapter 5 provides a summary and presents overall conclusions resulting from this work. Areas requiring further study and suggestions for extending this research are discussed.

Attributions

Unless otherwise indicated, all work contained in this dissertation was planned and conducted by Rosara Payne. Sue B. Clark provided advice and scientific direction for all aspects of the research described herein.

Jim Elliston of the Nuclear Radiation Center, assisted by maintaining the alpha spectrometry system. He provided advice and scientific direction for

chapter 2 and chapter 3. Dorothy Stuit of the United States Transuranium and Uranium Registries provided advice and assistance in chapter 2. Daniel Dugan of the Nuclear Radiation Center at WSU maintained the gamma spectrometry system used in chapter 2 and chapter 3.

The Radiation Safety Office at WSU provided the LSC instrument in chapter 2. The Geoanalytical Laboratory at WSU maintained and assisted in the use of the sector field ICPMS and LAMS instruments in chapter 3 and chapter 4. The 1 MW research reactor at WSU was used for the FTA analysis in chapter 4.

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CHAPTER TWO

RADIOANALYTICAL APPROACH TO DETERMINE ^{238}Pu, $^{239+240}$Pu, ^{241}Pu AND ^{241}Am IN SOILS

Abstract

Until 1970, the Idaho National Laboratory (INL) operated a disposal facility for solid radioactive waste called the Subsurface Disposal Area (SDA). Soils from various perimeter locations around SDA were collected in the early 1970's and analyzed for ^{238}Pu, $^{239+240}$Pu, and ^{241}Am. In this study, we have reanalyzed some of these historic soil samples from two different locations and depths, using a combination of traditional and new radioanalytical methodologies.   The methods used to determine ^{241}Am, ^{238}Pu, $^{239+240}$Pu and ^{241}Pu are described, along with estimates of the limits of detection for gamma and alpha spectrometry, and liquid scintillation counting. The data from these two locations demonstrate that the amount of ^{241}Am activity in these soil samples is greater than would be expected due to ingrowth from ^{241}Pu decay.

Introduction

The Idaho National Laboratory (INL) is a Department of Energy facility that was established in 1949 for the development and testing of various nuclear technologies intended for civilian and defense applications[1]. The Subsurface Disposal Area (SDA) at INL was used from 1952-1970 to dispose of containers of low-level transuranic waste, many of which originated from operations at the

Department of Energy Rocky Flats Site (RFS) in Colorado. Waste from RFS comprised of weapons grade Pu metal from machining processes, lathe cutting oil, and chlorinated solvents[2]. Other sources of activity include global and regional fallout, the SNAP-9A accident in 1964, and releases from onsite activities.

In the early 1970's soil samples were collected surrounding the SDA[3]. Markham et al. analyzed the samples for ^{241}Am, ^{238}Pu and $^{239+240}$Pu by alpha spectrometry, and reported isopleths for these isotopes, with the highest activities occurring at the northeastern corner of the SDA. These samples were then stored until we acquired them for this work.

As a result of storage, these soils were isolated from the environment for over 30 years, thereby "preserving" the amount of radioactivity contamination they contained. The earlier work by Markham et al. did not report activity levels for ^{241}Pu, which decays to ^{241}Am (t $_{1/2}$ = 14.35 yr; β = 21 keV; 99.99%). If ^{241}Pu is present in the samples, reanalysis of the ^{241}Am more than 30 years later should show measurable increases in ^{241}Am activity. Furthermore, direct determination of ^{241}Pu should be possible, and is essential for estimating the maximum quantity of ^{241}Am expected in the sample after a given time period. Liquid scintillation counting (LSC) allows for direct determination of the ^{241}Pu activity.

The focus of this work is to optimize an approach to systematically determine ^{241}Am, ^{238}Pu, $^{239+240}$Pu, and ^{241}Pu from the same aliquots of small e.g. 0.5 g soil samples. Possible sources of the contamination can be elucidated by distinguishing between ^{241}Am present due to ingrowth from ^{241}Pu and that from

other contamination events. Although our methodology is useful for small samples, it can impose limitations on quantifiability. In some cases, detection of an isotope may be sufficient, but quantitation requires a defined level of statistical discrimination between random noise, e.g. background, and detection of actual activity. Knowledge of the activity detection and determination limits can assist in evaluating instrumental and experimental parameters that may affect statistical determination of actual activity. For this purpose we have defined the limits of detection and quantitation for each type of analysis completed on these samples.

Experimental

Soils were obtained from the Lithologic Core Storage Area located at INL. The sampling approach is described in Markham et al.[3] The soils were agitated in their containers to re-mix the previously homogenized soil. From each location and depth, ten to fifteen 500 mg aliquots were weighed out into individual, 2/5 dram polyethylene vials. To determine ^{241}Am activity, each sample was counted for 24 h on either an Ortec high purity germanium (HPGe) detector (0-4 cm depth), or a low energy photon spectrometer (LEPS) HPGe detector (4-8 cm depth). Genie 2K software suite (v. 2.0; Canberra) was used for data acquisition. Raw data was analyzed with an Excel™-based program developed in-house.

Following analysis for ^{241}Am, each sample was transferred to a high purity carbon crucible along with 4 g of lithium metaborate (LiBO$_2$, Puratronic, 99.997%) and thoroughly mixed. To ensure complete transfer of the sample, the 2/5 dram vials were rinsed three times with 250-500 µL of 10% HNO$_3$ which was added to the flux mix. The crucibles were placed in a preheated muffle furnace (150°C),

and the temperature was raised to 500° C. The sample was maintained at this temperature for 15 min and then raised to 750° C and held for another 15 min and finally raised to 1000° C for 20 min. A clear melt signaled complete dissolution of the soil matrix.

The resultant liquid borate bead was allowed to cool and added to 2 M HNO_3 with heat. Once the bead was dissolved, ^{242}Pu (NIST SRM 4334G) was added as a tracer (0.15 Bq/sample) and the solution was transferred to a Teflon beaker. Concentrated HF was added dropwise with stirring until the solution cleared. The sample was evaporated to dryness and wet ashed three times with concentrated HNO_3. The sample was reconstituted in 4 M HNO_3 and carbon powder from the crucibles was removed by filtering with a Whatman GFA filter supported on a Whatman No. 542 filter. Concentrated HNO_3 was then added to bring the HNO_3 concentration to 8 M.

Approximately 0.5 g of $NaNO_2$ was added to each beaker and the contents were brought to a boil to stabilize the Pu in the 4+ oxidation state prior to ion exchange separation. Initial elution of the sample solution through an anion exchange column of Biorad AG 1 x 4 resin (1 x 10 cm) afforded a Th-containing fraction. The Pu-containing fractions were eluted with 3.5 column volumes of 0.6 M HCl followed by 2.5 column volumes of 0.05 M NH_4I in 0.6 M HCl[5]. Following evaporation to dryness, the Pu samples were prepared for alpha spectrometry by electrodeposition from a dilute sulfate based solution on 5/8" diameter stainless steel planchets using the method of Glover et al. [6].

The activities of ^{238}Pu and $^{239+240}$Pu were determined using an EG&G Octet PC alpha spectrometers and AlphaVision 4.02 software. All chambers were equipped with 450 mm^2 passive ion implanted Si (PIPS) semiconductor surface barrier detectors. Samples were counted for 300,000 s to achieve < 2% error in the ^{242}Pu tracer activity.

To determine the ^{241}Pu activity, Pu was stripped from the planchets using boiling 8 M HNO$_3$ for an hour. Small amounts of Ni and Fe leached from the planchet were removed by the anion exchange column as described previously (1 x 5 cm). Elution was performed with 0.36 M HCl/0.01 M HF directly into 20 mL scintillation vials, which were brought to dryness with heat. The sample was reconstituted over a 24 hr period by dissolution in 1 mL of 0.1 M HCl. Then 19 mL of Ecoscint scintillation cocktail (National Diagnostics) was added and the samples were counted for 6 hr.

A Packard Tri-Carb 2100TR liquid scintillation counter (LSC) equipped with a coincidence detector was used to discriminate between the Pu alphas and ^{241}Pu beta. Discrimination was accomplished by energy separation. The ^{241}Pu activity concentration was calculated using the expression of Paatero et al.[7]:

$$A_1 = \frac{A_2 \ R_1 \ 100\%}{\varepsilon \ R_2 \ \alpha \ m \ 60} \qquad (1)$$

Where A$_1$ = the activity of ^{241}Pu in the sample (Bq/g)

A$_2$ = activity of ^{242}Pu tracer (dpm)

R$_1$ = net count rate of ^{241}Pu (cpm) from LSC

ε = counting efficiency of ^{241}Pu (%)

R$_2$ = total alpha net count rate (cpm) from LSC

α = ratio of ^{242}Pu alpha counts/total alpha counts

m = mass (g)

The ratios of ^{242}Pu alpha counts/total alpha counts were obtained from the alpha spectra obtained previously.

Method Validation

The usual approach to achieve validation for an analytical method is to demonstrate precise and accurate results with a standard reference material (SRM). No single standard reference material was found that was certified for all the isotopes of interest in this study and that contained sufficient ^{241}Am activity to allow quantitation by HPGe and LEP gamma spectroscopy. Therefore we have verified the approach used for each isotope independently.

The gamma spectrometers are routinely energy and efficiency calibrated using NIST standards. Background spectra are acquired monthly. To quantify the ^{241}Am concentration, the counts under the 59.5 keV peak were compared to the peak area of a standard. Approximately 500 µg of 1.93 Bq/g solution from NIST SRM 4322B was weighed into a 2/5 dram vial. The volume of the standard matched the counting geometry of the samples. When the standard was counted and analyzed as a sample, it was found to be consistently within 5% of the true value after data analysis.

The alpha spectrometry system is also routinely calibrated and background counts analyzed. More than 50 counts of background in 300,000 s are considered unacceptable for Pu and Am analyses under these conditions the detectors are not used until decontaminated and background counts are < 50

counts in 300,000 s. A ^{242}Pu tracer was added to each sample to track losses and identify the percent recovery of the Pu. Recoveries were typically greater than 70%. Method blanks were analyzed with each batch of samples, and were subjected to all aspects of sample processing beginning at the soil fusion step thru final quantitation. The matrix consisted of the LiBO$_2$ with no soil added.

The LS counter was calibrated with NIST SRM 4340A ^{241}Pu standard (13 Bq) and the counting efficiency in the beta window (channels 0 – 70) was determined to be approximately 30% with typical background count rates of 28-30 cpm. Solutions were also made that contained a known amount of ^{241}Pu and ^{242}Pu. These samples were subjected to the same procedures that the soil Pu would undergo starting at column separation followed by electrodeposition, alpha counting, stripping and ending with the LSC analysis. The ^{242}Pu was used to track losses and provide the information necessary to utilize equation 1. Using the predetermined efficiency, the ^{241}Pu activity was calculated to be within 1-4% of the true value. This small deviation could be accounted for by dilution and weighing error.

Results and Discussion

The ^{238}Pu, $^{239+240}$Pu, ^{241}Pu and ^{241}Am activities determined at each location and depth are given in Table 2.1. The total Pu activity is higher at location 1 than location 2 for the surface samples which contain higher activities of Pu and than the samples at the 4-8 cm depth. Although the Pu activities are higher at location 1, the ^{241}Am activity is higher at location 2.

Results obtained for all our samples showed isotopes were detectable but not necessarily quantifiable. The activity detection and quantitation limits were calculated and used to evaluate the data obtained. In terms of radioactivity detection, the activity detection limit, a_D, is the activity at which the analytical procedure may be relied upon to provide detection. The activity determination limit, a_Q, is the activity at which the given procedure or method will be sufficiently precise to allow quantitative analysis.[4] The activity limits for each method are given in Table 2.2 by the equations used in Currie[4] for paired observations.

$$a_D = \frac{2.71 + 4.67\sqrt{\mu_B}}{\varepsilon\, T} \qquad (2)$$

$$a_Q = \frac{50\,\{1 + \sqrt{1 + \dfrac{\mu_B}{12.5}}\,\}}{\varepsilon\, T} \qquad (3)$$

Where μ_B is the background counts during count interval, ε is the efficiency and T is the effective counting interval.

While examining the data obtained from any method in terms of activity limits, it is important to remember that the values are given in Bq/g and here analyses were performed on only 0.5 g of soil per sample. The activity present in each sample also depends on the % recovery for the pre-analysis preparation. Figure 2.1 shows the activity detection and determination limits for each method in reference to the amount of activity present in the half gram samples.

Two different detectors were used to determine the ^{241}Am activity in the soils. A LEPS was used for the lower activity samples, 4-8 cm depth, because the efficiency is about twice that of the HPGe detector at the lower energy.

Figure 2.1a and 2.1b show graphically the lower activity limits of the LEPS than the HPGe detector. In the case of the soil samples from the 4-8 cm depth at location 1, the decreased activity limit of the LEPS is still insufficient to quantify the activity present because the measured activity coincides with the activity detection limit. Hence, the reported [241]Am activity for this location and depth is more qualitative than quantitative. The activities present in the 0-4 cm depths are well above all of the activity limits for the HPGe detector, as seen in Figure 2.1b.

Published data show that results obtained for [241]Am by gamma spectrometry and alpha spectrometry on soil matrices are in general agreement.[9,10] Although alpha spectrometry has activity limits that are lower than gamma spectrometry by two or three orders of magnitude for the determination of [241]Am, the sample processing is more laborious.[10] Gamma spectrometry has the potential to be quicker if multiple detectors are available. It is less labor intensive than alpha spectrometry, but sensitivity is sacrificed.

Activity limits for alpha spectrometry were calculated using multiple method blanks. The amount of [239+240]Pu present in the method blanks was found to increase the background counts enough to raise the intrinsic activity limits. However, the activity determination limit is still two orders of magnitude lower than the activity present in the samples.

Although the activity limits for [238]Pu are lower than those for [239+240]Pu, the [238]Pu activities in the samples are also much lower. Figure 2.1c shows that the [238]Pu activity for each sample is above the activity determination limit allowing

quantitation; the lower activity of the 4-8 cm depth samples requires high recoveries to be quantifiable. This is a realistic expectation because greater than 70% recovery was typical from digestion through electrodeposition.

Our liquid scintillation approach is intended for use with routine equipment, while minimizing the generation of mixed waste. These two factors impose activity limits an order of magnitude higher than reported elsewhere[7,8]. Despite this, Figure 2.1d shows that the samples from both locations at the 0-4 cm depth are above the elevated activity detection limit for our LSC method. Location 1 at the 4-8 cm depth must have greater than 80% recovery in the lower range of activities to be above the activity detection limit. This is again reasonable since the recovery through the alpha spectrometry process was high. Very little loss is observed to occur from stripping the planchets and removal of the Fe and Ni. Stripped planchets showed no quantifiable counts above background after 300,000 s count times.

Although there is detectable activity by LSC in the samples representing the lower depths, the data is mostly qualitative. Increasing the LSC count time to 1000 min would lower the activity determination limit from 0.23 Bq to 0.14 Bq. In this case, the samples from the lower depths would still not be quantifiable unless near 100% recoveries were obtained. This minimal decrease of the activity determination limit does not warrant the corresponding increase in analysis time. To allow quantitation of ^{241}Pu in the samples collected at 4-8 cm depths, the background counts must be reduced by about two thirds in conjunction with increasing the LSC count time to 1000 min.

The soils analyzed in this study were originally collected in the 1970's by Markham et al.[3] Table 2.1 shows that the maximum activities reported by Markham are consistent with our data for the 0-4 cm depth samples. One sigma Errors were not reported by Markham et al. and there is no indication of the exact sample location, although they were in the same general area as ours. A further comparison with the published data shows that reported $^{239+240}$Pu activities from the north and south sides of the SDA beyond the perimeter are an order of magnitude lower than those reported in this study.[2] This does not contradict our data because the soils used in each study were not in locations that are likely to have been subjected to the same local contamination events.

Most of the waste buried at the SDA was from the RFS. Contamination events also occurred at the RFS due to leakage of drums containing weapons grade Pu. Extensive studies have been done on these soils.[11,12,13,14] One such study in 1995 reported maximum $^{239+240}$Pu and ^{241}Am activities of 53.6 Bq/g and 9.99 Bq/g respectively.[14] The assumption made was that, based on the contents of the drums, the full complement of ^{241}Am present was due to ingrowth from ^{241}Pu. The Pu and Am activities determined are higher than those reported for SDA soils, but the proximity of these highest activity soil samples to the contamination source is uncertain.

The assumption used while analyzing soil from Rocky Flats that all the ^{241}Am present is due to ingrowth from ^{241}Pu is not valid for SDA soils as ^{241}Am waste from Rocky Flats was also disposed of at the SDA. However, this study

demonstrates that ingrowth of ^{241}Am from ^{241}Pu over a 25-30 yr period is sufficient to give rise to measurable ^{241}Am activity.

Accurate determination of the ^{241}Pu activity in these samples allows us to distinguish between the ^{241}Am that was present from the contamination event and that due to ingrowth. Figure 2.2 shows the percentage of the total ^{241}Am present in soil samples that can be attributed to ingrowth and that due to the original contamination event. Locations 1 and 2 have statistically different ^{241}Am ingrowth distribution profiles with location 1 displaying greater than 20% of ^{241}Am activity due to ingrowth and location 2 displaying less than 10% due to ingrowth. The qualitative nature of the data at the lower depth at location 1 and at both depths at location 2 from the ^{241}Pu analysis make it difficult to definitively say that the activities are different; however, the contribution from ingrowth indicates that the ^{241}Am contamination cannot be accounted for exclusively by weapons grade Pu. This implies that ^{241}Am from either waste disposed of in the SDA or onsite activities plays a larger role in the overall environmental contamination of the soil than the contribution from ^{241}Pu.

Conclusions

The determination of ^{241}Am by gamma spectrometry was successful. Only location 1 at the 4-8 cm depth was below the activity determination limit for ^{241}Am. ^{238}Pu and $^{239+240}$Pu activities were quantifiable at both locations and depths for the sample dissolution and preparation technique employed. Determination of ^{241}Pu by LSC was plagued with the most difficulties due to high activity detection and determination limits imposed by instrumentation factors and

the scintillation cocktail. Although the activity observed for the 4-8 cm depth samples at both locations was detectable, quantitation of this activity was not achievable. Increasing the shielding and use of specialized cocktails would improve the sensitivity.

The activities determined in this study were consistent with the highest activities reported in 1978[3]. Greater than 20% of the ^{241}Am at location 1 is due to ingrowth while less than 10% at location 2 is due to ingrowth. It appears that location, not depth is responsible for this difference. Overall the fraction of the total ^{241}Am that can be attributed to ingrowth is much smaller than would be expected if the contamination source was solely weapons grade Pu. It is reasonable that the waste buried at the SDA was not only weapons grade Pu waste and in fact a large amount of ^{241}Am was present, possibly from Pu pit reprocessing waste streams at the Rocky Flats Site.

Radiometric analyses are limited by the difficulty to discriminate between ^{239}Pu and ^{240}Pu alpha energies and the inability to detect low levels of activity in isotopes with long half-lives. Mass spectrometric analyses are able to provide complementary information. Future work will focus on the determination of the ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu atom ratio and the ^{137}Cs activity on these soils. These data along with the work here will help to narrow the possible sources of contamination by exploring activity and atom ratios and comparing them to other literature studies.

Acknowledgements

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Table 2.1 Activities determined for ^{241}Am and Pu isotopes compared with literature values in related soils

Location	Depth	^{241}Am (Bq/g)	$^{239+240}$Pu (Bq/g)	^{238}Pu (Bq/g)	^{241}Pu (Bq/g)
1	0-4 cm	0.78 ± 0.11	1.41 ± 0.16	0.024 ± 0.003	1.70 ± 0.37
2	0-4 cm	2.26 ± 0.28	0.48 ± 0.09	0.012 ± 0.003	0.81 ± 0.32
1	4-8 cm	0.10 ± 0.02	0.21 ± 0.01	0.004 ± 0.001	0.30 ± 0.11
2	4-8 cm	0.78 ± 0.12	0.20 ± 0.04	0.005 ± 0.001	0.38 ± 0.13
SDA[3]		1.89	1.35	0.03	
SDA[2]			0.023		
RFS[14]		9.99	53.6		

Table 2.2 Parameters employed to determine activity limits

	γ - Spec. (LEPS)	γ - Spec.	α - Spec. ^{238}Pu	α - Spec. $^{239+240}$Pu	LSC
Count Time	86,400 s	86,400 s	300,000 s	300,000 s	21,600 s
Efficiency	6%	3%	25%	25%	30%
Background	2730	1440	10	125	10400
a_D	0.048 Bq	0.075 Bq	0.0003 Bq	0.0007 Bq	0.073 Bq
a_Q	0.16 Bq	0.24 Bq	0.0015 Bq	0.003 Bq	0.23 Bq

Figure Captions

Figure 2.1: The activity detection, a_D and activity determination, a_Q limits in Bq for
a. ^{241}Am as determined by LEPS,
b. ^{241}Am as determined by HPGe,
c. ^{238}Pu as determined by alpha spectrometry,
d. ^{241}Pu as determined by LSC;
compared to the activity present in the 0.5 g samples. A comparison of the activity limits and the activity present for $^{239+240}$Pu are not included as the activity present is 2-3 orders of magnitude higher than the activity limits. n = 10-15, 1 sigma error.

