A TWO PART THESIS:

RADIONUCLIDE CONCENTRATIONS IN FOREST SURFACE FUELS AT THE SAVANNAH RIVER SITE

AND

PRELIMINARY STUDY OF INFLAMMATORY EFFECTS OF WOOD SMOKE EXPOSURE AMONGST WILDLAND FIREFIGHTERS

by

ANNA MARIE HEJL

(Under the Direction of Luke Peter Naeher)

ABSTRACT

The first study characterizes anthropogenic and natural radionuclides in litter and duff samples across selected areas at the Savannah River Site (SRS), South Carolina. Spatial analyses were conducted using kriging to describe spatial patterns in radionuclide levels in litter and duff across SRS. ^{137}Cs had the highest number of samples reported above minimum detectable concentration in litter and duff. Spatial trends do not appear to directly link areas with higher activity concentrations with onsite facilities.

The second study investigates inflammatory effects in wildland firefighters working at prescribed burns at SRS. Blood samples collected via dried blood spot (DBS) were taken from twelve firefighters. Inflammatory biomarkers in DBS samples were analyzed using Meso Scale Discovery assay. Linear mixed models were used to test whether there were cross-work shift

differences in IL-1β, IL-8, CRP, SAA, ICAM-1, and VCAM-1. A significant cross-work shift increase in IL-8 was observed in healthy seasonal wildland firefighters.

INDEX WORDS: Litter, Duff, Surface Fuels, Radionuclides, Kriging, Dried Blood Spot, Interleukin-8, Inflammation, Wood Smoke

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DEDICATION

I would like to dedicate this work to my beloved father, mother, and brother.

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CHAPTER 1

INTRODUCTION

This thesis consists of two independent studies and therefore is discussed in two parts. Part 1 consists of a study which investigates anthropogenic and natural radionuclide constituents found in litter and duff samples taken in 2004 across areas within the United States Department of Energy's Savannah River Site (SRS), South Carolina. Part 2 consists of a study conducted in 2011, which looks at the effects of particulate matter and carbon monoxide on inflammatory biomarkers found in whole blood samples of wildland firefighters at SRS. Chapter 1 provides a general description of each chapter. Chapter 2 consists of a background and literature review of part 1. Chapter 3 contains an article submitted for publication to *The Journal of Environmental Management* in 2011. This study characterizes and quantifies the radionuclide constituents from forest surface fuels at SRS. Chapter 4 provides a background and literature review for part 2. Chapter 5 includes an article in preparation to be submitted for publication to *Epidemiology*. This study investigates the effect of wood smoke exposure by looking at inflammatory responses in wildland firefighters working at prescribed burns in southeastern United States. Chapter 6 gives concluding remarks for part 1 and 2 of this thesis.

PART 1

RADIONUCLIDE CONCENTRATIONS IN FOREST SURFACE FUELS AT THE SAVANNAH RIVER SITE

CHAPTER 2

LITERATURE REVIEW FOR PART 1

NATURE OF RADIOACTIVITY

Radioactive Decay in the Environment

A nuclide is a specific atom defined by its atomic number and mass number (Cooper et al., 2003). Some nuclides may undergo changes due to their imbalance in their number of protons and neutrons. When unstable nuclides exist, they emit radiation in order to achieve a more stable state: Such nuclides are classified as radionuclides. This spontaneous process of decomposition via radiation emission to gain a more stable state is termed radioactivity or radioactive decay (USEPA, 2007). Transmutation occurs when a parent nucleus undergoes changes of atomic number therefore becoming a daughter nucleus/product—a new nucleus of a different element (Cooper et al., 2003). Initially, when a daughter nucleus is formed, it is considered in an unstable state and must resolve into a stable state by emitting radiation particles. While radioactive decay occurs, there are types of nuclear radiations that commonly emit from the nucleus. Such occurrences involve three types of nuclear radiation: alpha (α), beta (β), gamma (γ) (USEPA, 2011c). Originating in the nucleus of a radionuclide, γ-rays, usually accompanied by α and β particle radiation, do not have charge or mass and have a greater range in matter allowing them to travel long distances into material (USEPA, 2011c). Gamma-rays are therefore considered indirectly ionizing radiation as opposed to directly ionizing radiation which consists of charged particles (i.e. α and β particles) (Cooper et al., 2003). Directly ionizing

radiation, when emitted from radionuclides, has a relatively short range in energy and therefore does not penetrate deep into matter (Cooper et al., 2003).

Precise prediction of when a nucleus will decay is unfeasible because decay occurs randomly for a given radionuclide which can have an infinite number of radioactive nuclei. The rate of decay varies widely among radioactive elements, and inasmuch, one gram of a radioactive substance that decays rapidly may contain the same amount of activity as several tons of another radioactive substance that decays slowly (Sloto, 2000). Therefore, statistical means are used to estimate the probability of decay for a specific radionuclide. Radioactive decay is calculated using the following equation,

$$N_t = N_0 e^{-\lambda t} \quad (1)$$

where N is the number of parent nuclei present at time, t, N_0 is the initial number of radioactive nuclide at time (t) zero, and λ is the decay constant for a give radionuclide (ANSI, 1999; Cooper et al., 2003). To correct for the decay that can occur during the time period between sampling date to analysis date, it is important for radioisotope concentrations to be decay-corrected to the sampling date. The decay process can neither be speed up nor slowed down because of the probability of a nucleus decaying at a given time (t) (Cooper et al., 2003).

Sources of Radionuclides

Radionuclides may originate from natural or manmade processes. Radionuclides classified as naturally occurring, may arise from either primordial or cosmogenic origin. Primordial radionuclides—responsible for most of radiation exposure to individuals (Cooper et al., 2003)—existed since the creation of the Earth, while radionuclides of cosmogenic origin are continuously formed in the upper atmosphere via cosmic rays (Papastefanou and Ioannidou, 2004). Some examples of primordial radionuclides include ^{40}K, ^{232}Th, ^{238}U, and ^{235}U (Ghiassi-

Nejad et al., 2001). Examples of radionuclides of cosmogenic formation include ^{7}Be, ^{3}H, ^{14}C, and ^{22}Na (Cooper et al., 2003). While a number of radionuclides are naturally occurring, there are also manmade sources of radionuclides which circulate in the environment: nuclear weapons tests (i.e. atomic bombs), nuclear power and discharges from reprocessing, nuclear medicine, and from fossil fuel mining and combustion (i.e. coal, radon, phosphate rock) (McBride et al., 1978; Hu et al., 2010; UNSCEAR, 2000).

Exposure Pathways and Health Risks

There are several general exposure pathways in which humans may be exposed to radionuclides: inhalation, dermal, and ingestion. External or internal exposure of radionuclides in air, soil, and water are concerns (Peterson et al., 2007). Inhalation of radionuclides may occur through air or soil routes, while ingestion of contaminated soil, water, and foodstuffs can occur (Peterson et al., 2007).

With radioactive elements, there can be health risks associated with given radioactive emissions. Half-lives of radionuclides may contribute to associated health risk. For instance, a combination of long half lives, low specific activities, decay rates and decay energies may classify such radionuclides as low hazards (Peterson et al., 2007). Rather, relative short lived radionuclides tend to be most radioactive (Cooper et al., 2003).

Cancer is the primary health concern associated with radioactive exposure, where radionuclides may disrupt cellular function and tissue growth (Cooper et al., 2003; USEPA, 2007). A comprehensive epidemiological study was conducted to estimate cancer risks relative to external exposure to ionizing radiation (X and γ rays ranging from 100 to 3000 keV) in over 400,000 nuclear industry workers from 15 countries (Cardis et al., 2007). They found a significant association between radiation dose and all-cause mortality; the relative risk was

calculated as 1.04 at 100 millisieverts (mSv) (Cardis et al., 2007). Severity of health outcomes due to ionizing radiation depends on duration of exposure, amount of energy absorbed by living tissues, and the penetrating degree of the radiation.

Exposure concerns for α, β and γ radiation are discussed in brevity hereafter. Alpha particles have little penetrating power due to their relatively large size and property to lose energy quickly. However, greater concern arises if exposure to α particles via inhalation or ingestion occurs. Once inside the body, α particles disturb the body's cells, increasing the risk of cancer (Krewski et al., 2006; USEPA, 2010a). Beta particles are much smaller than α particles and can penetrate the human skin by 1 to 2 centimeters and travel further into tissues. Therefore, direct exposure to β particles is a potential hazard. Inhalation or ingestion of β particles poses concern by increasing the risk of cancer to an even greater extent (USEPA, 2010b). Gamma-rays are of greatest health exposure concern due to their highly electromagnetic energy. Gamma-rays can penetrate through the body, sometimes several centimeters into tissue and therefore possess external and internal bodily hazards (Shilnikova et al., 2003; USEPA, 2010c).