Figure 2.2: Percent of the total current ^{241}Am activity attributed to ingrowth and the original contamination event. n = 10-15, 1 sigma error.
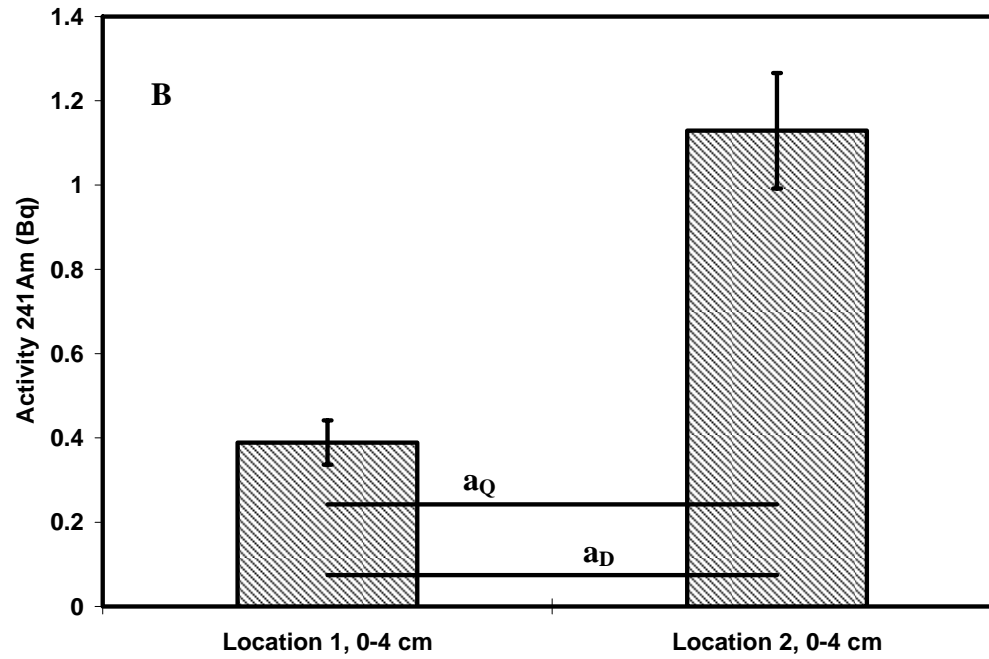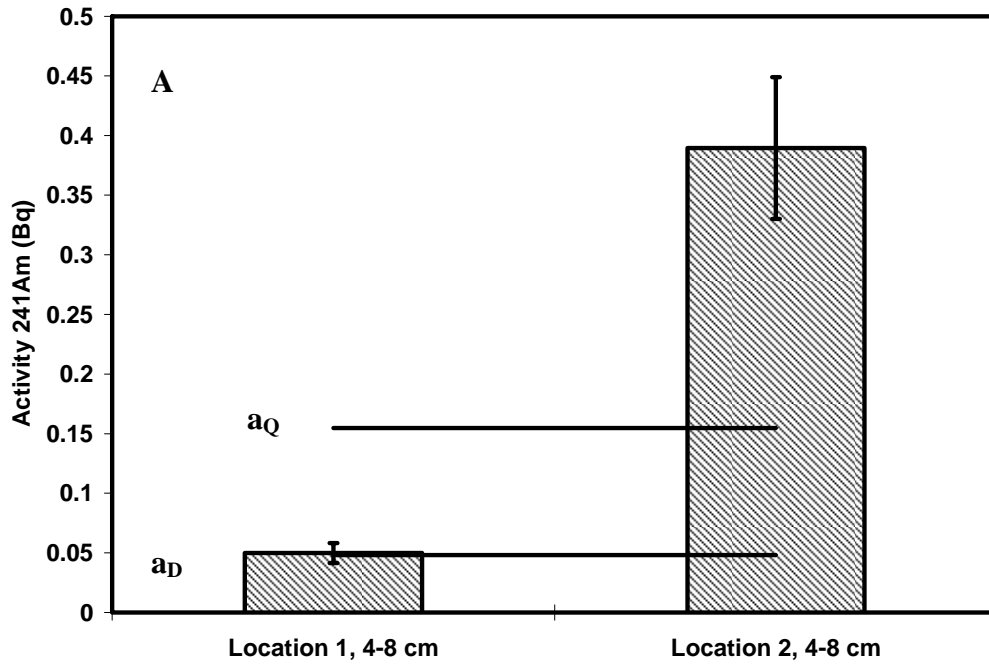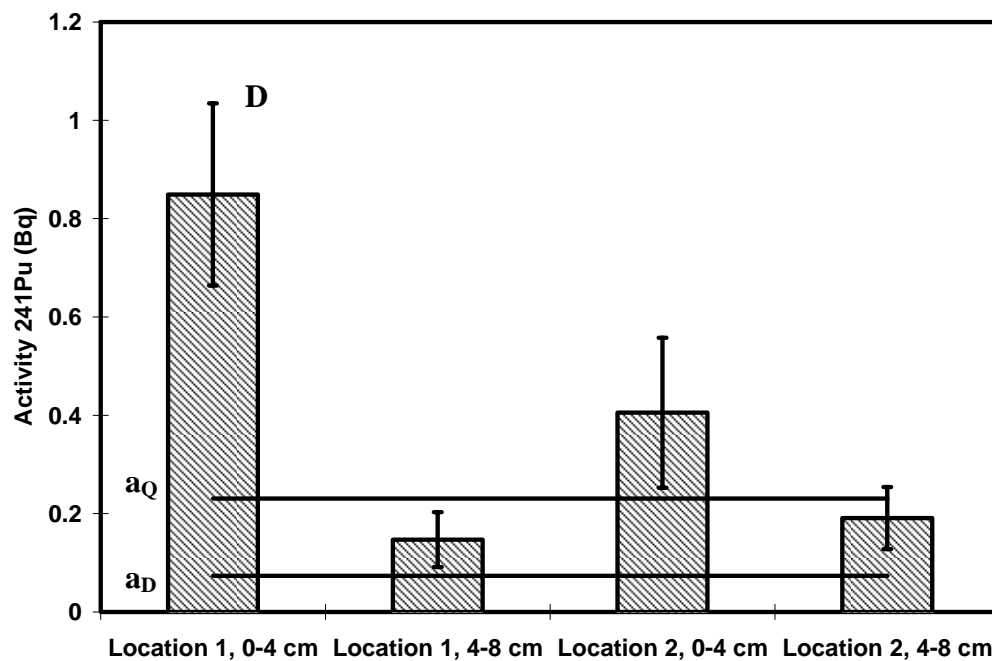
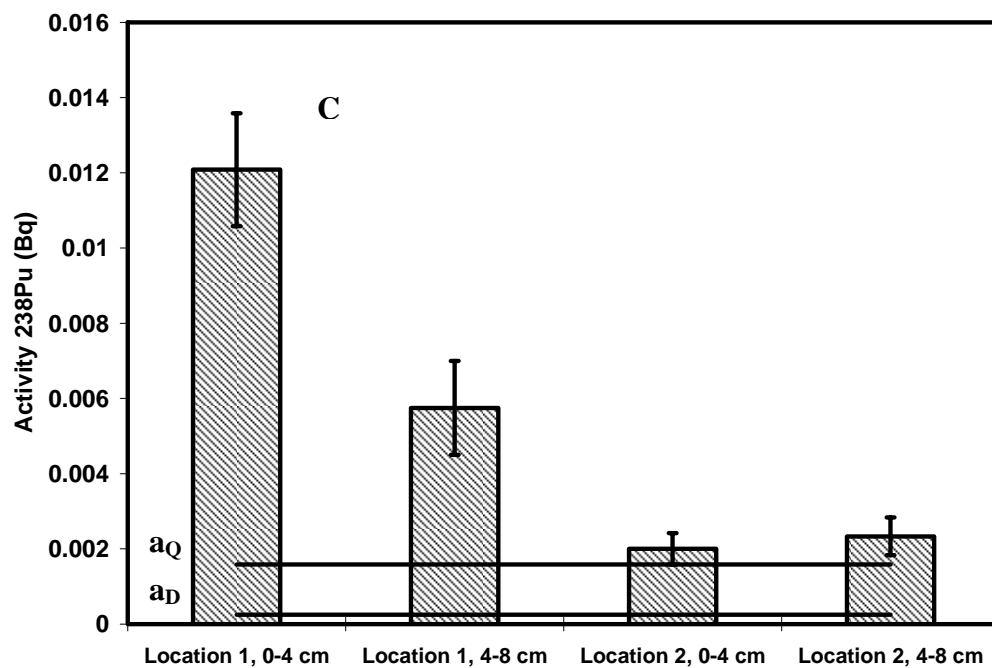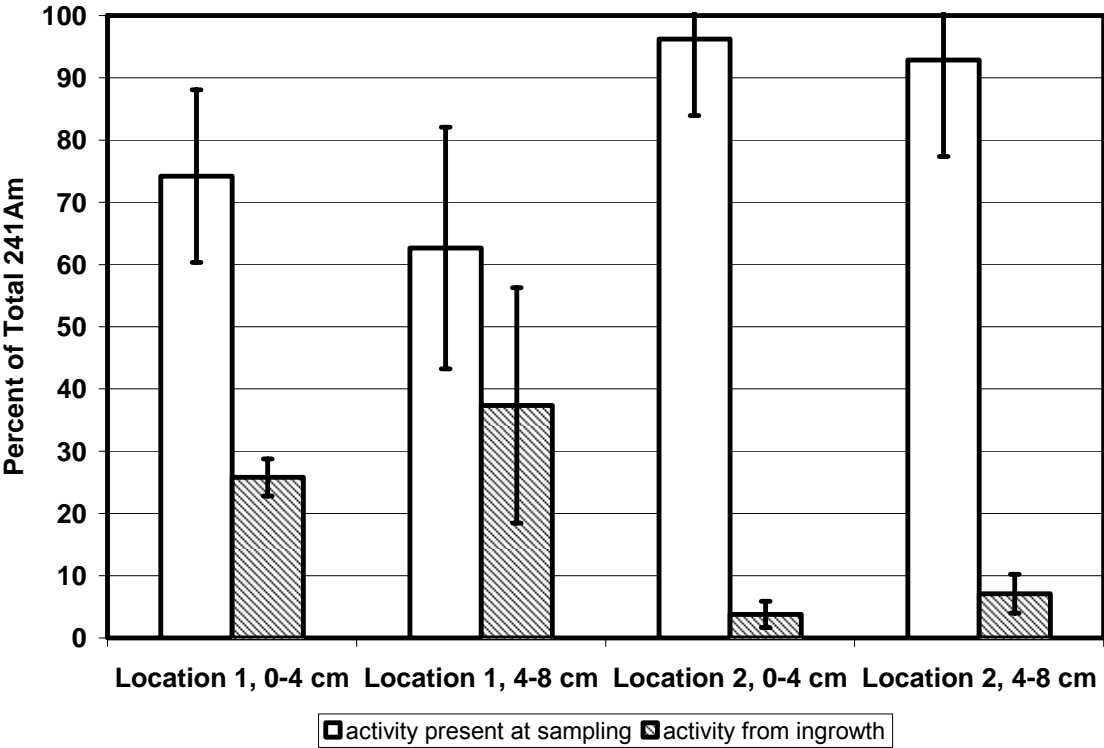# Figure 2.1

Figure 2.1

Figure 2.2

CHAPTER THREE

EXAMINATION OF Pu, Am AND Cs ACTIVITY AND ATOM RATIOS IN SOILS FROM THE IDAHO NATIONAL LABORATORY

Abstract

The determination for ^{137}Cs, ^{241}Am, and isotopes of Pu activities and comparison of atom ratios can provide information on the source of contamination. There are four possible sources of actinide and fission product deposition in soils collected from the Idaho National Laboratory (INL). These sources are integrated global fallout, regional fallout, stack releases from the Idaho Chemical Processing Plant (ICPP) and radioactive waste management activities at the Subsurface Disposal Area (SDA). The soils used in this study were collected near the SDA in 1972. We analyzed activities and atom concentrations in soil from two different locations, and at two depths at those locations, e.g. the surface soil (0-4 cm) and the soil just below the surface (4-8 cm). The ^{137}Cs activities in the surface soils are elevated above that expected for fallout, whereas the activities in 4-8 cm depths are consistent with fallout. This suggests that a local, atmospheric source is responsible for the elevated ^{137}Cs in the surface soils. The Pu contribution was detectable in all samples and elevated above that expected for global or regional fallout, with more than 99% from non-fallout sources. Activity and atom ratios indicate a signature consistent with weapons-grade Pu. The ^{241}Am activity in all samples is significantly larger than can be accounted for by fallout or

ingrowth from ^{241}Pu, suggesting that ^{241}Am has been introduced from sources other than weapons grade Pu.

Introduction

Over the last 50 years actinides have been deposited in the soil through stratospheric, tropospheric, and local contamination events. Radiometric analyses to determine the activities of ^{238}Pu, $^{239+240}$Pu, ^{241}Pu, ^{241}Am and ^{137}Cs in conjunction with mass spectrometric (MS) analyses to determine Pu atom concentrations can used to determine appropriate activity and atom ratios. Each contamination event is characterized by distinct activity and atom ratios. An example of this is seen in Figure 3.1, adapted from Taylor et al. (Taylor et al., 2001). The atom ratio of ^{240}Pu/^{239}Pu is indicative of the operation or event history of the Pu. An atom ratio of 0.18 is considered typical of integrated global fallout (Krey, 1976). Combining the ratios determined in this work with this information provides insight to possible contamination sources.

The soils analyzed were collected in the early 1970's from the U.S. Department of Energy (DOE) facility now known as the Idaho National Laboratory (INL). There are four possible sources of contamination for these particular soils: integrated global fallout, regional fallout, stack releases from the Idaho Chemical Processing Plant, and the disposal of solid radioactive waste via shallow land burial in the Subsurface Disposal Area (SDA).

These pathways will be explored in greater detail within the results and discussion. Briefly, regional fallout is classified as fallout from nuclear testing at

the Nevada Test Site (NTS). The NTS fallout is characterized by having ^{240}Pu/^{239}Pu atom ratios smaller than fallout (0.03-0.08) and high $^{239+240}$Pu/^{137}Cs activity ratios (Beasley et al., 1998). Integrated global fallout is primarily from nuclear weapons testing, but also includes a satellite failure. In 1964, a satellite powered by a ^{238}Pu thermal generator (SNAP-9A) burned up as it re-entered the atmosphere in the southern hemisphere. This increased the ^{238}Pu/$^{239+240}$Pu activity ratio in the northern hemisphere to 0.036 ± 0.011 (Beasley et al., 1998; Brunzl et al., 1992; Irlweck and Hrneceke, 1999; Cooper et al., 2000).

The ICPP was built as a multipurpose facility used to recover highly enriched uranium from various fuel types and began operation in 1953 (Beasley et al., 1998; Lenhard et al., 2004). Fission products and isotopes of the actinides were released from the ventilation stacks, but the earliest isotopic measurements of these releases were recorded in 1974, which occurred after the collection of these soils. The activity contribution and specific characteristics of the contamination through this pathway are largely unknown.

The SDA received waste from various nuclear processes at the INL, and other sites e.g. Rocky Flats Site (RFS) in Colorado. The Rocky Flats facility was one of the sites responsible for actinide partitioning, producing weapons-grade components made from enriched ^{239}Pu. The waste was disposed primarily in unlined pits with a majority of the waste from RFS for the years 1967-1969, placed in a specific location called Pit 9. The soils in this study were collected from inside the INL boundary, outside the northeastern corner of the SDA, very close to Pit 9 (Markham et al., 1978). This Pit covers a 1 acre area and contains

3,100 m^3 of transuranic mixed waste and 1,100 m^3 of mixed waste from INL operations (Schwartz, 1995). This constitutes 30 kg of transuranic radionuclides (3-4% of the total transuranic inventory in SDA) and 114,000 L of organic waste (> 30% total organic inventory of the SDA) (Schwartz, 1995). A flood in 1969 at Pit 9 caused the release of radionuclides from the buried waste drums resulting in contamination of the surrounding INL soils (Markham et al., 1978; Beasley et al., 1998). The characteristics of the waste released from these flooding events are enhanced $^{239+240}$Pu activity, ^{240}Pu/^{239}Pu atom ratios of approximately 0.07 and modest ^{137}Cs activity (Beasley et al., 1998).

The goals of this study were to determine activity and atom ratios of ^{241}Am, ^{238,239,240,241}Pu and ^{137}Cs and compare them to literature and known values. Comparison to fallout values can show how much additional radionuclide contamination exists. This data will provide insight to the possible sources of the radionuclide contamination. Utilizing knowledge of half-lives will show the activities present at the time of sampling and the expected activities that will be present in the future.

Experimental

A detailed description of the soils, sampling, sample preparation and the experimental methods used for the determination of ^{238}Pu, $^{239+240}$Pu, ^{241}Pu and ^{241}Am activities are found elsewhere (Payne and Clark, submitted). Briefly, 500 mg aliquots of soil were measured into 2/5 dram polyethylene vials. The samples were then counted for 24 hr on high purity germanium (HPGe) detectors

to determine ^{241}Am activity. The 4-8 cm depth samples were counted on a LEPS HPGe detector fitted with a beryllium window to reduce the background at the low energy. Following analysis the samples were transferred to carbon crucibles and completely digested using a modified lithium metaborate fusion method. The resultant borate bead was dissolved and 0.14 Bq of ^{242}Pu (SRM 4334F) added as a tracer.

Anion exchange was employed to separate the Pu fraction from the soil and LiBO$_2$ matrix. This was accomplished using Biorad 1 x 4 resin (1 x 10 cm) and eluting with dilute HCl and dilute NH$_4$I. An alpha spectrometry source was made by electrodeposition of the Pu fraction from a sulfate based matrix (Glover et al., 1998). ^{238}Pu and $^{239+240}$Pu activities were determined by counting on an EG&G Octet PC alpha spectrometer for 300,000 s using 450 mm^2 surface barrier detectors.

After counting the Pu was stripped from the stainless steal planchets by boiling for 1 hr in 8 M HNO$_3$. A short (1 x 5 cm) anion exchange column removed Fe and Ni from the remaining Pu, as described above. Elution into scintillation vials was accomplished using a dilute HCl and HF mixture. After the samples were dried, they were reconstituted into 1 mL of 0.01 M HCl to which 19 mL of Ecoscint scintillation cocktail (National Diagnostics) was added. Samples were counted for 6 hr on a Packard Tri-Carb 2100TR liquid scintillation counter (LSC). Determination of ^{241}Pu was accomplished by energy resolution.

Due to the low activity of the ^{137}Cs, 3-10 g sample sizes were employed. Samples were weighed into 5 dram polyethylene vials. The samples were

placed on the face of the HPGe detectors and counted for 24 h. Data reduction
was performed with the Genie 2K software suite (version 2.0; Canberra) and the
analysis was accomplished using an Excel™-based program developed in
house.

For this work we compared our samples with a standard to determine
activities. The standard used was a multi-source gamma standard (#62955-590;
Analytics, Atlanta, GA) certified for ^{137}Cs among other gamma emitters. The
standard was counted for 15 min achieving < 0.5% counting error. When the
standard was counted as a sample and after data analysis, the calculated activity
was within 0.3-4% of the true value which is within the tolerance of the standard.
The face of the detector was used for both the samples and the standard, but the
standard and sample geometries are still different because the standard is a
point source. In addition, the samples have a larger diameter and volume.

To determine the $^{239, 240, 241}$Pu atom concentrations, three 500 mg aliquots
of soil from each location and depth were digested and separated as done for the
alpha activity analysis. In this case 2.38 x 10^{11} atoms of ^{242}Pu were added as an
internal standard to determine atom numbers. The literature reports that ^{242}Pu
exists in the soil around INL (Beasley et al., 1998). The number atoms of ^{242}Pu
present are on the order of 10^5 atoms per gram of soil. Native ^{242}Pu content is
therefore negligible and constitutes less than 5 x 10^{-5} % of the tracer. After
separation, the samples were dried and transferred into 10 mL volumetric flasks
with 4% HNO_3. Analyses were completed on a ThermoFinnigan Element2 sector
inductively coupled plasma mass spectrometer fitted with an Aridus membrane

desolation attachment.   This attachment removes of H_2O prior to sample introduction into the plasma. We determined that this reduced UH^+ formation to 0.01% which is analogous to the PuH^+ formation that can be expected. Each location and depth was run in triplicate with each of sample analyzed on the mass spectrometer twice with a 2.5 min 4% HNO_3 rinse between every analysis to reduce carry over.

The small number of atoms of ^{238}Pu in the samples and isobaric ^{238}U, complicates the mass spectrometric measurements at this mass.   No decontamination factors were calculated for the anion exchange; therefore, a small amount of U contamination could exist. This would be unnoticeable in alpha spectrometry due to the small activity that would be present. It would cause a bias with mass spectrometry because the mass spectrometer used cannot differentiate between the isobars ^{238}U and ^{238}Pu. Alpha spectrometry is therefore necessary to quantify ^{238}Pu and atom concentrations were not determined. A 1 ppb solution of ^{238}U was analyzed to determine relative count rates.   A comparison at mass 238 shows in our analyses that count rates correspond to approximately 0.04 and 2 ppb of ^{238}U exist in the HNO_3 solvent and sample process blanks respectively. The blank counts at mass 238 for the mass spectrometry were low and consistent and were corrected in the data analysis.

Quality Control

The activity detection and determination limits were calculated for the two gamma detectors used for ^{137}Cs analysis in this work. Samples from the 4-8 cm

depth were analyzed on a lower background detector (0.004 vs. 0.04 cps). The activity detection limit, a_D, is the activity at which the analytical procedure may be relied upon to lead to detection. The activity determination limit, a_Q, is the activity that the given procedure or method will be sufficiently precise to allow quantitative analysis (Currie, 1968). The activity limits for each detector were calculated by utilizing the equations given in Currie for paired observations. The a_D and a_Q (0-4 cm) was calculated to be 0.053Bq and 0.167 Bq respectively. Samples from the 0-4 cm depth had sufficient activity to quantify the results using the higher background detector and 3 g sample sizes. The a_D and a_Q (4-8 cm) were calculated to be 0.034 Bq and 0.122 Bq respectively. The lower background detector provided adequate activity limits to quantify ^{137}Cs activity at the 4-8 cm depth when larger (10 g) sample sizes were employed.

Previous work has shown that ^{241}Am, ^{238}Pu, $^{239+240}$Pu, and ^{241}Pu activities in these samples (0.5 g) are detectable for the 0-4 and 4-8 cm depth for the methods and instrumentation employed (Payne and Clark, submitted). The activity determination limits were sufficiently low to allow quantitation for all sample activities except ^{241}Am at location 1 for the 4-8 cm depth and ^{241}Pu at both locations for the 4-8 cm depth (Payne and Clark, submitted).

Further confidence in the alpha spectrometric measurements for $^{239+240}$Pu was provided by the MS analyses. All MS count rates were adjusted to account for background and the abundance sensitivity. Abundance sensitivity is the contribution of the neighboring peak to the intensity of the measured isotope (Becker, 2005). The corrected atoms/g for each isotope are shown in Table 3.1.

From the data given, the activity of the $^{239+240}$Pu was determined using the general relationship that A = λN, where A is the activity, λ is the decay constant and N is the number of atoms. Figure 3.2A shows that this calculated activity for $^{239+240}$Pu corresponds to the activity determined by alpha spectrometry.

This calculation can also be applied to the activity of ^{241}Pu. In Figure 3.2B it is seen that the calculated activity of ^{241}Pu is also statistically the same as the LSC determined activity for each sample site and depth except location 2 at the 4-8 cm depth. The LSC data at the lower depths was not quantifiable, explaining the observed difference. In the case of ^{241}Pu although there is statistical agreement between the two techniques, it appears as though the MS results show a positive bias compared to the LSC activities. Efforts were made to exclude ^{241}Am from the system, but any remaining ^{241}Am would cause an increase in the atom concentration determined by MS. Self-absorption in the LSC analysis could result in an apparent systematic decrease in the LSC results compared to the MS results. Overall, mass spectrometric techniques confirmed the $^{239+240}$Pu and ^{241}Pu activities determined by alpha spectrometry and LSC.

Results and Discussion

^{137}Cs activity

The activity of the ^{137}Cs in the 4-8 cm depth was found to be in agreement with fallout values (0.013-0.038) (Beasley et al., 1998; Hulse et al., 1999). A slight enhancement of ^{137}Cs activity is seen in the 0-4 cm depth (Table 3.2). The ^{137}Cs activity is correlated with depth rather than location for these samples. The

excess of ^{137}Cs in the upper layer suggests another contamination source must exist.

Pu and ^{241}Am from previous work

The activities of ^{238}Pu, $^{239+240}$Pu and ^{241}Pu were determined previously and are given in Table 3.3 (reference date 1/2006) (Payne and Clark, submitted). All of the Pu isotopes are highest at location 1 for the 0-4 cm depth. The 4-8 cm depth has statistically the same activity at both locations. The Pu activities are above fallout levels in both the 0-4 and 4-8 cm depths for both locations, but the ^{137}Cs activity is elevated only in the 0-4 cm depth at both locations. This indicates that the lower layer has been impacted by processes and activities at INL.

The activity of ^{241}Am is highest at location 2 and both locations show a decrease in activity with depth. The ^{241}Am activities are elevated compared to expected fallout values. Previous determination of the ^{241}Pu activity in these samples allowed differentiation between the ^{241}Am that was present from the contamination event and that due to ingrowth. Locations 1 and 2 have statistically different ^{241}Am ingrowth distribution profiles with location 1 displaying greater than 20% of ^{241}Am activity due to ingrowth and location 2 displaying less than 10% due to ingrowth. The contribution from ingrowth at both locations and depths indicates that the ^{241}Am contamination cannot be accounted for exclusively by ^{241}Pu (Payne and Clark, submitted).

^{137}Cs and $^{239+240}$Pu activity ratios

The ratios of Cs activity to $^{239+240}$Pu are higher at location 1 and location 2 than the expected fallout ratio of 0.035 (Beasley et al., 1998) as seen in Table 3.1. The enrichment in $^{239+240}$Pu is expected due to the local contamination events that the soils experienced. The DOE reports $^{239+240}$Pu background fallout activities at INL from 1970-1994 are between 0.00037-0.00089 Bq/g with an average of 0.0007 Bq/g (Mitchell, 1995). Utilizing this average background activity and the activities determined for our samples we find that between 99.7-99.94% of the $^{239+240}$Pu activity is attributable to non-fallout sources at both locations and depths. Additionally, the ratio of the published fallout activity of $^{239+240}$Pu (Mitchell, 1995) to the determined ^{137}Cs activity is consistent with expected fallout values for INL (Beasley et al., 1998), with an enrichment in ^{137}Cs activity in the 0-4 cm depths. This can be accounted for because it is likely that all onsite locations contain some ^{137}Cs from the ICPP and higher $^{239+240}$Pu/^{137}Cs than fallout is expected from testing low yield Pu fueled devices (Beasley et al., 1998). This indicates that ^{137}Cs is attributable to on-site activities.

^{137}Cs and ^{241}Am activity ratios

The ^{241}Am/^{137}Cs activity ratios found in this work are higher than the ratio of 0.007 estimated using fallout activities reported by the U.S. DOE (Mitchell, 1995). When only the ^{241}Am from ingrowth, which was determined from previous work (Payne and Clark et al., submitted) is considered, the value is still high (0.57-2.32). This is due to the large activity of non-fallout Pu present.

Pu and Am activity ratios

There are two stratospheric sources of ^{238}Pu. The satellite nuclear auxiliary power source (SNAP-9A), which failed to reach orbit and burned up in 1964, and fallout from weapons testing. The fallout ^{238}Pu/$^{239+240}$Pu activity ratio after 1964 is 0.03 ± 0.005 (Cooper et al., 2000). Table 3.4 shows that the range of ^{238}Pu/$^{239+240}$Pu ratios in this work is lower than fallout. This suggests an increase in the $^{239+240}$Pu activity relative to fallout.

All of the Pu activity ratios differ significantly from expected fallout values. Comparison of Pu atom and activity ratios observed in the samples to that from a known WGP contamination event shows that the Pu contamination in these soils appears to be a mix of WGP with fallout contributions (Table 3.4) (Lee and Clark, 2005). The ^{241}Am/$^{239+240}$Pu activity ratio in this work is elevated (0.45-4.75) compared to fallout (0.35) (Eriksson et al., 2004), providing further confidence that an additional source of ^{241}Am existed for these soils. The source of the radiological contamination would not be able to be elucidated if only $^{239+240}$Pu, ^{241}Am, and ^{137}Cs activities and the corresponding activity ratios were considered. The determination of ^{241}Pu would assist in assigning source information to the ^{241}Am.

^{241}Pu atom and activity ratios

Detonation of nuclear weapons produces ^{241}Pu, which decreases the ^{241}Pu/$^{239+240}$Pu activity ratio relative to WGP. The half-life of ^{241}Pu is 14.35 y, such that all ratios involving this isotope must be decay-corrected to the same date (01/2006). The ^{241}Pu/$^{239+240}$Pu activity ratios for the samples analyzed in this work are larger than expected for fallout (Irlwick and Hrnecek, 1999).

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Similarly, the atom ratio of ^{241}Pu/^{239}Pu is larger than expected due to fallout in the northern hemisphere, indicating possible WGP (Kelley et al., 1999). The WGP fabricated at RFS contains < 0.58% ^{241}Pu with negligible ^{241}Am (Hulse et al., 1999) at the time of manufacture, but the ^{241}Am activity increases with time due to decay of ^{241}Pu. In our previous work, we determined the activity of ^{241}Am due to ingrowth from ^{241}Pu that was present when the soil was collected (Payne and Clark, submitted). The ratio of the ^{241}Am from ingrowth (as opposed to total) to $^{239+240}$Pu is in line with expected WGP ratios reported in both Lee and at RFS (0.15-0.24). This ratio is not a good indicator to distinguish between fallout and WGP because of these similarities. Plutonium atom ratios would aid in the designation of the Pu source between fallout and WGP. Figure 3.1 is an example of how atom ratios can be used to fingerprint source information.

Pu atom ratios

The ^{240}Pu/^{239}Pu atom ratios have been well-characterized globally and for specific events and processes. Global fallout in the northern hemisphere is reported to be 0.18 ± 0.014 (Kelley et al., 2003). More specifically, the integrated global fallout plus NTS for ^{240}Pu/^{239}Pu atom ratio for INL is 0.166 ± 0.004 (Beasley et al., 1998). The soils in this work were found to have ^{240}Pu/^{239}Pu isotopic ratios between 0.06 and 0.07 (Figure 3.1 & Table 3.4). The ^{240}Pu/^{239}Pu isotopic composition of the waste buried at the SDA through 1969 is characteristic of weapons grade Pu (WGP) and could span values between 0.03 and 0.08 (Beasley et al., 1998).

The fallout contribution has often been determined by utilizing knowledge about ^{240}Pu/^{239}Pu atom ratios. From this information it is possible to determine the fractional contribution of a two source mixture if their isotopic ratios differ significantly. Following the example of Krey the ratio of the $^{240+239}$Pu activities from the two sources can be expressed as follows (Krey et al., 1976):

$$\frac{A_1}{A_2} = \frac{(R_2 - R_m)}{(R_m - R_1)} \frac{(1 + 3.67R_1)}{(1 + 3.67R_2)} \qquad (3)$$

Where:

A_1, R_1 = activity and ^{240}Pu/^{239}Pu isotopic ratio from source 1 (fallout)

A_2, R_2 = activity and ^{240}Pu/^{239}Pu isotopic ratio from source 2 (INL local events)

R_m = ^{240}Pu/^{239}Pu isotopic ratio from the mixture

The ratio of the half lives of ^{239}Pu to ^{240}Pu is 3.67. Recognizing that $A_1 + A_2 = A_m$, it is possible to solve for the activity of $^{239+240}$Pu from each source. Using R_1 = 0.166 and R_2 = 0.055 (Beasley et al., 1998) we find that $^{239+240}$Pu from non-fallout sources consists of > 90% of the Pu at location 1 and > 80% at location 2 with 10-20% error. This model overestimates the fallout contribution for the locations analyzed and introduces large errors by propagating the error associated with each of the terms used, and the assumptions incorporated in R_2. This model is a good first approximation to understand the fallout contribution in a contaminated sample but the associated error is large.

Decay with time

Employing knowledge of decay the activities of Pu, ^{241}Am and ^{137}Cs can be calculated as seen in Figure 3.3A. The ^{241}Pu decays rapidly compared to the other isotopes. The ^{241}Am shows a slight increase in activity due to this decay

around the year 1984 (Figure 3.3B). When the samples were collected, ^{241}Pu dominated the total activity present but after 50 years the ^{241}Am becomes a more significant contributor to total activity. It is evident that the activity ratios will also change with time.

Radiometric and MS analyses on small soil samples complement each other. Using the combined data sets, contaminant source information can be elucidated. In this soil, the Pu is WGP primarily from the SDA. There is a larger than expected ^{241}Am activity probably derived from waste streams at RFS. The primary source of ^{137}Cs is from fallout and other possible on-site activities such as the ICPP.

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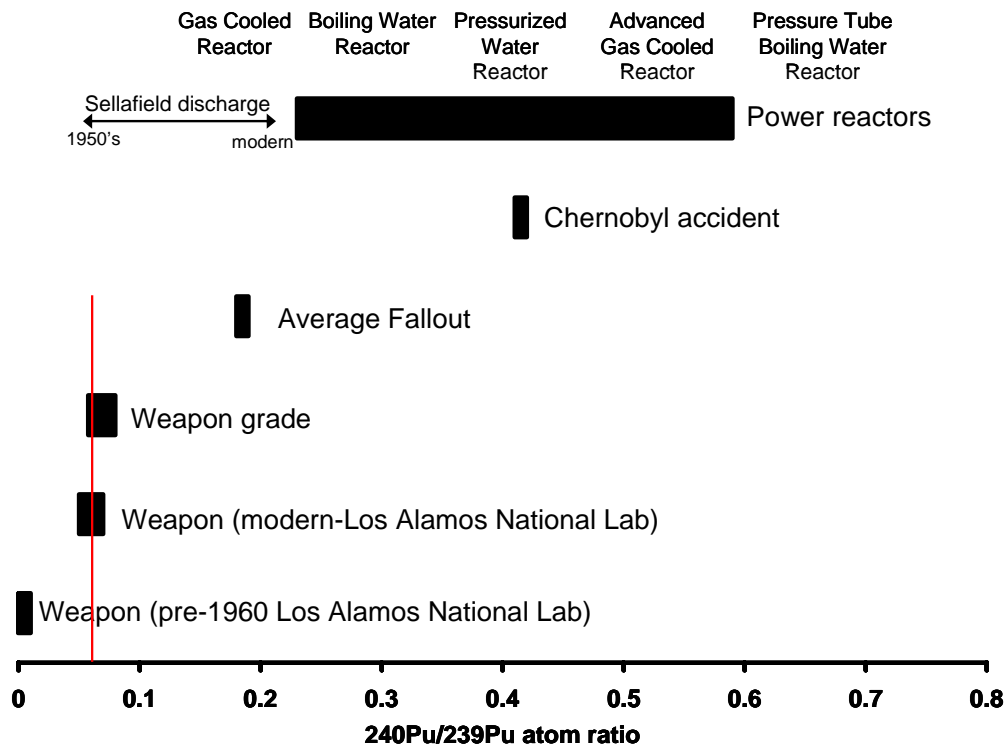
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Figure 3.1. ^{240}Pu/^{239}Pu atom ratios expected from various nuclear events. The vertical line indicates the atom ratios determined in this work. Reproduced by permission of The Royal Society of Chemistry.
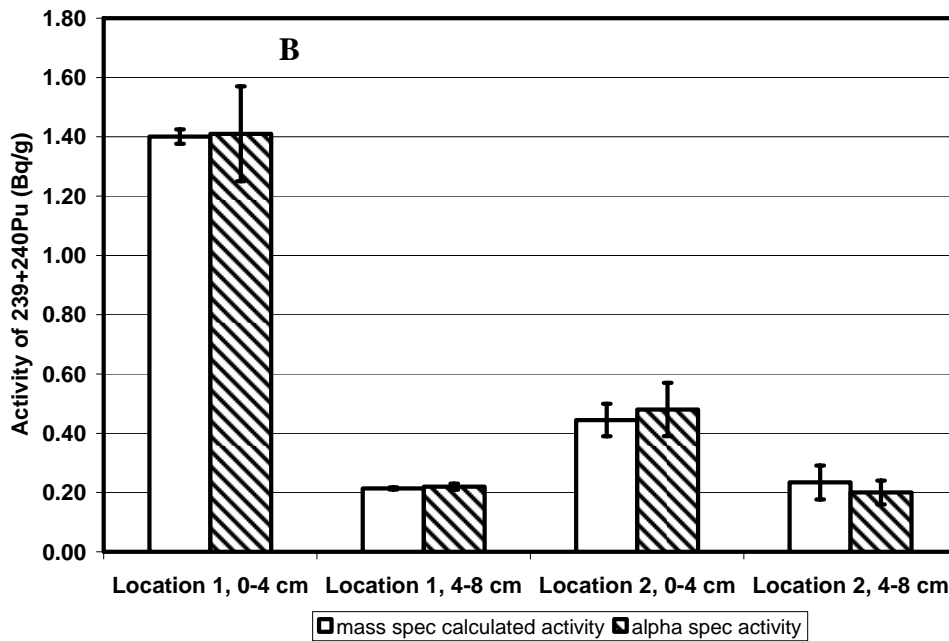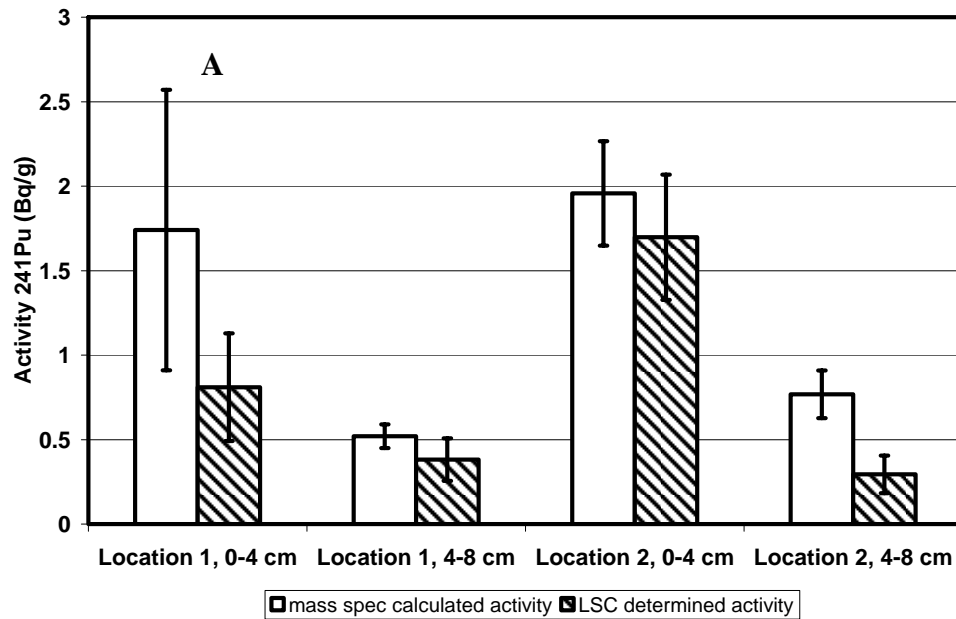
Figure 3.2A. Comparison of $^{239+240}$Pu (Bq/g) for each sample location and depth as determined by alpha spectrometry and mass spectrometry.
Figure 3.2B. Comparison of ^{241}Pu (Bq/g) for each sample location and depth as determined by LSC and mass spectrometry.
Error is 1 sigma, n = 10 for alpha spectrometry and LSC, n = 3 for mass spectrometry.
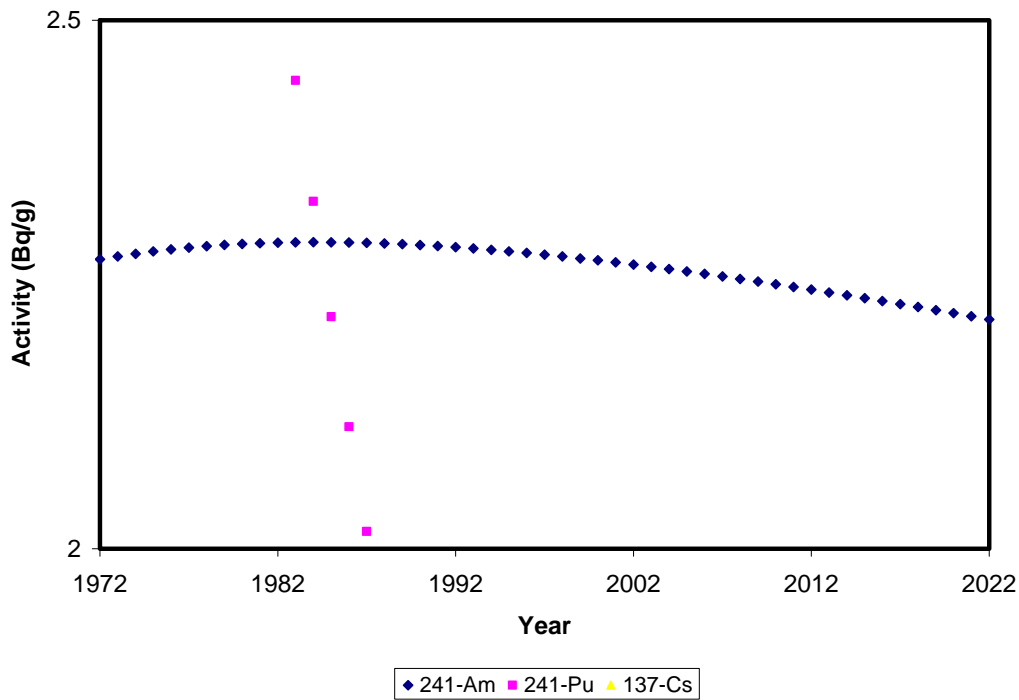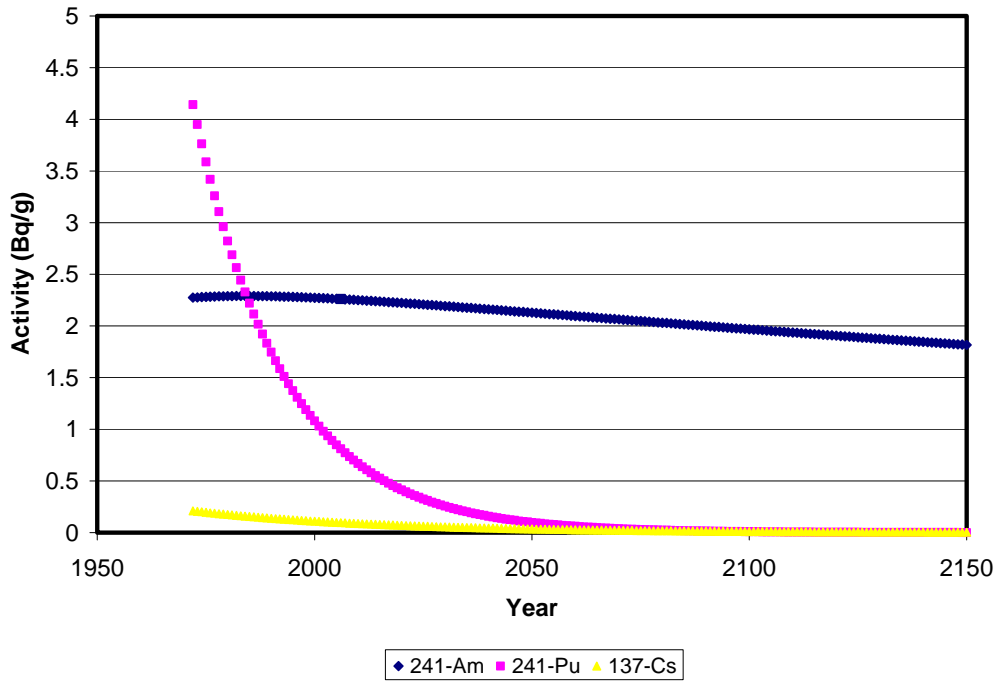
Figure 3.3A. Decay of ^{241}Am, ^{241}Pu and ^{137}Cs at Location 2, 0-4 cm, since the time of sampling.

Figure 3.3B. Enlargement of Figure 3.3A, showing the increase of ^{241}Am in 1984 from the decay of ^{241}Pu.

Table 3.1. ^{239}Pu, ^{240}Pu and ^{241}Pu atoms/g as determined by mass spectrometry, error is 1 sigma, n = 3

Location	^{239}Pu (atoms/g)	^{240}Pu (atoms/g)	^{241}Pu (atoms/g)
1, 0-4 cm	3.84 (0.5) x 10^{11}	2.82 (0.2) x 10^{10}	1.14 (0.5) x 10^9
1, 4-8 cm	1.99 (0.5) x 10^{11}	1.57 (0.5) x 10^{10}	6.02 (3) x 10^8
2, 0-4 cm	1.26 (0.02) x 10^{12}	7.68 (0.1) x 10^{10}	1.23 (0.2) x 10^9
2, 4-8 cm	1.89 (0.03) x 10^{11}	1.24 (0.02) x 10^{10}	5.22 (0.9) x 10^8

Table 3.2. Activity of ^{137}Cs (Bq/g) for each location and depth, ^{137}Cs ratios with $^{239+240}$Pu and ^{241}Am in this work and literature fallout values, Error is 1 sigma, n = 10.

Location	^{137}Cs (Bq/g)	$^{239+240}$Pu /^{137}Cs	^{241}Am /^{137}Cs
1, 0-4 cm	0.0864 ± 0.004	16.32 ± 2.02	9.03 ± 1.35
1, 4-8 cm	0.0169 ± 0.002	13.02 ± 1.84	5.92 ± 1.35
2, 0-4 cm	0.0963 ± 0.011	4.99 ± 1.10	23.49 ± 3.83
2, 4-8 cm	0.0441 ± 0.004	4.54 ± 0.95	17.69 ± 3.12
Fallout	0.013-0.038[a]	0.052 ± 0.012[b]	0.007[c]

[a] Beasley et al., 1998. [b] Hulse et al., 1999. [c] DOE report.

Table 3.3. Pu and Am activities (Bq/g) determined previously by Payne and Clark, 2006. ^{241}Pu reference date 1/2006, error is 1 sigma, n = 10.

Location	$^{239+240}$Pu (Bq/g)	^{238}Pu (Bq/g)	^{241}Pu (Bq/g)	^{241}Am (Bq/g)
1, 0-4 cm	1.41 ± 0.16	0.024 ± 0.003	1.70 ± 0.37	0.78 ± 0.11
1, 4-8 cm	0.22 ± 0.014	0.004 ± 0.0008	0.29 ± 0.11	0.10 ± 0.019
2, 0-4 cm	0.48 ± 0.091	0.012 ± 0.003	0.81 ± 0.32	2.26 ± 0.27
2, 4-8 cm	0.20 ± 0.038	0.0047 ± 0.001	0.38 ± 0.13	0.78 ± 0.12

Table 3.4. Pu and Am activity and atom ratios from fallout, this work and literature weapons grade plutonium in soil.

Ratios	$^{240}Pu/^{239}Pu$[a]	$^{241}Pu/^{239}Pu$[a]	$^{241}Pu/^{239+240}Pu$[b]	$^{238}Pu/^{239+240}Pu$[b]	$^{241}Am/^{239+240}Pu$[b]
Fallout	0.166[e]	0.0014 ± 0.0002	0.38-0.67	0.03 ± 0.005	0.35 ± 0.02
WGP[f]	0.05	0.005	0.79-1.29	0.017-0.033	0.15-0.24
1, 0-4 cm	0.074 ± 0.005	0.0032 ± 0.002	1.21 ± 0.30	0.017 ± 0.003	0.55 ± 0.10
1, 4-8 cm	0.078 ± 0.012	0.0029 ± 0.002	1.32 ± 0.51	0.018 ± 0.004	0.45 ± 0.09
2, 0-4 cm	0.061 ± 0.0005	0.0010 ± 0.0002	1.69 ± 0.74	0.025 ± 0.008	4.71 ± 1.06
2, 4-8 cm	0.066 ± 0.0008	0.028 ± 0.0005	1.90 ± 0.74	0.024 ± 0.007	3.90 ± 0.95

[a] atom ratio. [b] activity ratio. [c] only ^{241}Am contribution form ingrowth. [d] total ^{241}Am present. [e] Beasley, 1998. [f] Lee, 2005

CHAPTER FOUR

DEVELOPMENT OF AN EPOXY PREPARATION TECHNIQUE AND

LOCATING SYSTEM FOR FISSION TRACK ANALYSIS AND SUBSEQUENT

LASER ABLATION MASS SPECTROMETRY OF SOILS

Abstract

Fission track analysis (FTA) is an important technique used to directly detect nuclides with high fission cross sections in many matrices including soils. Locating the particles of interest using FTA and further analyzing the particle by laser ablation mass spectrometry (LAMS) is a quick method for gathering important compositional data with little sample preparation and almost no waste. We have developed an epoxy sample preparation technique and a particle locating system using boron carbide (B_4C), which is easily coupled to LAMS. The B_4C creates an image in the fission track detectors in the form of decreased etching at that location. Exploiting this response allows the B_4C chip and images to be used as coordinates to locate the fission tracks to their corresponding soil aggregates. This protocol successfully allows particles containing ^{235}U and ^{239}Pu to be located and analyzed. Our analyses have shown that LAMS on soil aggregates that contain fissile nuclides provides information on the identity of the nuclide (^{235}U or ^{239}Pu). The elemental signature of the particles containing ^{235}U or ^{239}Pu is also considered.

Introduction

Fission track analysis (FTA) is a technique that allows the detection and spatial resolution of isotopes with high fission cross sections such as ^{235}U and ^{239}Pu in varying matrices.[1] In FTA, a sample containing fissile atoms is placed in close contact with an insulating material, called a detector, which is then irradiated with thermal neutrons. The induced fission causes damage to the adjacent insulating detector. This damage can then be magnified by chemically etching the detector in a warm caustic solution and the magnified tracks are observable by optical microscopy.[1]

Fission track analysis has been applied to many disciplines of science such as anthropology, astrophysics, botany, chemistry, geochemistry, geochronology, metallurgy, nuclear physics and nuclear engineering.[1] Furthermore, it provides the ability to map the location of ^{235}U and ^{239}Pu contamination within a given sample. While tracks indicate the presence of ^{235}U and ^{239}Pu, fission track analysis is typically not used to distinguish between the two isotopes; consequently, further analysis is necessary. The challenge with such an analysis is to detect and locate small amounts of contaminated material in an excess of uncontaminated matrix particles. FTA has been reported to be quantifiable down to femtogram (10^{-15} g) quantities of ^{239}Pu.[2] Another challenge is distinguishing between natural U and anthropogenic U or Pu.

To obtain specific information about isotopes of interest in specific locations, FTA and alpha track analyses have been augmented by single particle analysis using alpha spectrometry[2], energy dispersive x-ray analysis (EDX)[3],

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secondary ionization mass spectrometry (SIMS)[4], and thermal ionization mass spectrometry (TIMS) .[5] Alpha spectrometry, SIMS, and TIMS primarily provide information on the actinide isotopic signatures, while EDX analysis allows identification of stable elements contained in the contaminated particles. Previous attempts to couple FTA with mass spectrometric analysis techniques have been done with TIMS or SIMS using swipe samples for the determination of uranium enrichment levels.[4-8] The disadvantage of this approach is that sample preparation for further analysis is labor intensive and analyses are often not completed for days. Laser ablation mass spectrometry (LAMS) is an attractive option as sample preparation tends to be minimal with little to almost no waste produced. The technique developed here allows FTA samples to be directly analyzed on LAMS with no further sample preparation.

Another challenge facing single particle analysis after FTA is the ability to accurately locate the position of the particles responsible for track production. Significant advances on this aspect have been achieved by workers interested in dating materials or investigating tissue and bone samples.[1, 9-13]

Pressed pellets are often employed for FTA on environmental samples such as pulverized rock and soils. Pellets can be prepared either with[14-17] or without[18-20] a binding agent; this approach has also been employed prior to LAMS.[21-26] Although success has been achieved for both FTA and LAMS using pellets, the pellet method does not accommodate a combined FTA LAMS analysis incorporating a locating system. Part of the difficulty in combining these methods is that the soils must be immobilized in order to more accurately

analyze only the particles subjected to the laser, thereby not introducing unwanted soil particles. Using a grid as a locating system[13] could hinder the close contact needed to register fission tracks. In addition, any particles which are not located on the surface of the pellet will not record fission events in the detector, nor will they be accessible for further analysis.

We have developed a new method, which couples FTA with LAMS. This allows us to investigate the elemental composition of the soil aggregates that preferentially sorb U and/or Pu. Understanding this elemental composition opens an opportunity to learn more about the interactions between fissile nuclides and the soil. The FTA/LAMS protocol described herein has been applied to the analysis of soils collected from the Idaho National Laboratory's (INL) Radioactive Waste Management Complex (RWMC), now known as the Subsurface Disposal Area.[28] The soils were contaminated by shallow land disposal and subsequent flooding events. Between April 1954 and late 1970 an estimated 65,000 – 153,000 m^3 of transuranic waste was shipped from the DOE Rocky Flats facility in Golden, Colorado to INL. The waste was packaged in steel drums, wooden boxes, cardboard, or plastic bags and placed mostly in unlined pits or trenches. Flooding of open pits and trenches in February 1962 and January 1969 allowed transuranic waste to seep into the soil.[28-31]

The purpose of this work is to explore the compatibility of FTA and LAMS. Using LAMS, the primary source of induced fission events will be determined. The elemental signatures of the soil aggregates containing fissile nuclides will also be investigated.

Experimental

Between 1972 and 1974 Markham et al. collected soil samples from 72 locations around the RWMC in the 0-4 cm and 4-8 cm depths.[29] The soil samples were then oven dried, thoroughly mixed, ground, and sieved with a 0.5 mm mesh. The samples were analyzed for $^{239+240}$Pu, ^{238}Pu and ^{241}Am and packaged for storage.[29]

We obtained the samples from storage and then determined the soil pH and cation exchange capacity (CEC) by standard methods.[32] The observed pH and CEC were 7.21 ± 0.05 and 21.4 ± 2.2 cmolc/kg (cmolc = centi-moles of charge), respectively. The surface area as determined by BET analysis was 3.8 ± 0.1 m^2/g and the major crystalline minerals observed by powder x-ray diffraction were quartz, smectite, kaolinite, illite and mica. The homogenized soils contain 47% sand, 36% silt, and 17% clay. These physical properties are consistent with previous studies on INL soils collected from similar locations.[30, 31] After total digestion of 0.5 g of soil using ^{242}Pu as a tracer and a modified lithium metaborate fusion[34], Pu was separated from the matrix using anion exchange.[35] The $^{239+240}$Pu was determined using alpha spectrometry[36] and was found to be distributed within the samples with an average activity of 1.41 ± 0.16 Bq/g. The soil contains 4.09 ± 0.38 μg/g of primordial uranium and the ^{235}U content, as determined by inductively coupled plasma mass spectrometry and alpha spectrometry, was found to be 0.0023 ± 0.0002 Bq/g and 0.0023 ± 0.0008 Bq/g respectively.

For FTA to be compatible with LAMS, sample preparation must

accomplish the following:

• The sample must be immobilized to prevent particles other than those of

interest from being introduced into the MS system.

• The surface of the sample must be flat to provide close contact to the detector

during FTA.

• A reliable method for locating the particles that created fission tracks in the FTA

detector must be integrated into the fission track sample.

• It must be possible to go from detector back to original sample.

The result of the sample preparation development with respect to these

conditions leads to the procedure described herein.

Sample preparation

Tastrak™ (Track Analysis Systems Ltd., Bristol, UK), a CR-39 (allyl

diglycol carbonate) plastic manufactured for nuclear track detection, was ordered

precut into 15 x 15 x 1 mm slides. Pieces of Tastrak™ were used as sample

mounts and the sample detectors. A paste was prepared by mixing 400 grit

silicon carbide (SiC) with a small amount of 18 MΩ water. The sample mounts

were then roughened on one side by rubbing the mount and paste against a

glass plate. This provides an irregular surface to which the epoxy will adhere.

The epoxy resin was heated for less than five minutes in a plastic beaker

while being stirred. After heating, triethylenetetraamine (TETA) was added as a

curing agent in approximately 1:8 ratio of cure to resin. The TETA was

thoroughly mixed with the epoxy resin. One drop of the resulting mixture was

then placed on the frosted side of the sample mount, which was kept on a hotplate at 50 °C for the remainder of the sample preparation. Approximately 2 mg of soil sample were added and stirred into the epoxy mixture. Three boron carbide chips (Electro Abrasives, Buffalo, NY), were added to each sample, all three in the epoxy near each of corners of the slide, which was to be used as a locating system. The slide was then removed from the heat and allowed to harden overnight.

During hardening, the soil particles settle to the bottom of the epoxy. The soil particles must be exposed to register fission tracks and to be set for LAMS analysis. This was achieved by grinding and polishing the epoxy in a similar manner to that employed to roughen the sample mounts. First the sample was ground with 400 grit SiC, followed by 600 and 1200 grit. The larger grits correspond to progressively smaller particle sizes therefore increasing the smoothness of the epoxy surface. Diamond compound (Diafin, La Jolla, Ca) was used as a polishing agent. Polishing provides a mechanism for eliminating surface defects in the sample mount and is compatible with reflected light microscopes, such as the one used with the LAMS. A minimal amount of diamond compound was dabbed on butcher paper, which covers a glass plate. One drop of polishing oil was added and the epoxy sample was rubbed on the mixture in circular motions. This procedure was employed with 3µm followed by 1µm particle size diamond compound. The sample was then rinsed with 18 MΩ deionized water, followed by a reagent grade methanol rinse. A fresh Tastrak™ slide, used as a track detector, was placed on top of the sample and taped

together creating a 'sandwich' assembly (Figure 4.1).   The sandwiched

Tastrak™ samples were placed in individual polyethylene bags, which were heat

sealed and placed in 4 dram polyethylene vials for irradiation.

Irradiation with thermal neutrons

Irradiations of samples were undertaken at the 1 MW TRIGA fueled

reactor at Washington State University. The thermal neutron flux of the position

used in the reactor was ~ 4 x 10^{12} n•s^{-1}•cm^{-2}. Fission tracks were produced

during a 12 minute irradiation with a fluence of approximately 3 x 10^{15} n•cm^{-2}.

Previous experimentation showed that this fluence was sufficient to observe

fission tracks.[13, 35, 37]

Processing detectors

Following irradiation and a minimum 1 hr decay period, the plastic track

detectors were separated from the sample mounts. Each detector was then

chemically etched by immersing it in a solution of 6 M NaOH at 70 °C for ten

minutes. After etching, the detectors were rinsed with 18 MΩ deionized water

and allowed to air dry.

Detector slides were examined under an optical microscope equipped with

a motorized stage (Autoscan AS3000B) and CCD camera running image

analysis software (Autoscope Version 2.0). Each detector was observed under

the microscope to identify the locations of the B_4C chips and fission tracks. The

location of the B_4C in the sample was recorded in the detector simultaneously

with sample produced fission tracks. Boron has a high neutron absorption cross

section, 750 barn, undergoing $^{10}B(n,\alpha)^{7}Li$ reaction, but Tastrak is insensitive to

alpha damage therefore the effect that the B_4C has on the detector is a deficiency in etching efficiency. This is due to the decrease in neutron flux on the detector where the B_4C chip is located, resulting in decreased radiation damage of the detector at the region as shown in Figures 2a and 2b. The unique shape of the B_4C chips and the difference in detector response to polished and unpolished B_4C allow locations (within 10 μm) to be identified as coordinate markers. One point of a B_4C chip would be set to (0,0) and the coordinates of the other two chips were determined relative to the defined origin. Fission tracks were also given x and y coordinate designations (μm) in relation to the origin and other B_4C markers.

LAMS

Samples were examined using a ThermoFinnigan Element2 sector ICP-MS fitted with a Nd:YAG UP-213 laser ablation sample introduction system by New Wave Research (Fremont, CA). The laser was operated using the fifth harmonic at 213 nm. The system was purged under He gas, which also functions as a carrier into the argon plasma. Laser spot sizes of 2-160 μm may be employed with varying intensity. Typically, 8-12 μm laser spot sizes were employed, producing approximately 10 J/cm^2 at a laser pulse rate of 10 Hz.

The LAMS instrument has visual and tracking capability similar to that employed during examination by optical microscopy. The boron carbide chips were located on the screen and their x and y values entered into the imaging suite software. This three point triangulation allowed the exact position of the soil particles or aggregates that are responsible for fission events to be located

during LAMS. A 30 x 30 μm square area around the location of interest was then ablated at a scan rate of 10 μm/s by the laser and analyzed for several m/z including 235 and 239.

Method Validation

Samples containing 5-10 shavings of pure natural U and boron carbide chips were irradiated and examined to ensure fission events could be detected and the location of the particle would not be misidentified using the B_4C locating system. This procedure provides evidence that the post-irradiation tracking system is successful and the microscope used to locate the fission tracks and the CCD camera used with the LAMS have comparable resolution and spatial accuracy. Solid boric acid (HBO_3) was irradiated to determine the detectors sensitivity to alpha damage. Sparse damage was observed that could not be positively identified as detector defects or tracks. Detectors that were etched after irradiation show less than 10 marks per detector, which are assumed to be detector defects or dust particle background.

Each grit of SiC was irradiated for 6 hours to determine the ^{235}U content. It was found to have a non-uniform ^{235}U concentration of 7.33 ± 0.58 μg/g in the 400 grit, 12.29 ± 7.44 μg/g in the 600 grit and 5.39 ± 2.35 μg/g in the 1200 grit. The SiC can potentially provide a major source of contamination tracks; therefore, it is very important to ensure that the sample preparation procedure removes traces of SiC.

For initial testing, polished, unpolished blanks, oil, methanol and various combinations were irradiated and analyzed at least three times to determine their

effect on the number of background tracks on prepared, polished epoxy blank samples. In three samples of irradiated polishing oil only one cluster of tracks was found indicating that the oil used for polishing does not contribute significantly to the background. Methanol was also irradiated and it was found to contribute approximately 2-3 starburst patterns of tracks and 3-6 clusters of tracks per sample. Epoxy blanks with no soil added, ground but unpolished and cleaned with methanol and water showed a multitude of starbursts and clusters of tracks. This reveals that the cleaning procedure alone does not sufficiently remove SiC. Blanks with no soil added, which had been polished and cleaned with methanol and water, were also made to insure that the epoxy would not contribute to high background counts and that the polishing and cleaning procedure would rid the sample of the SiC. In three irradiated blanks, one had one starburst and each had a few locations with individual damage marks, which again could not be positively identified as tracks or detector defects. This indicates that the combined polishing and cleaning procedure removes traces of SiC sufficiently.

Results and Discussion

The processing and analysis of the fission track detectors requires separation from the sample mounts as described above. When analysis of a fission track detector suggests that a particle contaminated with ^{235}U or ^{239}Pu is present, relocating that particle in the sample mount for subsequent LAMS analysis can be challenging. In over 175 processed samples, the fission track detector response to the B_4C chips during irradiation was predictable and

reproducible, as shown in Figures 4.2a and 4.2b. The images of the B_4C chips

recorded in the fission track detectors provide markers in the detector that can be

used to define locations in the sample mounts for subsequent LAMS, as

described above. Figure 4.3a shows a portion of a detector where no tracks are

seen; this is an image taken from a method blank sample. Figure 4.3b is a

typical starburst image of fission tracks created from a soil particle. The starburst

pattern of tracks demonstrates that fissile nuclides are not homogenously

distributed throughout the sample, rather they are preferentially associated with

certain soil particles or exist as discrete particles. Naturally occurring U-

containing minerals often contain a more homogeneous distribution of fissile ^{235}U

within individual aggregates. The tracks produced from this type of association

are seen in Figure 4.3c as random tracks not starbursts as seen in many of the

samples in this work.

Fission track analysis cannot discriminate between fission tracks produced

from ^{235}U or ^{239}Pu. In this respect, LAMS provides information that complements

FTA. To fully understand the potential of LAMS, the following equation must be

considered:

$$N_{products} = N_{target} \cdot \Phi \cdot \sigma \cdot t \qquad (1)$$

where $N_{products}$ is the number of nuclei that have undergone fission and therefore

produced fission tracks, N_{target} is the number of target atoms exposed to the

incident neutrons, Φ is the neutron flux (4 x 10^{12} n/s•cm^2); σ is the cross section

of the target (^{235}U = 585 b, ^{239}Pu = 750 b); and t is the time of irradiation (720 s).

For every five million atoms of ^{235}U or ^{239}Pu present in the sample, 8.4 or 10.8

number of tracks are seen, respectively. This means that although ^{235}U and ^{239}Pu are considered to have very high fission cross sections, at the end of a 12 minute irradiation, most of the atoms did not capture a neutron and fission. Hence, there are sufficient atoms of the ^{235}U or ^{239}Pu remaining to determine the elemental composition of the fission track source using LAMS. Similarly the other elements experienced an insignificant loss of atoms of due to the irradiation process; 10^{-5} - 10^{-11} % of the atoms experienced nuclear changes.

After identifying the locations by FTA, the only piece of information obtained is that soil containing ^{235}U or ^{239}Pu exists in a certain location. By examining that location with LAMS and utilizing its multi-element capability, compositional information can be elucidated. If a discrete particle of U or Pu oxide caused the fission tracks then it would be logical to hypothesize that only a background signal would be seen at masses for trace elements that are typically seen in soils and the count rates at masses 235 or 239 would be high, although sufficient laser resolution would be required. On the other hand if the Pu or U is associated with a soil particle, ion signals much higher than background would be expected for elements that make up the soil particle composition.

Moving the laser around the sample location reduces the time dependent fractionation that could be observed due to the ablation process.[38] As a laser bores a hole in a sample the signal will drop off due to the difficulty of extracting atoms out of the hole and maintaining laser power at successively deeper depths. Each run lasts approximately 60 s including a 10 s background at the start of each run. Figure 4.4 shows a condensed version of the LAMS data collected for

a soil spot, which had been located with FTA. Although the count rates change

for each mass as the laser is moving along the area, it is evident that differences

exist among masses. The data in Figure 4.4 was generated from a cluster of

tracks similar to the one seen in Figure 4.3c.

Based on the known activities of the ^{235}U and ^{239}Pu by ICPMS and alpha

spectrometry, the number of atoms of each per gram of sample are in the order

of 10^{13} and 10^{11}. Each sample contained between 30 and 45 regions of interest

consisting of a mixture of starburst and clusters of tracks, which were located and

analyzed on the LAMS. On each located aggregate of soil, ^{235}U was observed

across the majority of the mass scan time points, although at much lower count

rates than the other mass to charge ratios (m/z) analyzed. The ^{239}Pu was only

seen in a few time points along a scan as seen in figure 4.4. When the 239 mass

was observed it was often accompanied by counts in the 240 mass window. This

suggests that this observation at mass 239 is ^{239}Pu$^+$ not ^{238}UH$^+$ This could

indicate that ^{239}Pu is present but in very small quantities, or that it was on a

particle, which only possesses a small portion of the surface area of the soil

under examination. The limited observation of counts in the 239 m/z window do

not account for the large number of atoms that should be present in each sample

if near homogeneous distribution of the Pu exists in the sample. This indicates

that preferential Pu sorption or Pu rich particles or oxides must exist in these

soils. No Pu rich particles were found using the FTA and LAMS technique, which

is not surprising because the bulk analysis to determine activities was conducted

using 500 mg sample sizes and the FTA was done on 2 mg sample sizes. The

probability of finding a hot particle in 2 mg is much less than the probability of finding one in 500 mg. If the Pu is homogenously distributed, a 2 mg sample would contain on the order of 2×10^8 atoms. Employing equation 1, this would produce 432 tracks. This is not observed and in the case of these soils the ^{235}U dominates the observed fission tracks.

Despite the heterogeneous nature of soils, LAMS can still provide useful insight into the composition of the particles in comparison to the bulk composition. Even without information on ablation rates and efficiencies, data between runs can be compared. While the ablation efficiency can change in different materials, this is compensated for by looking at ratios of elements. In order to quantify the ablation efficiency, an internal standard must be used. This requires the assumption that an element has a homogeneous, well known concentration over the area of interest. Between spots, the ablation efficiency can also be different; for a first approximation, the ratios of elements between spots can be compared. This would not be an appropriate approximation if the elements being compared possessed different chemical properties i.e. refractory versus non-refractory. Another issue that must be considered is that the data for each mass is not acquired simultaneously, rather it is gathered incrementally; the mass spectrometer must change magnet settings to scan through the masses. In order to reduce the uncertainty in the ratios, it is important to look at element ratios that are close in mass, which therefore were ablated and gathered at similar times.

Figures 4.5a and 4.5b are comparisons of bulk atom ratios and count rate ratios of LAMS data collected on three locations identified by FTA as having either ^{235}U or ^{239}Pu associated with them. Bulk elemental concentrations were determined on the soil after total digestion using inductively coupled plasma mass spectrometry (ICPMS). These concentrations were reported as μg (10^{-6}) of the element per gram of soil. They were then manipulated to give concentrations of the isotope of that element that would match the mass used in LAMS. For example, mass 60 was used in LAMS to determine count rates for Ni but it is only 26.22 percent naturally abundant. From this data the number of atoms present for each mass, per gram of soil was determined and ratios of the numbers of atoms were calculated. Correction for irradiation was not needed due to the small atom change for the short irradiation time, 10^{-5} - 10^{-11} %. Count rates in LAMS are proportional to the number of atoms present therefore ratios of count rates and ratios of numbers of atoms are comparable. Ratios were determined for elements with similar masses to minimize the time delay between ablation and detection of each element. In general, atoms with similar masses are also going to experience similar space charge effects, positive ion repulsion, in the mass spectrometer. The difference in these effects will be minimized by looking at ratios of atoms with similar masses.

Although a few similarities exist, most of the bulk atom ratios and the count rate ratios from LAMS, differ significantly. At this time we are not able to speculate about the details of this observation, but it appears as though the soil which contains fissile nuclides is not representative of the bulk soil material. The

correlation plots in Figure 4.6 provide additional information. For all of the ratios seen in Figure 4.5 the correlation coefficients between the count rates for the LAMS data are greater than 0.6. This indicates that the metals are occurring together in the waste material. At the higher count rates the soil has a more uniform composition from the high waste influence. In soil which has not been as heavily influenced by waste, lower count rates and more scatter is observed. Correlation coefficients for Ni/Cu, Rb/Pb and Pb/Cs would not be expected to be high in natural soils. This has been observed in California benchmark soils with correlation coefficients for these ratios of 0.46, 0.57 and 0.57[39]. The high correlation coefficients observed in this work are in part influenced by the method that was used to gather the data. For the LAMS, one mass was used to gather information about an element; in this case that element is not the only contributor to the mass. For example, mass 60 was used to look for Ni while mass 63 was used for Cu. Not only were Ni and Cu used in the waste packing material in the SDA (stainless steel drums), but ^{60}Co and ^{63}Ni were present in the waste.[40] At mass 60 there are contributions from natural Ni present in the soil, Ni from the waste and ^{60}Co, also in the waste. Isobars are not discernible by this MS instrument. Relevant isobaric interference for Cu at mass 63 is ^{63}Ni, for Rb at mass 85 are ^{85}Kr and ^{85}Sr, and ^{133}U and ^{133}Ba are interferences for Cs at mass 133.

Conclusions

The primary objective of this work was to develop a sample preparation method, which is compatible for both FTA and LAMS. The main conditions for successful sample preparation include obtaining a sample in which the soil of interest is imbedded in a flat and polished epoxy resin with the surfaces of the particles exposed and a technique to locate particles after irradiation. The B_4C chips embedded in the epoxy leave an impression in the detector in the form of decreased radiation damage and therefore less etching at that location. Exploiting this detector response allows the B_4C chips to be used as coordinate markers. Fission tracks can then be assigned coordinates with respect to the B_4C image and the particles that created the image can then be located from the corresponding B_4C chips.

Our work preliminarily shows that LAMS can provide information about soil samples. The fissile isotope that created the fission tracks can be identified with this system. The form of the fissile nuclide, oxide or interaction with soil, can also be inferred. Initially it appears that FTA combined with LAMS provides an opportunity to learn more about the soil contamination. High correlation coefficients were observed at masses for metals that were present in the SDA. More work must be done to explore this idea. It is also important to investigate whether the differences observed between the bulk atom ratios and the LAMS count ratios is due to instrumental differences or real differences in the located particles. In our future work, we plan to exploit these two techniques to learn more about the preferred sorption of ^{235}U and ^{239}Pu in contaminated soils.

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Figure 4.1
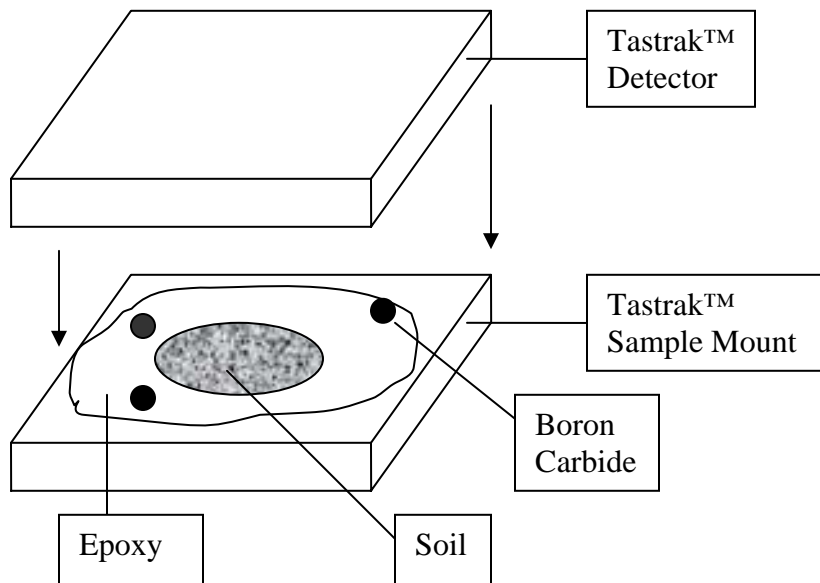
FIGURE 4.1. Sandwich assembly for FTA of a soil sample.

Figure 4.2
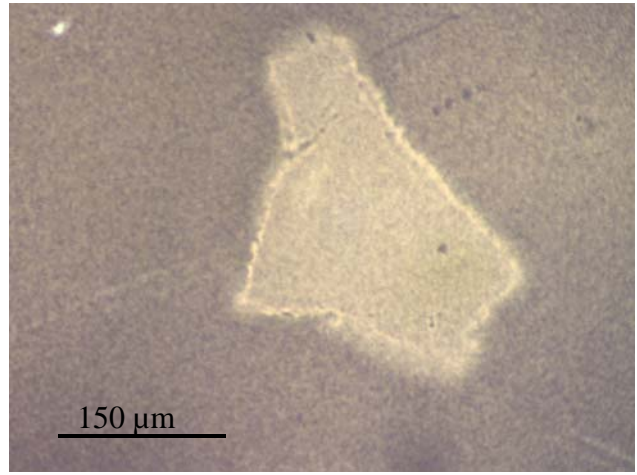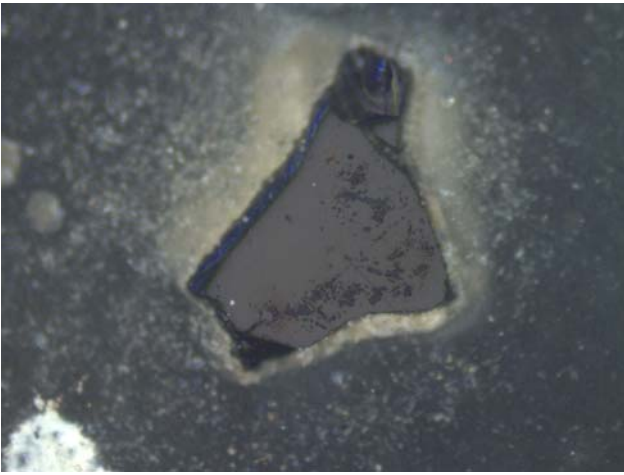
FIGURE 4.2
a. Image of a boron carbide chip that is mounted into the epoxy resin.
b. Image of the deficient etching produced in the Tastrak™ slide by a boron carbide chip as a result of irradiation.

Figure 4.3
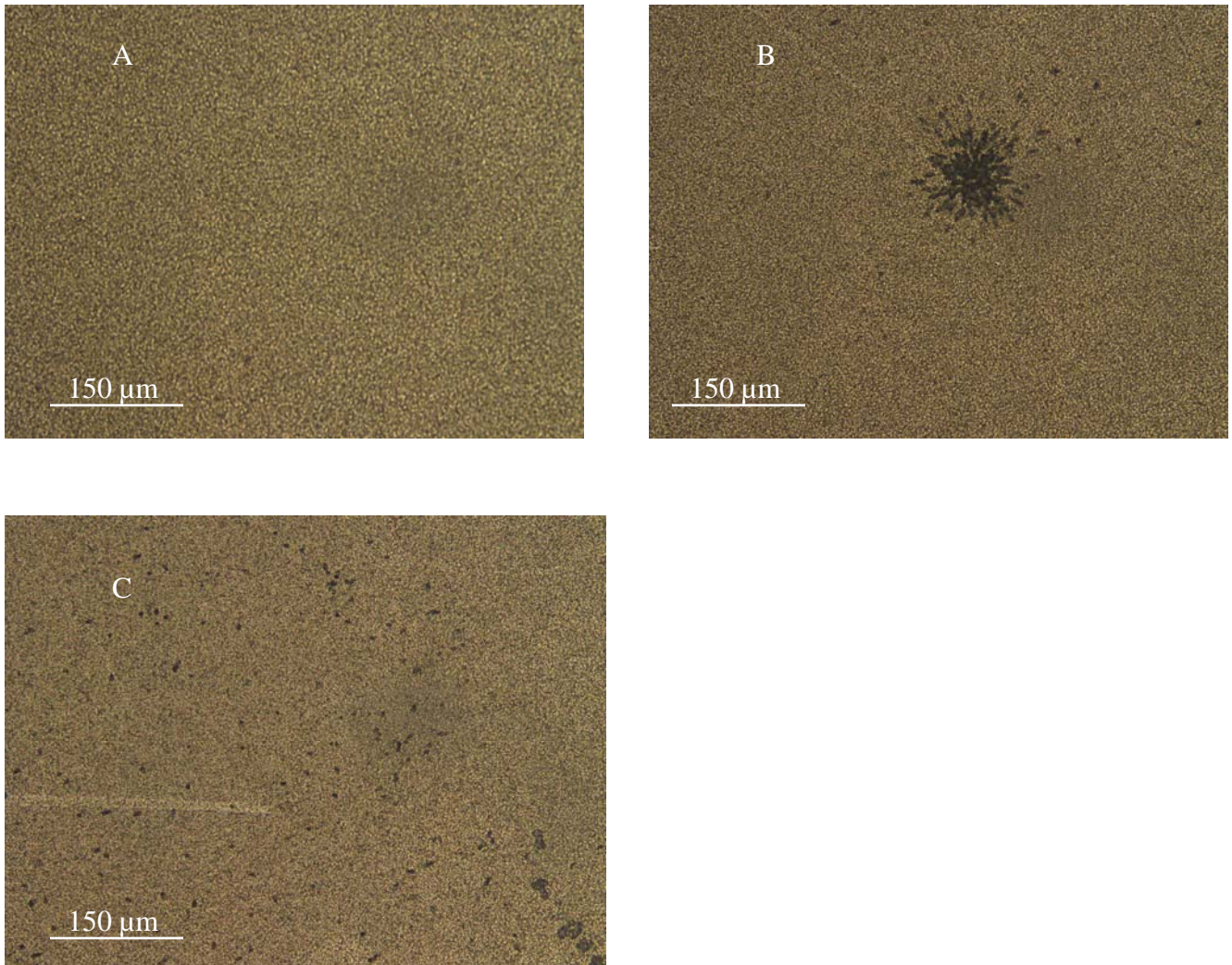
FIGURE 4.3
a. Typical background of an etched detector with no tracks
b. Typical starburst pattern associated with a preferential sorption on a soil
c. Typical homogenous distribution of tracks from a soil

Figure 4.4
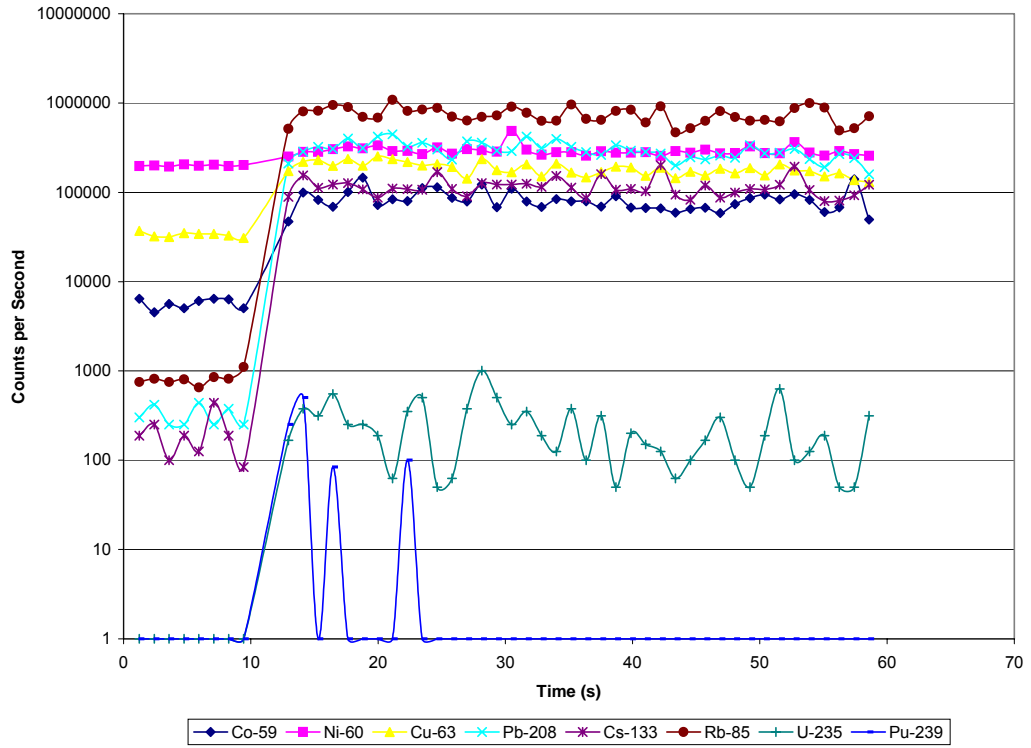
FIGURE 4.4. LAMS analysis of a contaminated soil. First 10 seconds represent
the background counts at each mass.

Figure 4.5
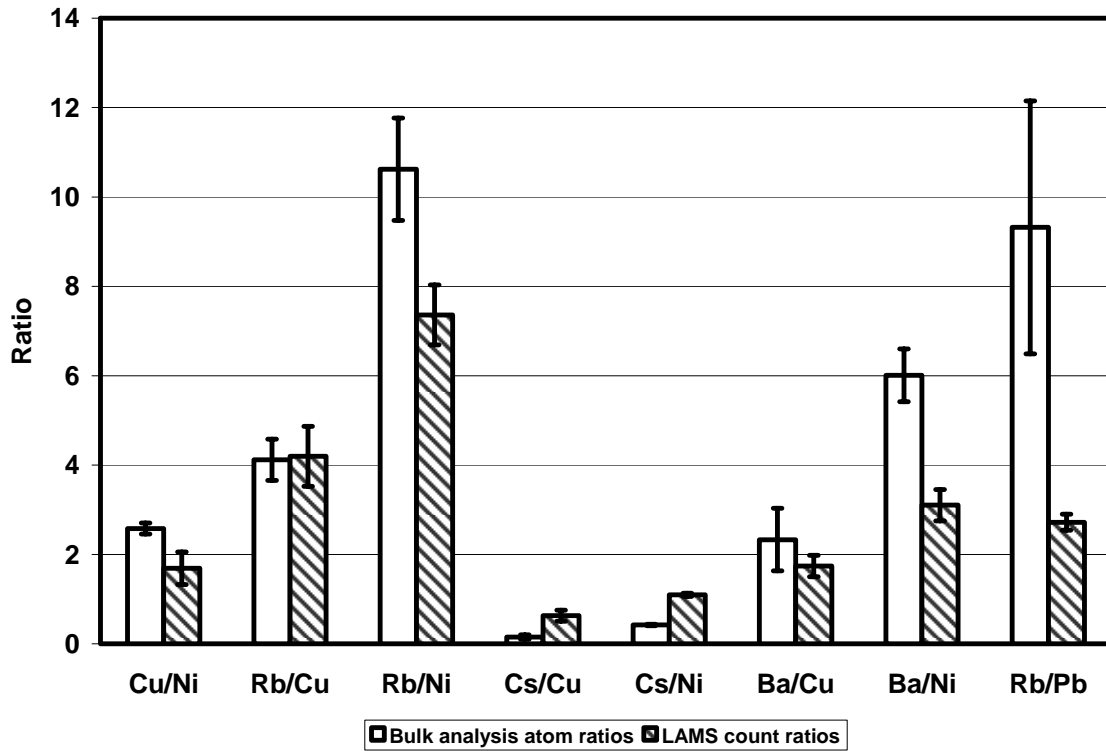
FIGURE 4.5. Comparison of bulk elemental ratios to LAMS elemental ratios on spots previously located by FTA.

Figure 4.6a
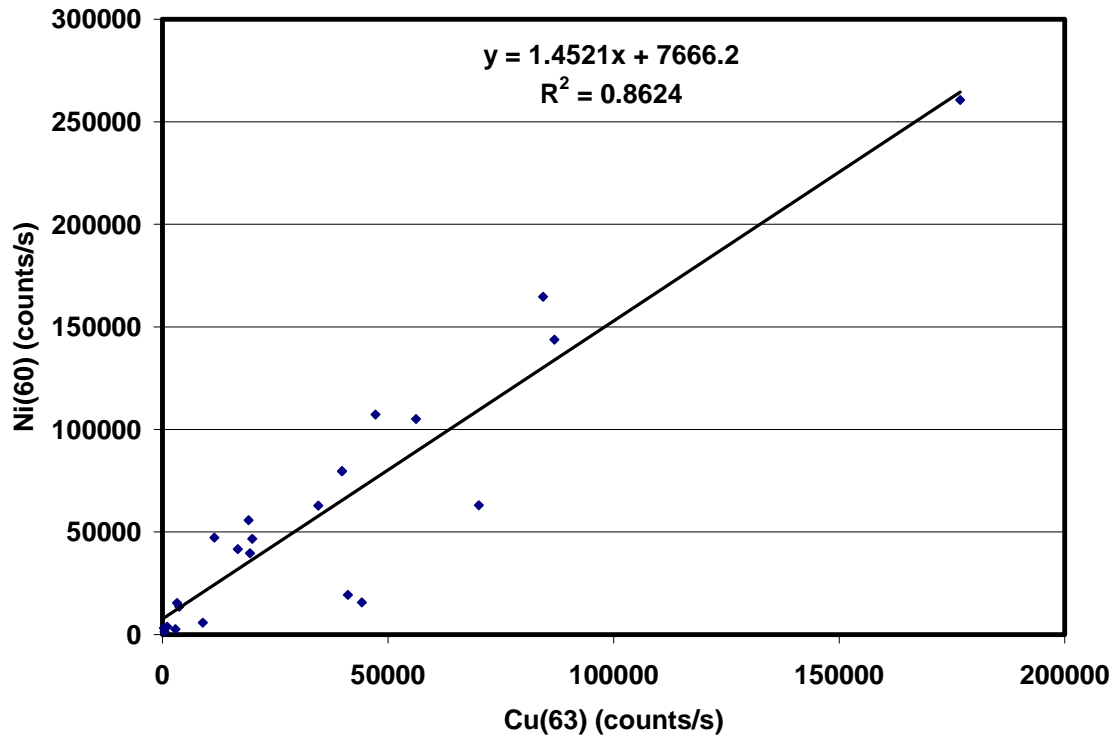
FIGURE 4.6a. LAMS correlation count data from several soil spots located by FTA for masses 60 and 63.

Figure 4.6b
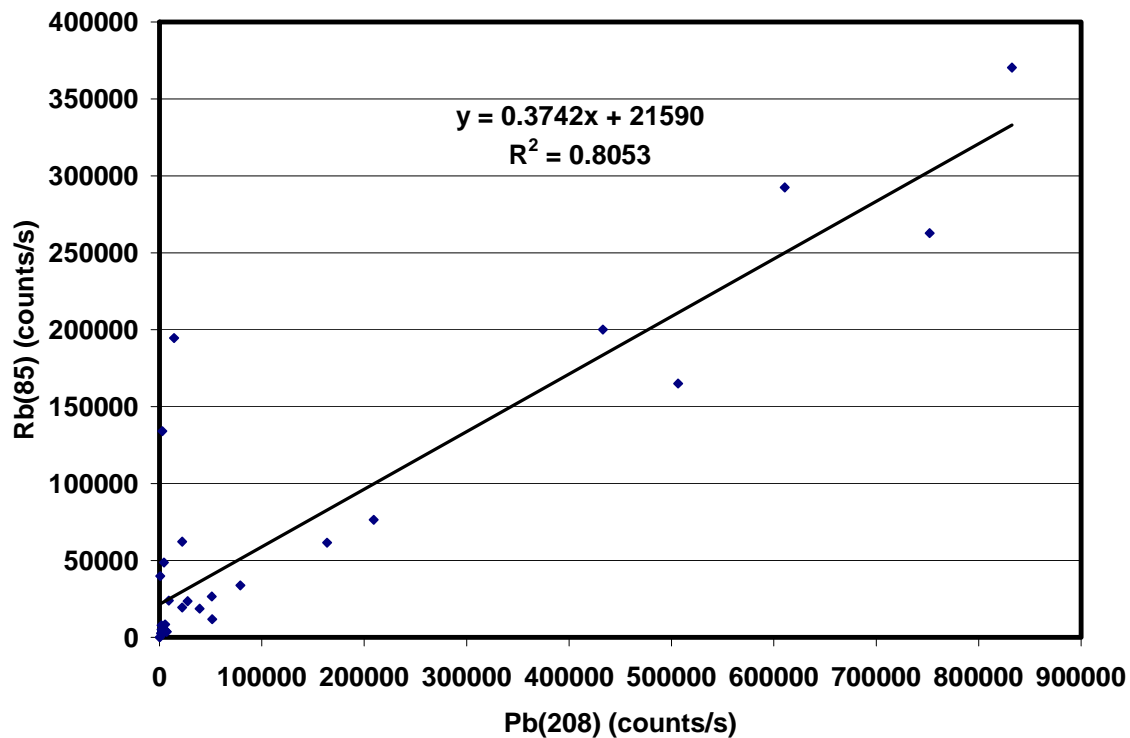
FIGURE 4.6b. LAMS correlation count data from several soil spots located by FTA for masses 85 and 208.

Figure 4.6c
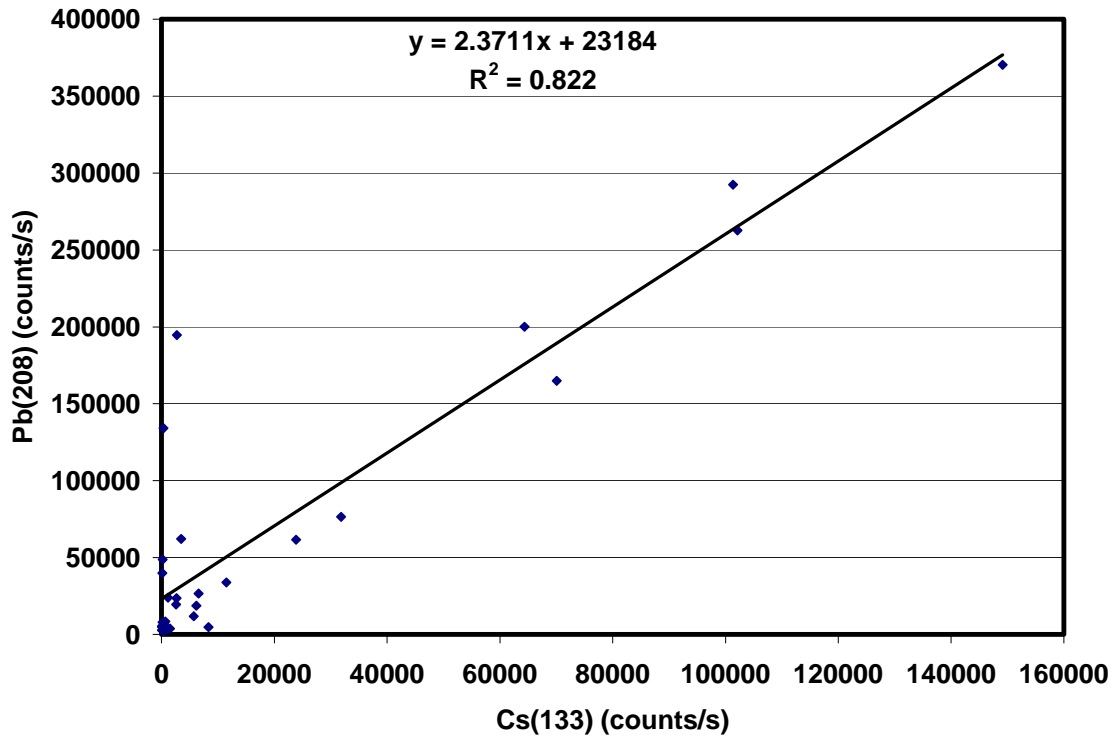
FIGURE 4.6c. LAMS correlation count data from several soil spots located by FTA for masses 208 and 133.

CHAPTER FIVE

CONCLUSIONS

Throughout the nuclear era, contamination of soils with radioactive materials has occurred through several pathways. An understanding of the behavior of the contamination in the environment is essential to assessing health and environmental risk. This behavior is influenced by the nature of the contamination and the specific interactions with the soil. An understanding of the physical and chemical properties of the contamination can provide insight into possible remediation strategies. If the mobility of the contaminant is limited, monitored natural attenuation may be a reasonable remediation approach (Newell and Wilson, 1999). This will require detailed knowledge of the activity present and the expected rate of decay. Other remediation approaches such as in-situ or ex-situ chemical treatment or ex-situ mechanical treatment require a prior knowledge of the chemical characteristics (ANL 1993; INEEL 2003; Khan and Husain, 2001) . In the case of the transuranic elements, identifying the process which created them lends insight into the chemical and physical form, providing a first step to understanding their behavior in the environment.

The overall objective of this work was to gain a better understanding of the radiological contamination in historic soils collected from INL by determining the source of the contamination. This required the development of radioanalytical methods to quantify certain isotopes that tend to be difficult to measure. Two locations were examined and two depths at each location, 0-4 cm and 4-8 cm.

The approach to accomplishing this goal was multifaceted. Insight into the contamination history was achieved through isotopic and activity ratios. Contaminant interactions with the soils were also investigated. The significant findings from this work are summarized below.

To better understand the source of the contamination present in the soils, it was first necessary to determine the bulk activities. A methodology to determine ^{241}Am, ^{238}Pu, $^{239+240}$Pu and ^{241}Pu activities was developed and described in Chapter 2. There were two major accomplishments in this work. The first was the sequential determination of these isotopes from a small (0.5 g) sample. Small samples tend to have larger variability in activity, demanding a more precise determination. This was done through the combination of several traditional radiochemical techniques, gamma spectrometry, anion exchange, alpha spectrometry and liquid scintillation counting. Limits of quantitation and detection were defined for each isotope. The second accomplishment was the determination of the ^{241}Pu beta activity. Activity of ^{241}Pu is rarely determined because of the inherent difficulty as described in Chapter 2, yet the knowledge of this activity provides very useful information for source term apportionment, and for estimating the impact of progeny contamination in the future. Accurate determination of the ^{241}Pu activity allows discrimination between the activity of ^{241}Am present at the time of sampling versus the activity present from the decay of ^{241}Pu. The methodologies and techniques used for these soils provided quantitative results in all cases except at the 4-8 cm depth of location 1 for ^{241}Am determination and the 4-8 cm depth at both locations for ^{241}Pu determination.

Results demonstrate that in general, activity levels for the isotopes determined herein are higher for the surficial (0-4 cm) depths than for the soils in the 4-8 cm depths. Furthermore, the activities for the soils below the surface are statistically equivalent, but have higher activities than expected based on local background. The surface soil at location 1 has a higher activity than the surface soil at location 2. Interestingly, the ^{241}Am activity is higher at location 2 than location 1 for both depths. From the ^{241}Pu activity, the activity of ^{241}Am present from ingrowth was calculated. It was found that greater than 20% of the ^{241}Am present at location 1 and less than 10% of the ^{241}Am present at location 2 was a product of ingrowth. This suggests an additional source of ^{241}Am in the soils contributed to the contamination. The Pu and the non-ingrowth ^{241}Am are from different waste streams.

To further investigate the possible sources of contamination we calculated Pu activity ratios, determined Pu isotope ratios, and ^{137}Cs activity. This work was described in Chapter 3. Determination of the Pu atom concentrations provided a mechanism to validate our analytical results described in Chapter 2. This was accomplished by calculating the activity from the atom concentration and comparing these results to the radiometric determination. Both methods, mass spectrometric and radiometric, provided statistically equivalent activities for ^{241}Pu and $^{239+240}$Pu. This provides evidence that the separations must have efficiently removed ^{241}Am from the Pu fraction, minimizing ^{241}Am contamination in the ^{241}Pu atom determination.

The source of the Pu was a combination of weapons grade and fallout Pu with the major contribution from WGP. The elevated ^{241}Am/$^{239+240}$Pu activity ratio corroborates our findings that ingrowth from ^{241}Pu is not the sole source of the ^{241}Am. The importance of determining the ^{241}Pu activity was exemplified in this work. If only the $^{239+240}$Pu and ^{241}Am activities were considered, WGP never would have been suspected as the source of the Pu.

The ^{137}Cs activity in the 4-8 cm depth samples was correlated to fallout while the 0-4 cm depth showed a slight enhancement in activity. This difference in activity profiles for the Pu and ^{241}Am compared to the ^{137}Cs suggests that the contamination mechanisms are different, elucidating that onsite operations at INL contributed to ^{137}Cs soil contamination.

The soil particles contaminated with fissile isotopes were located using fission track analysis by the development of a B_4C locating system to be used with fission track analysis as described in Chapter 4. These locations were then interrogated using laser ablation mass spectrometry. Ratios of metal concentrations in the bulk soil differ significantly from the count ratios of those same metals as determined by LAMS. High correlation coefficients were observed between metals that would not normally be correlated in natural systems. These metals have been documented as being present in waste buried at the subsurface disposal area. This infers that the soils were influenced by contamination released from the disposal pits at the SDA and other nuclear activities at the INL site. Additional correlation plots are given in Appendix A

along with the corresponding linear best fit. Appendix B is a compilation of the same correlation plots with the best fit line forced trough the origin.

Suggestions for further study

Because only four samples were analyzed in this study, it is not possible to make any inferences about potential transfer coefficients for ^{241}Am and Pu isotopes in the soil. It is probable that the Am and Pu were not in the same chemical and/or physical form in the materials disposed of in Pit 9 compared to other materials disposed of at the SDA and other releases of Am and Pu to the environment at the INL.   Therefore, we cannot describe the complex migration processes that led to the contamination of the soils.

To further examine the possible migration processes for ^{241}Am and Pu, it would be necessary to determine atom and activity ratios at many more sampling locations. Because the ranges of activities for these isotopes will increase significantly when more sampling locations are considered, the techniques and methods used in this work may not be applicable. The determination limits for the analysis of ^{241}Am and ^{241}Pu for the 0.5 g sample size used herein are relatively high. Lower activities of these isotopes are expected at more distant sampling locations, as reported by Markham et al. (Markham et al., 1978); therefore, quantitation of these isotopes would not be able to be quantified. Alternatively, the ^{241}Am could be determined using alpha spectrometry, which is a more sensitive approach than gamma spectrometry. Further modifications to the anion exchange procedure would also be required. The LSC determination

limits could be lowered by investing in more extensive shielding of the instrument, the use of specialized scintillation cocktail, longer count times and larger sample sizes.

To gain a better understanding of the origin of the contamination observed in the soils, it would be helpful to determine several additional atom ratios. The $^{237}Np/^{239}Pu$ atom ratio would provide additional insight into the contribution from the ICPP and the Nevada Test Site (NTS). Contamination contribution from the ICPP would be characterized by $^{237}Np/^{239}Pu$ atom ratios that are elevated (>> 10) relative to expected global fallout (0.45) in the northern hemisphere, while Nevada Test Site contributions would be lower (0.03) than expected fallout (EML 1998). The ICPP contribution could be further confirmed by looking at the $^{238}Pu/^{239}Pu$ atom ratio. Airborne emissions from the ICPP are assumed to be elevated in ^{238}Pu (EML 1998). These ratios could be determined by mass spectrometry with efficient sample preparation and chemical separations to produce chemically clean fractions for analysis. Not only should anion exchange techniques be considered, but a standardized Np tracer would also be necessary. Decontamination factors must be investigated to obtain ^{238}Pu atom concentrations. Even small amounts of ^{238}U that bleed through the anion exchange column and any ^{238}U contamination present in HNO_3 will result in overestimation of ^{238}Pu by mass spectrometry if the contamination is not well characterized and consistent. Such information on atom ratios for more locations would facilitate development of mixing lines to elucidate source apportionment as

shown by Ketterer et al. and Cooper et al. (Ketterer et al., 2004; Cooper et al., 2000).

It would also be informative and interesting to investigate U isotope ratios in the soils. The varied operations and events that contributed to the contamination in the soils have unique U signatures. Specifically, ^{236}U would serve as an indicator of irradiated ^{235}U, as ^{236}U does not occur naturally (Ketterer et al., 2003). In the soils used for this work, the atom concentrations of ^{236}U are thought to be on the order of 10^8 atoms/g of soil. This leads to the supposition that highly sophisticated mass spectrometric techniques should be employed, such as accelerator mass spectrometry, although other mass spectrometric techniques would work well when higher levels of ^{236}U are present.

In this work, the utility of FTA followed by LAMS was shown. Additional investigation is necessary to make this approach more reasonable for routine application and the interpretation of the results more reliable. Soil aggregates which do not contain fissile material from a contamination source should be interrogated using LAMS. This would provide a first step towards understanding whether the high correlation coefficients observed between many masses are a product of the contamination or the soil. The understanding of the interplay between fissile nuclides and soil components could be further investigated by completing a size fractionation on the contaminated soil and individually analyzing the samples with FTA followed by LAMS. This could validate the high mass correlations are related to the type of minerals present in the size fractions.

To better understand the information that FTA and LAMS could provide, it would also be informative to use 'background' soil from INL and to add fissile contamination (^{235}U or ^{239}Pu). This should be done on the total soil as well as different size fractions of the soil. Hopefully all of these steps would help to elucidate the interaction between the soil and fissile nuclides. Once this information is obtained on these particular INL soils, it would be helpful to make this technique applicable to other soils. Analysis of well characterized soils and minerals, with and without ^{235}U or ^{239}Pu should be completed to see if any trends can be determined. It will be important to verify whether the information obtained on the INL soils is unique to the soil or transferable to other soils.

Sequential extractions to elucidate the mineralogical associations of Pu and Am would provide a detailed comparison of these contaminants. This data would supply information on the assumption that Pu and Am were introduced in different chemical and physical forms. A comparison of the ^{241}Pu and ^{241}Am profiles would assist in determining if the ^{241}Am from the decay of ^{241}Pu behaves differently in the environment than ^{241}Am released from the buried waste.

Summary

The significant conclusions and contributions of this work are as follows:
Chapter 2

- Sequential determination of ^{241}Am, ^{238}Pu, $^{239+240}$Pu and ^{241}Pu activities with limited sample quantity

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- Determination of limits of detection and quantitation for each technique and isotope

- Provided evidence for multiple sources of ^{241}Am

Chapter 3

- Determined ^{239}Pu, ^{240}Pu and ^{241}Pu atom concentrations

- Provided further evidence of the analytical quality of the radiometric results

- The Pu contamination is from a weapons grade Pu source

- Determined ^{137}Cs activity is elevated above fallout in the surficial soils

Chapter 4

- Developed a FTA method compatible with incorporating a B_4C locating system

- Ability to locate soil particles responsible for track formation

- Identified the fissile isotope responsible for track formation using LAMS

- Provided LAMS data showing that the soil had been influenced by a contamination event

This information can be used to infer chemical and physical properties of the Pu and Am contaminants. The insight provided can assist in the development of remediation strategies. Comparison with newly collected samples from the same location would assist with the development of risk assessments.

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APPENDIX A

SOIL CHARACTERISTICS AND CORRELATION PLOTS FROM LAMS

Soil Characteristics	
pH	7.21 ± 0.05
Water Content	1.5 ± 0.03 %
Dry Bulk Density	1.42 ± 0.01 g/cm^3
Wet Bulk Density	1.77 ± 0.008 g/cm^3
Porosity	35.1 ± 2.1 %
Surface Area	3.78 ± 0.09 m^2/g
EC	1.25 ± 0.03 mmoh/cm
CEC	21.43 ± 2.19 mol$_c$/kg
Total Dissolved Solids	800 mg/L
Total Anions/Cations	12.5 mmol/L
OC	1.63 ± 0.76 %
OM	2.77 ± 1.25 %
C	0.95 %
N	0.12 ± 0.03 %
S	< 0.02 %

Soil Characteristics of bulk background soil collected at INL in 1972.

	ave (µg/g)	std	%rsd
Ca	18697.40	1009.92	5.40
Fe	39735.58	2459.56	6.19
V	75.91	8.75	11.52
Cr	120.91	9.41	7.79
Co	70.98	8.33	11.74
Ni	20.05	1.97	9.82
Cu	21.22	2.18	10.28
Rb	112.77	5.10	4.52
Sr	286.77	10.78	3.76
Cs	4.93	0.11	2.18
Ba	1120.84	6.68	0.60
Ce	91.06	4.01	4.40
Nd	43.36	2.22	5.12
Gd	6.05	0.33	5.42
Pb	19.68	2.79	14.20
U	4.09	0.38	9.27

Average elemental concentrations in bulk background soil collected from INL in 1972.
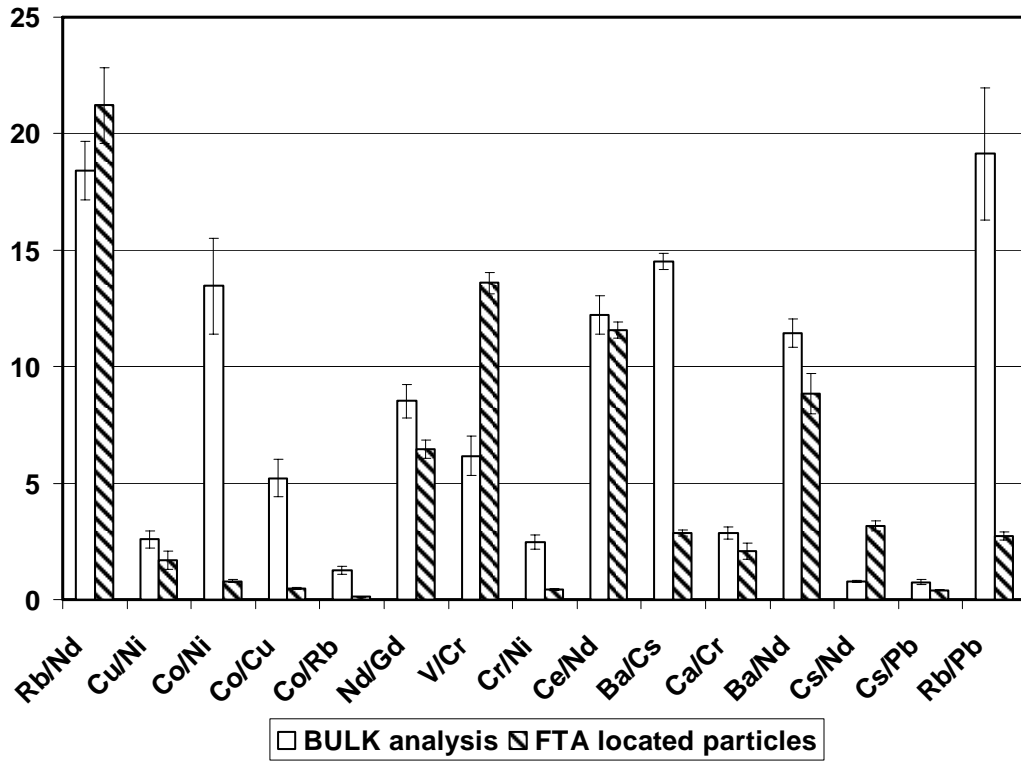
Comparison of bulk analysis atom ratios and count ratios from FTA located soil
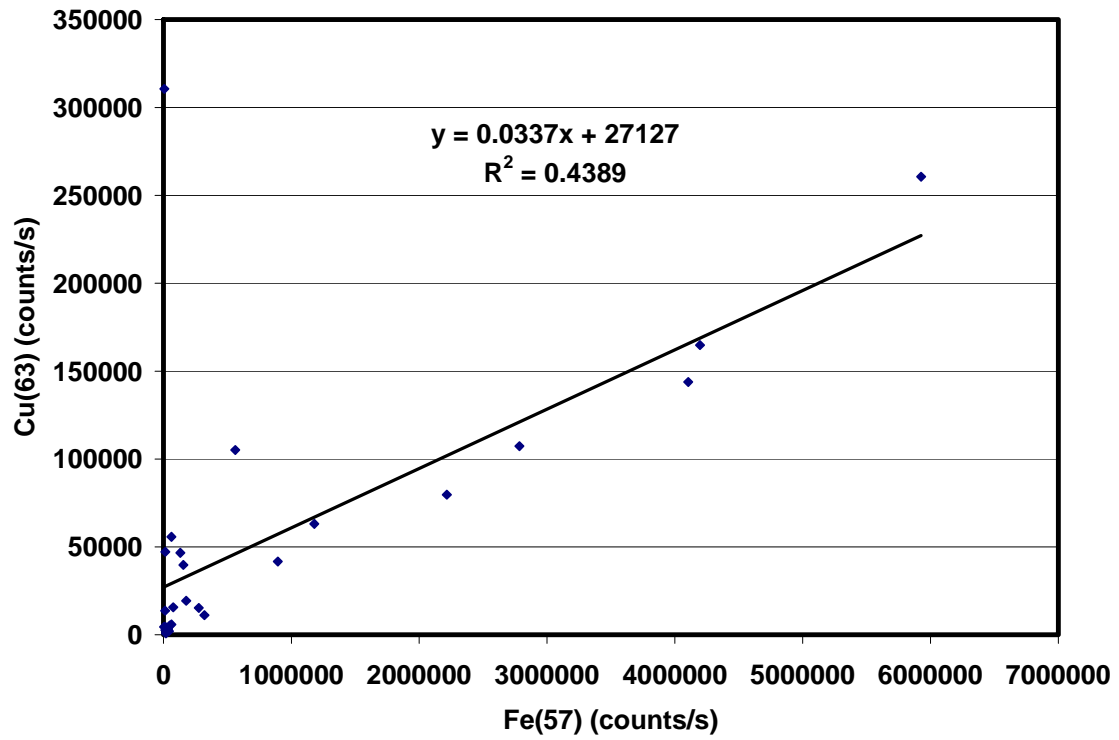
Correlation plot for Cu and Fe. Relevant mass interferences ^{63}Ni and ^{57}Co.
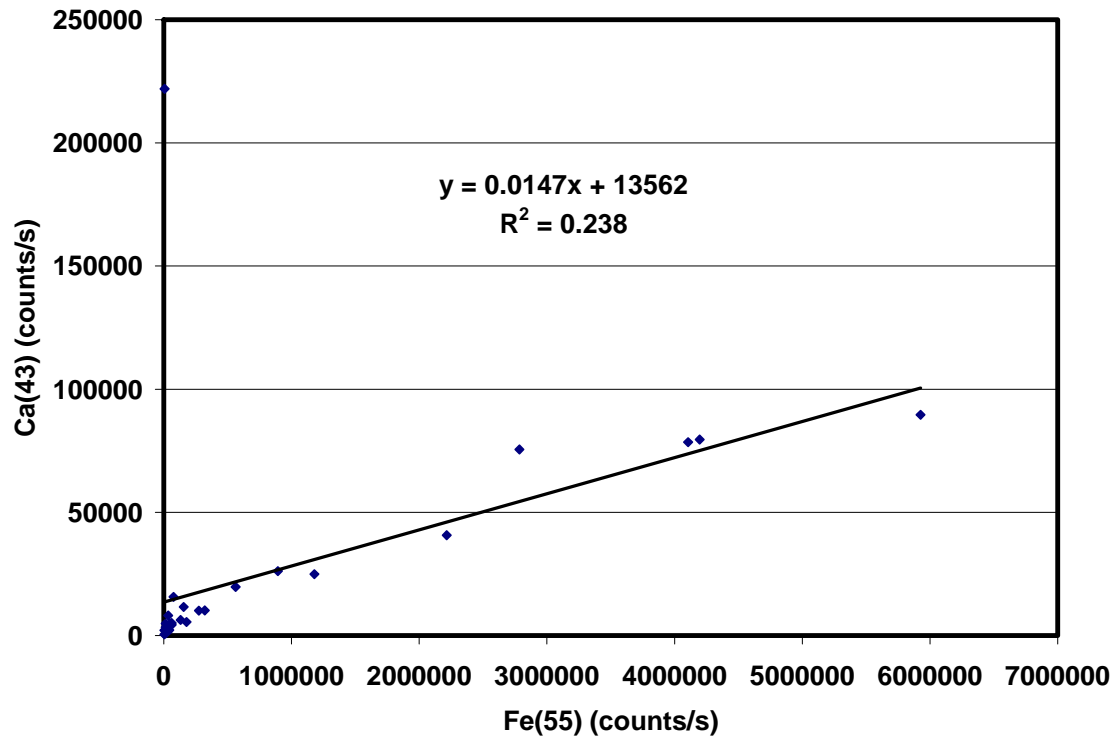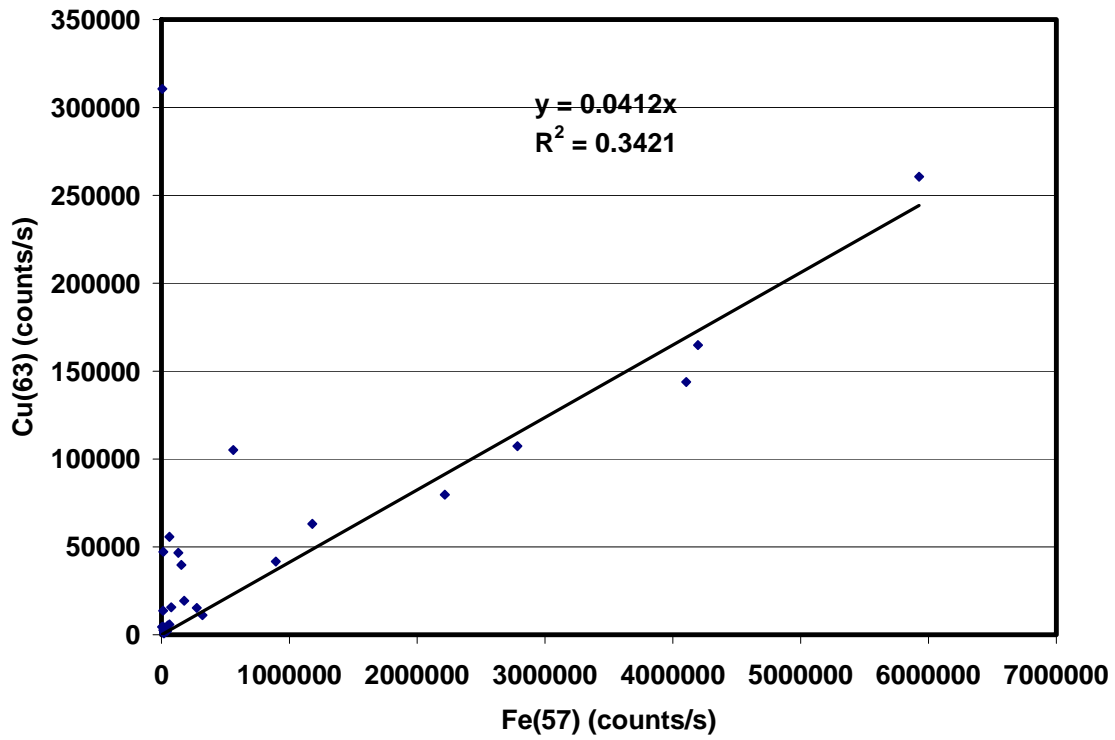
Correlation plot for Ca and Fe. Relevant mass interferences [57]Co.
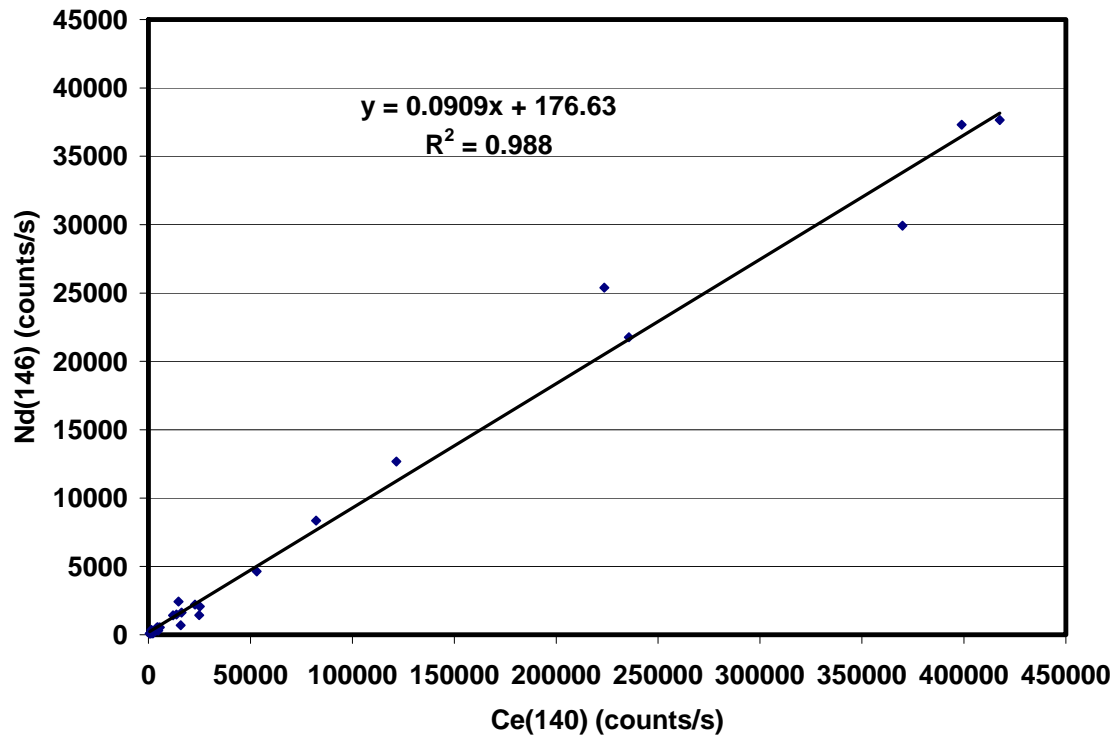
Correlation plot for Nd and Ce. Relevant mass interferences ^{140}La and ^{140}Ba.
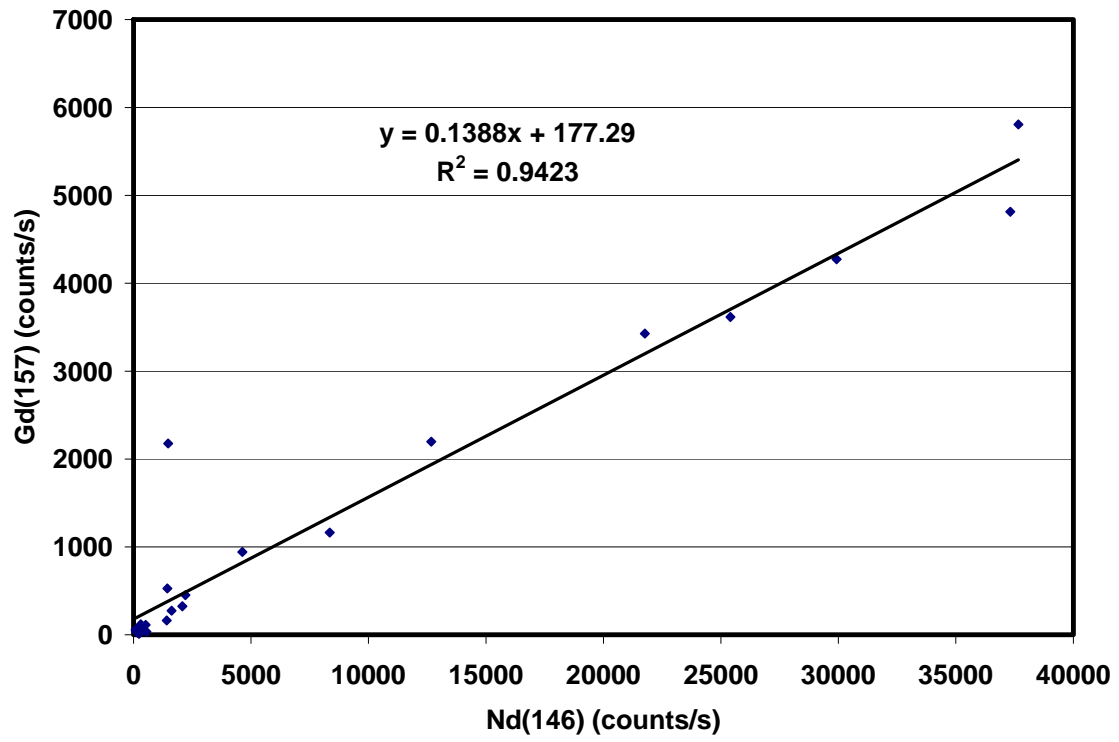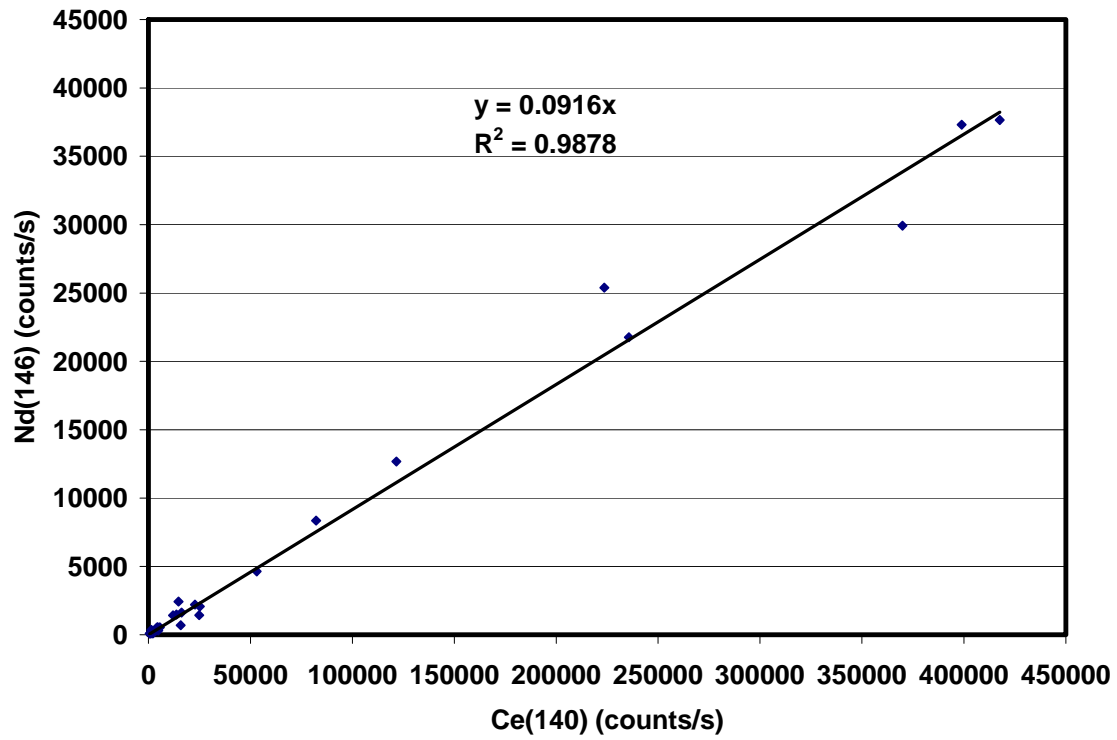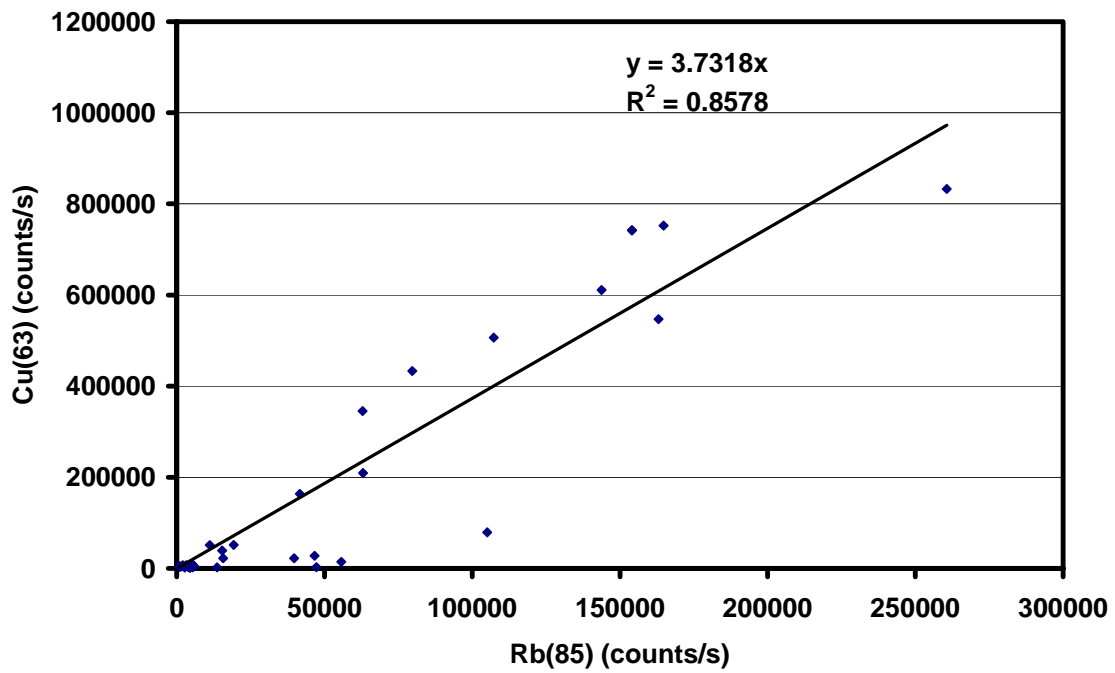
Correlation plot for Gd and Nd.
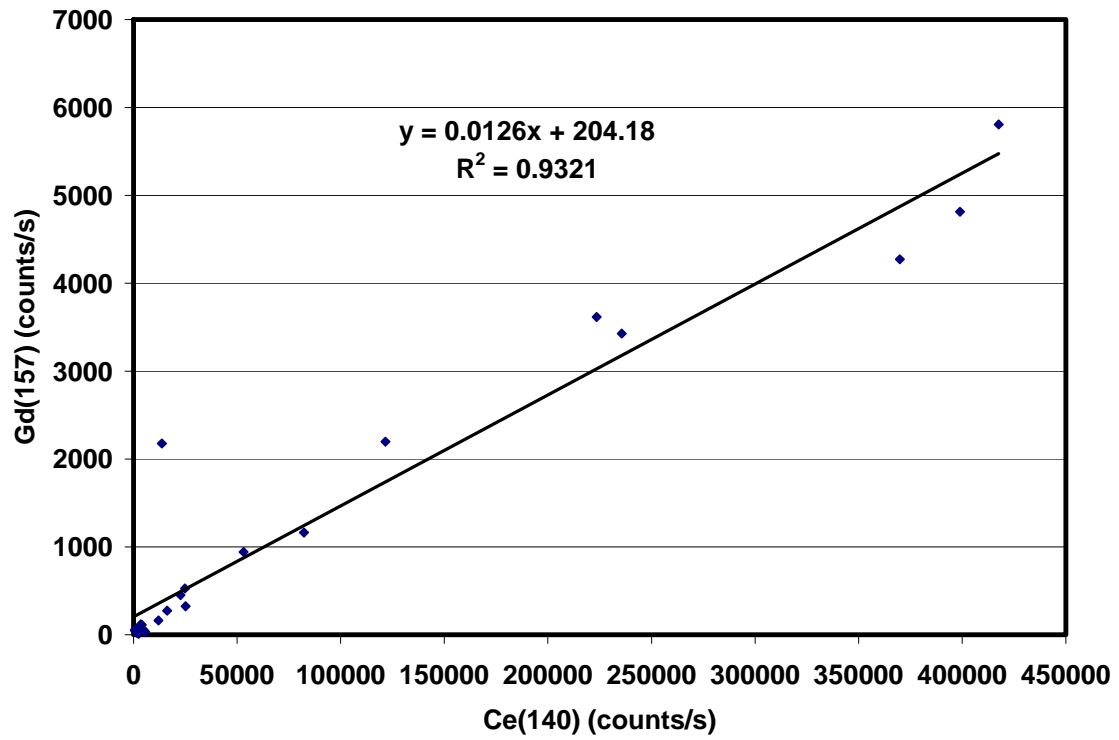
Correlation plot for Gd and Ce. Relevant mass interferences [140]La and [140]Ba.
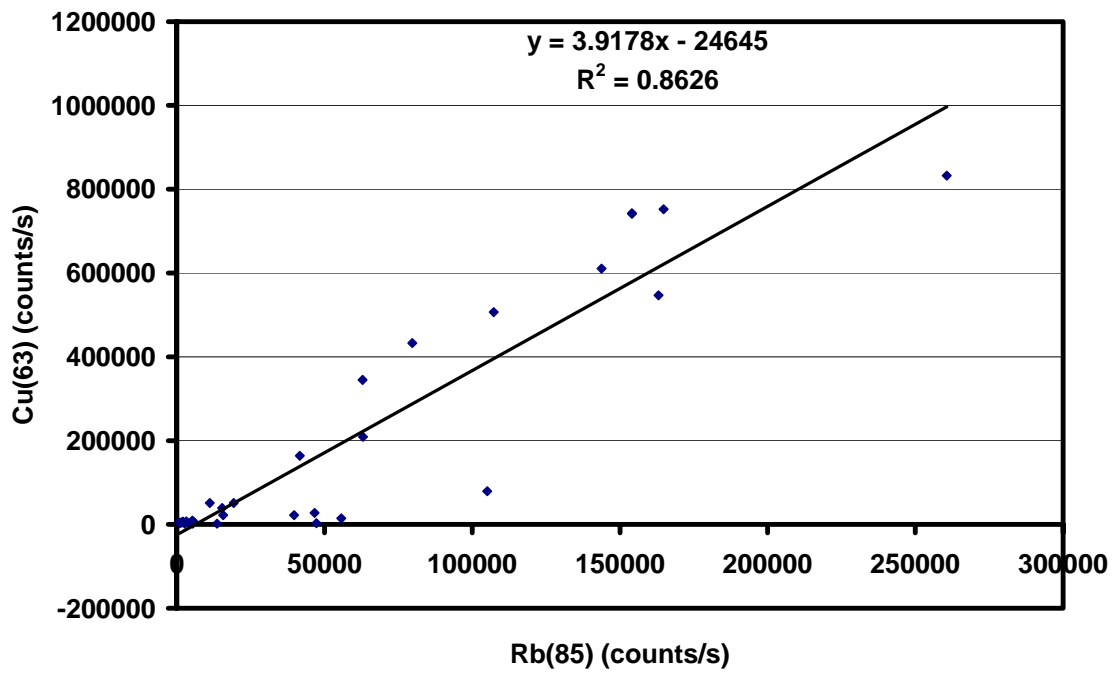
Correlation plot for Cu and Rb. Relevant mass interferences ^{63}Ni, ^{85}Kr and ^{85}Sr.
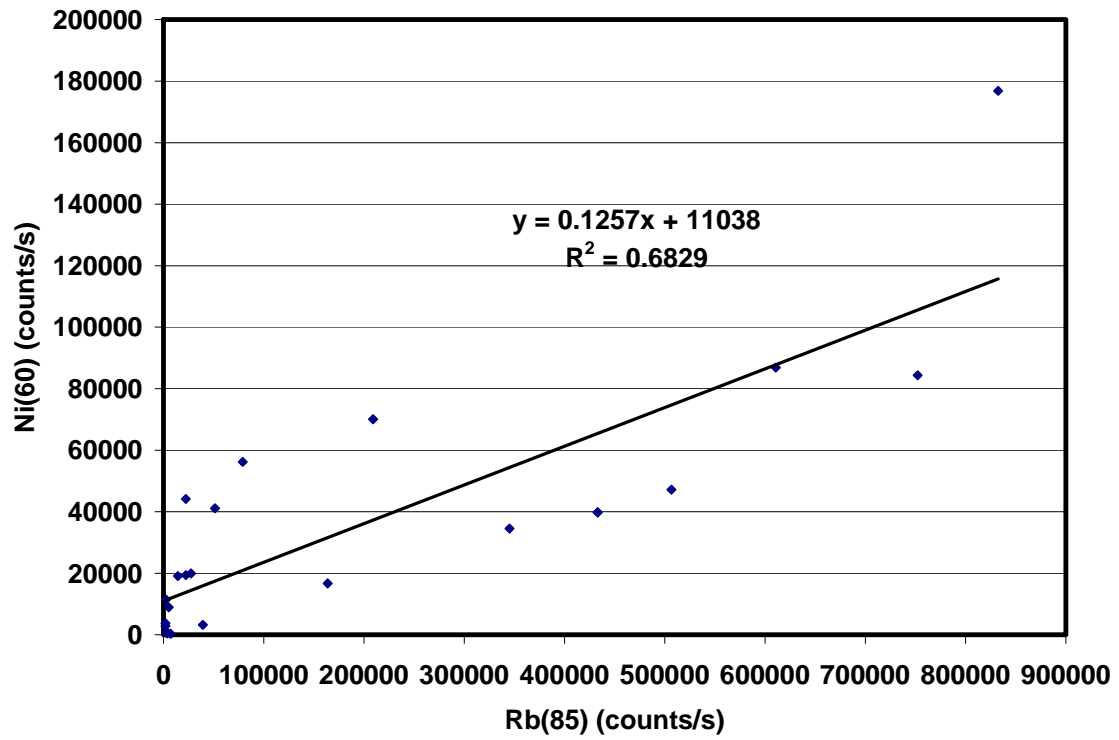
Correlation plot for Ni and Rb. Relevant mass interferences ^{60}Co, ^{85}Kr and ^{85}Sr.
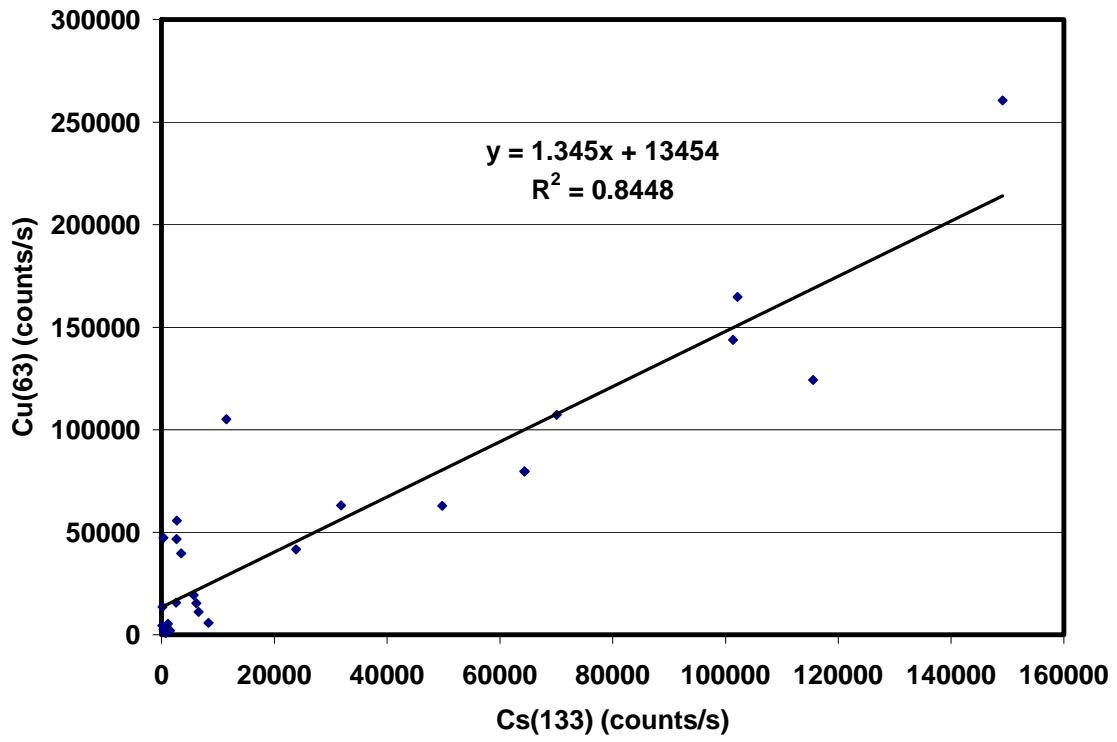
Correlation plot for Cu and Cs. Relevant mass interferences [63]Ni, [133]U and [133]Ba.
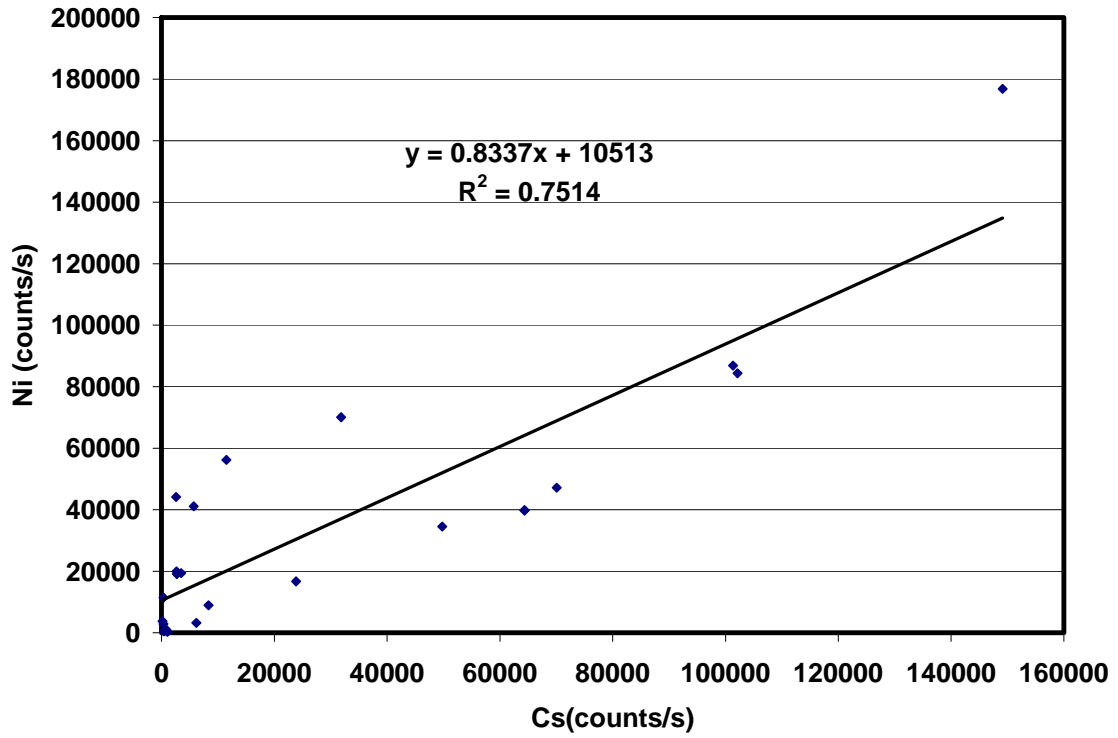
Correlation plot for Ni and Cs. Relevant mass interferences ^{60}Co, ^{133}U and ^{133}Ba.

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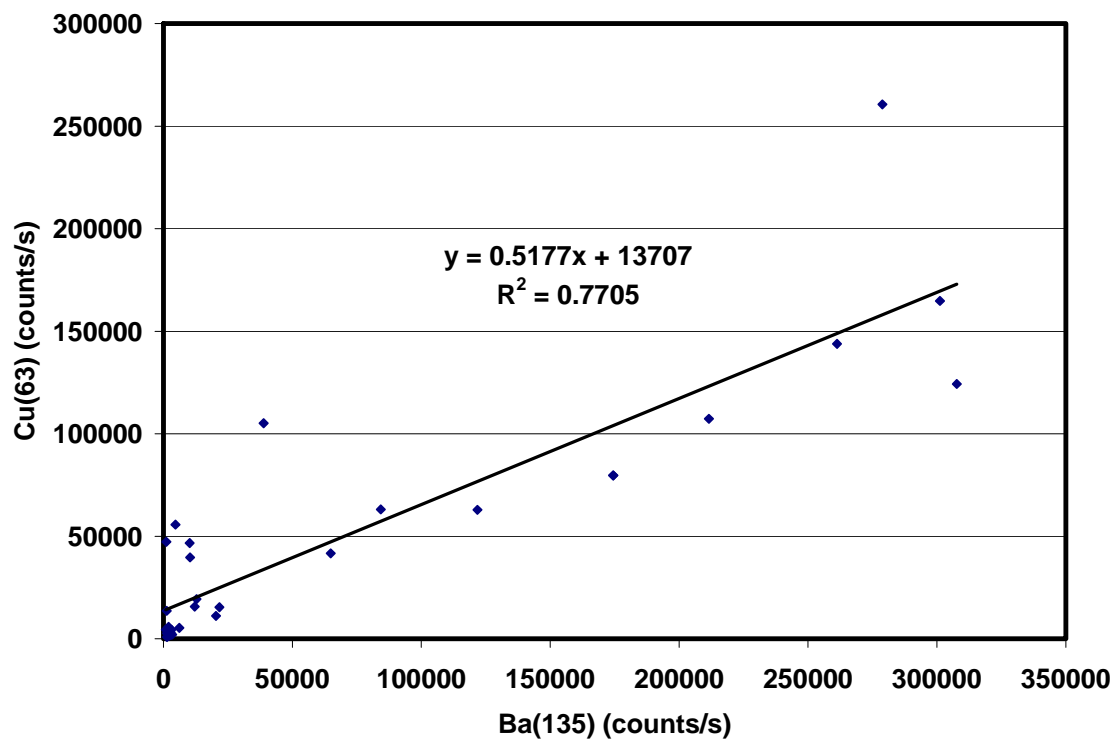
Correlation plot for Cu and Ba. Relevant mass interferences ^{63}Ni.

The chart shows a correlation plot with:
- y-axis: Ni (counts/s), ranging from 0 to 200000
- x-axis: Ba (counts/s), ranging from 0 to 350000
- equation: y = 0.3105x + 11768
- $R^2 = 0.6167$
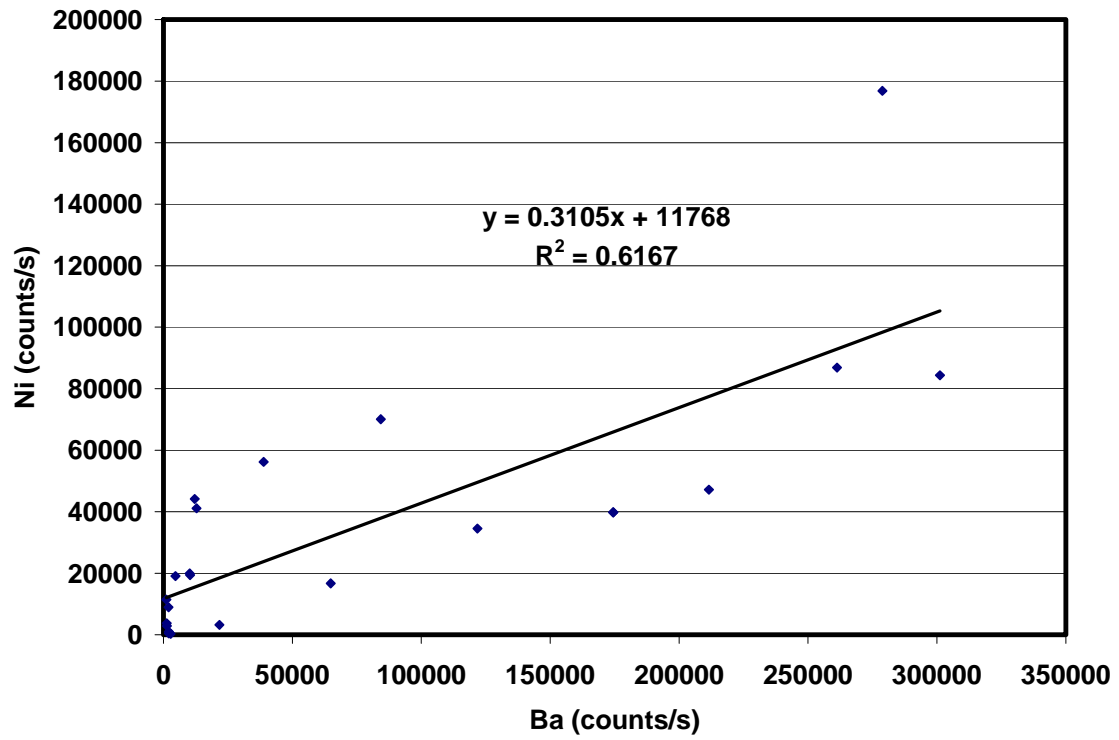
Correlation plot for Ni and Ba. Relevant mass interferences [60]Co.

APPENDIX B

CORRELATION PLOTS FROM LAMS FORCED THROUGH ORIGIN

Correlation plot for Cu and Fe forced through (0,0). Relevant mass interferences ^{63}Ni and ^{57}Co.
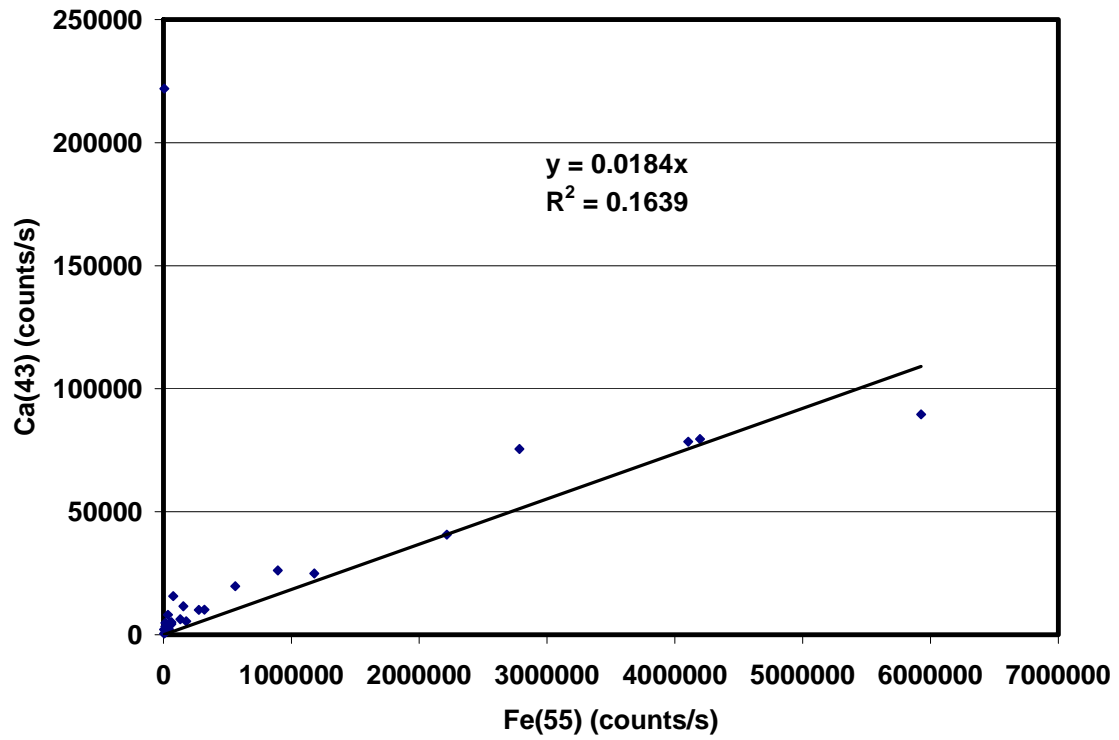
Correlation plot for Ca and Fe forced through (0,0). Relevant mass interferences ^{57}Co.

$y = 0.0916x$

$R^2 = 0.9878$

Correlation plot for Nd and Ce forced through (0,0). Relevant mass interferences ^{140}La and ^{140}Ba.
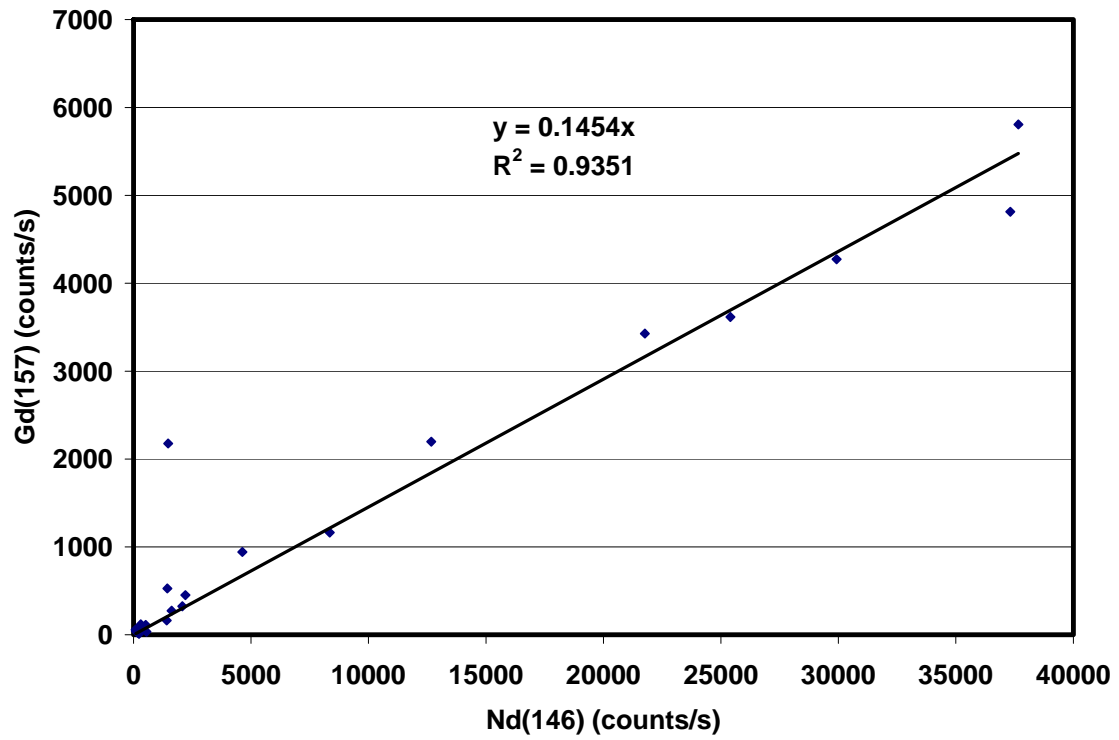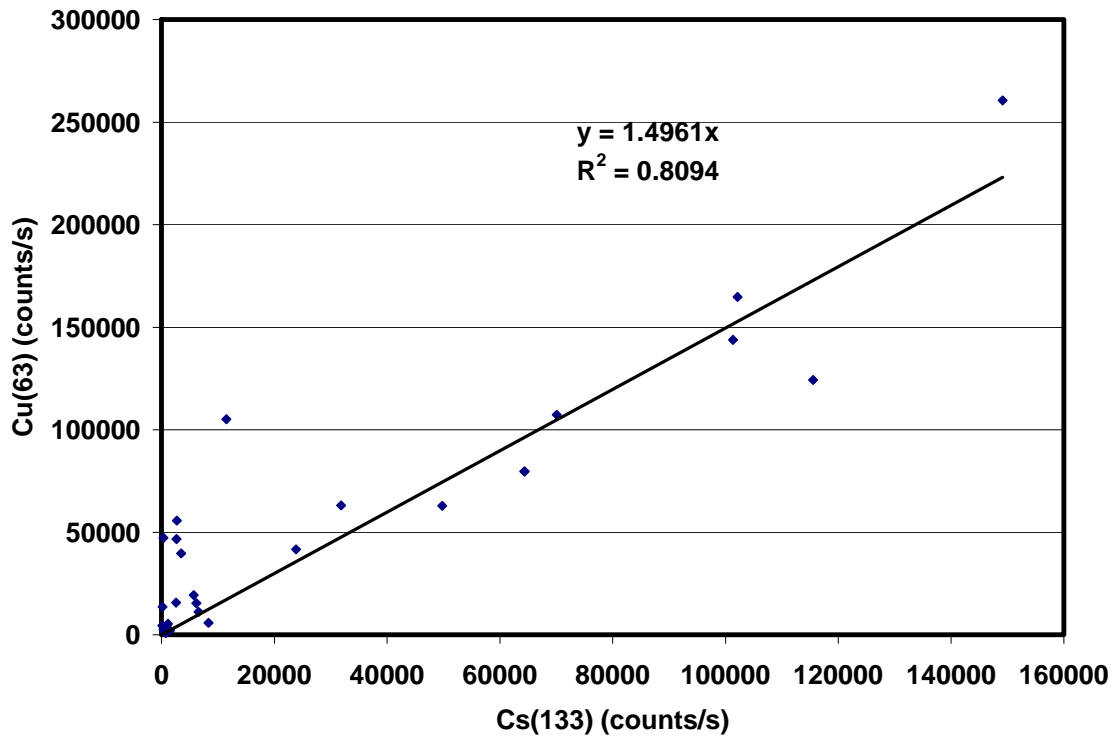
Correlation plot for Gd and Nd forced through (0,0).
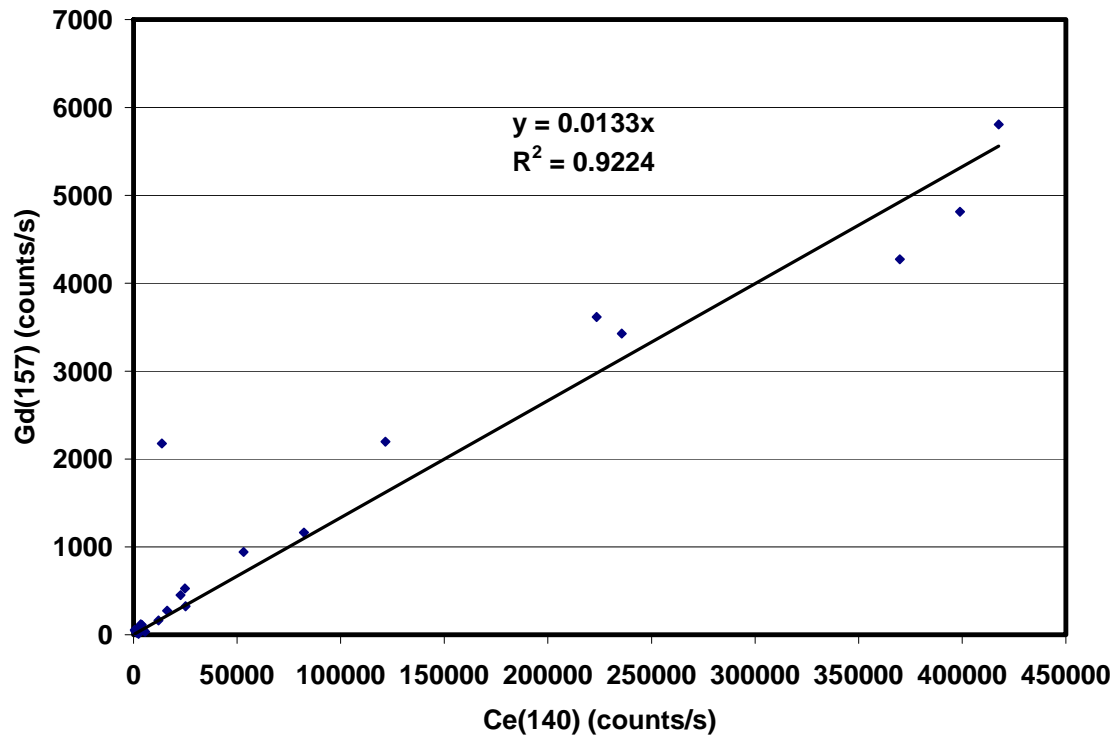
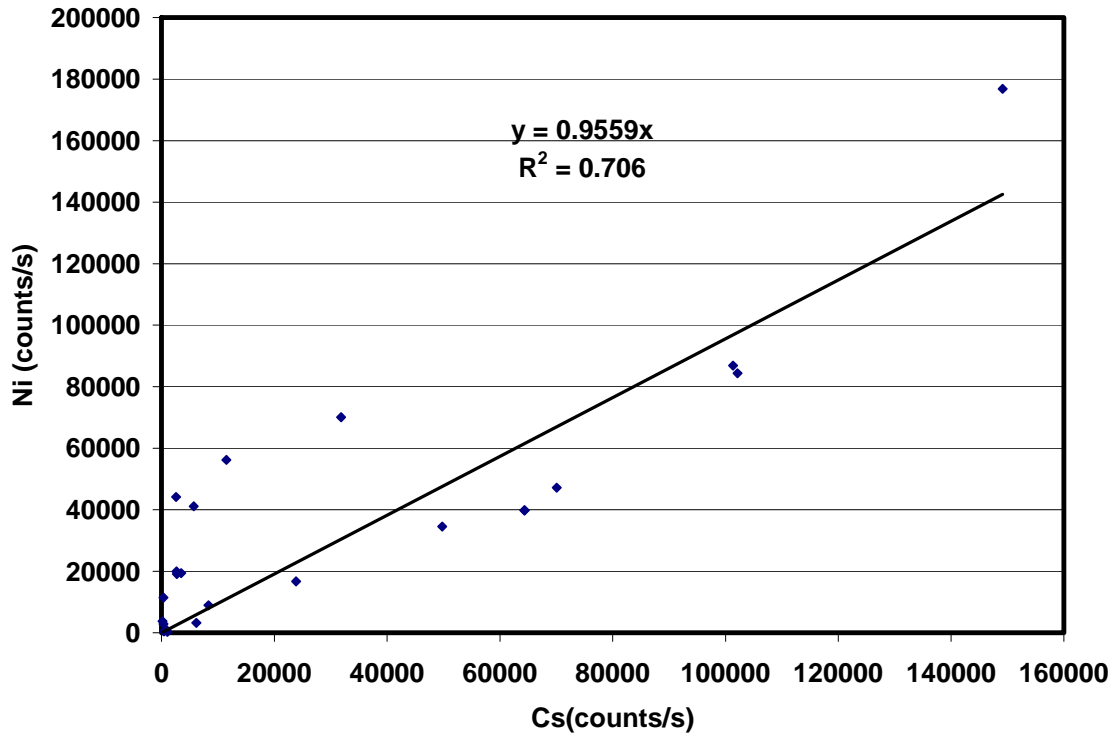Correlation plot for Gd and Ce forced through (0,0). Relevant mass interferences ^{140}La and ^{140}Ba.

Correlation plot for Cu and Rb forced through (0,0). Relevant mass interferences ^{63}Ni, ^{85}Kr and ^{85}Sr.
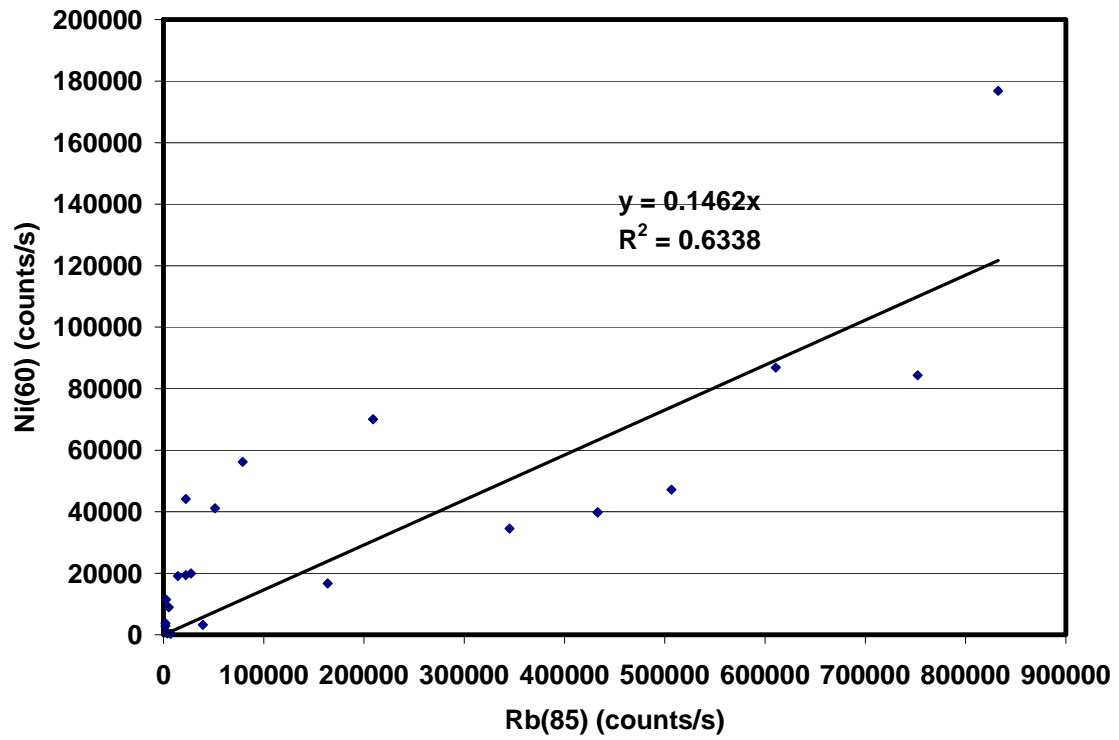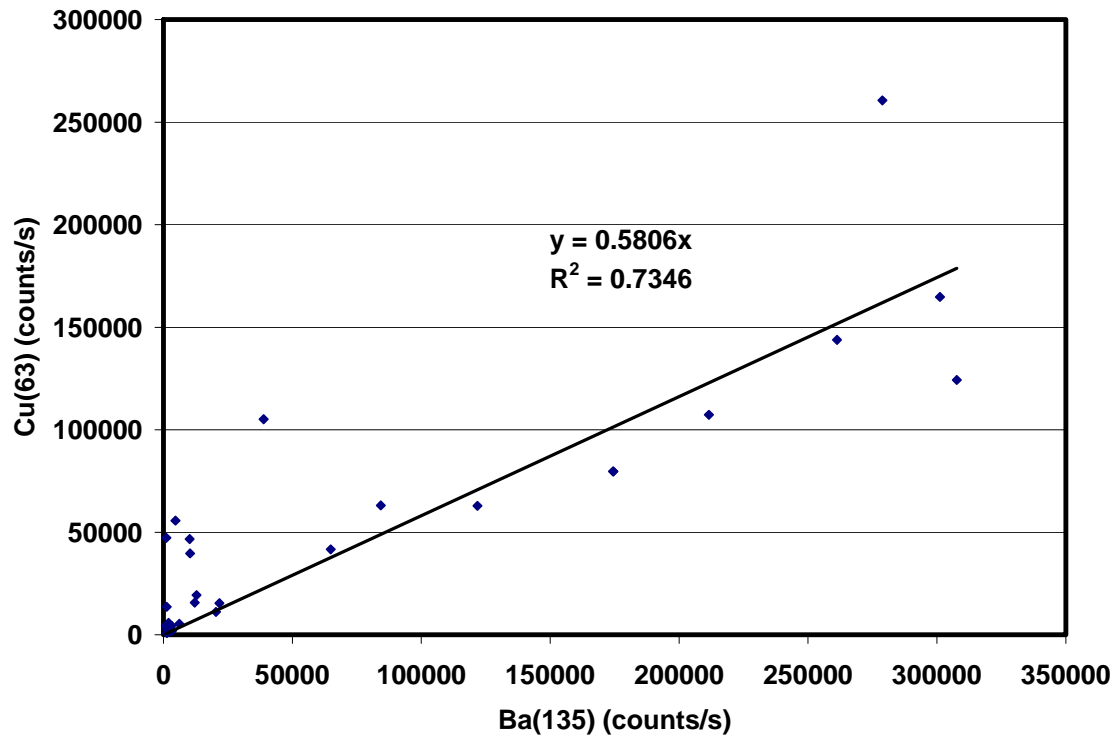
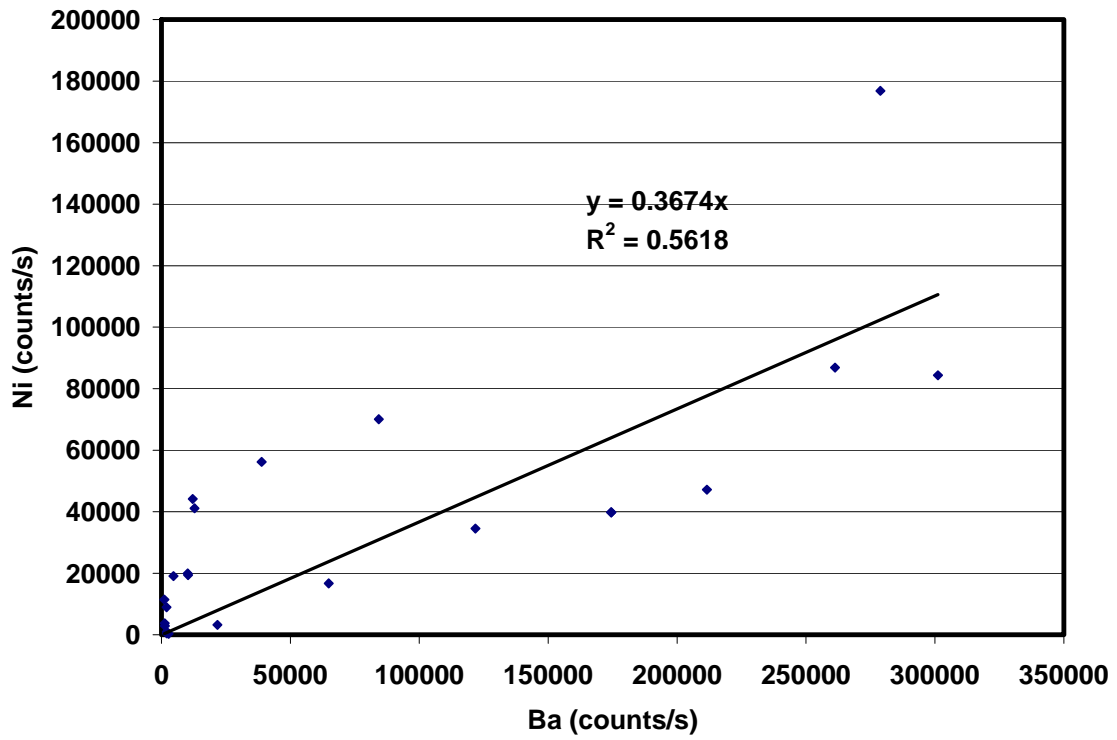Correlation plot for Ni and Rb forced through (0,0). Relevant mass interferences ^{60}Co, ^{85}Kr and ^{85}Sr.

Correlation plot for Cu and Cs forced through (0,0). Relevant mass interferences ^{63}Ni, ^{133}U and ^{133}Ba.

$$y = 0.9559x$$
$$R^2 = 0.706$$

Correlation plot for Ni and Cs forced through (0,0). Relevant mass interferences ^{60}Co, ^{133}U and ^{133}Ba.

Correlation plot for Cu and Ba forced through (0,0). Relevant mass interferences ^{63}Ni.

Correlation plot for Ni and Ba forced through (0,0). Relevant mass interferences ^{60}Co.