FATES OF RADIONUCLIDES IN THE ENVIRONMENT

Multiple pathways in which radionuclides can be dispersed such as atmospheric, water, soil/sediment, vegetation, and foodstuff contribute to a wide array of fates of radionuclides in the environment (Van Hook, 1979). For the purpose of this thesis, primary attention to radionuclide dispersion to atmospheric, soil, and vegetation are discussed.

Atmospheric

Anthropogenic processes and natural sources of radionuclides in the environment both contribute to past and present levels of radionuclides in the atmosphere. Due to nuclear weaponry testing and processing, nuclear medicine and industrial energy processes, and nuclear

catastrophic events such as the Chernobyl mishap, radionuclides remain ubiquitous in the environment. Meteorological processes such as precipitation and wind currents can further transport and distribute radionuclides in the atmosphere (Amiro and Davis, 1991). Release of radionuclides into the atmosphere post Chernobyl showed radioactive aerosol detection more than 1000 kilometers from the source (Lujaniene et al., 2007). Natural occurring radionuclides such as cosmogenic beryllium, after its formation in the atmosphere, adsorbs electrostatically to aerosols and thereafter may be transported to the earth's surface through wet and dry deposition (Kaste et al., 2002).

Settled radioactive particles found in soil or ground materials can be resuspended through various processes (Amiro and Davis, 1991). Resuspension—the re-entrainment of radionuclide particles into the atmosphere formerly deposited—may be accomplished by wind-driven means (Nicholson, 1988) or fire occurrence (Kashparov et al., 2000). Previous soil studies found that ^{238,239}Pu and ^{240}Pu decreased with soil depth and sampling distance from point source (McLendon et al., 1976), indicating aerial dispersal of radionuclides (Adriano and Pinder, 1977).

Soil/Sediment

Radionuclide concentrations in soil vary greatly among locations due to differences in rainfall patterns and in the mechanics of retention and transport in different types of soil (SRS Environmental Report, 2008). Microbes involved in the decomposition process may also alter the amount of radionuclides present in the soil and sediment. For example, Rafferty et al. (1997) explains the continuous presence of ^{137}Cs in forest litter post the Chernobyl incident by proposing a fungus mediated translocation. According to Simonoff et al. (2007) microorganisms found alongside radionuclides in environments with wide temperature and pH ranges compensate by employing redox reactions which convert many substrates including

radionuclides in organic matter into stable and non soluble forms. The result of these reactions may be radionuclide fixation or dissemination (Simonoff et al., 2007). Radionuclide particles may also adsorb onto suspended and bed sediments (Cooper et al., 2003). Physical composition of the soil profiles is also a factor determining of how radionuclides are translocated into vegetation. For instance, due to cation exchange processes, cesium adsorbs onto sediments and soils (Peterson et al., 2007).

Vegetation

Results of various studies indicate that radioactive contaminants present within uncultivated soils, floodplains, and surface and ground water could be transported into vegetation growing on contaminated areas (Adriano and Pinder, 1977; McLendon et al., 1976; Pinder et al., 1984; Whicker et al., 1999). The radioactivity deposited years ago and incorporated into the soil can be taken up by the trees and transported to their above ground tissues, incorporating into the needles that fall and become litter (Adriano et al., 1981).

Radionuclides transported through atmospheric dispersion also intercept on trees and other vegetative material (Copplestone et al., 1999). Capable of storing radionuclides, forest zones can serve as long-term repository sites (Cooper et al., 2003). Adriano and Pinder (1977) found that the deposition of aerosols on forest foliage seems to be dependent on roughness, pubescence, and moisture of the leaves.

FOREST SURFACE FUELS

Prescribed Burning

The practice of prescribed burning is used across the United States to reduce hazardous forest fuels, prepare sites for seeding, improve and sustain wildlife habitat, and to control for diseases (Van Lear and Waldrop, 1991). The United States Fire Services (USFS) applies fire

management procedures and safety precautions at all time when administering prescribed burns. Prescribed burning is the purposeful application of fire to a land under appropriate weather and burn conditions (Carter and Foster, 2003). Burning is restricted to forest floor and understory vegetation. The consumption of understory vegetation such as shrubs, grasses, litter, and duff is accomplished via prescribed burning due to lower flame height and flame temperatures (Kilgo and Blake, 2005). The overstory and upper canopy of the forest is seldom disturbed through prescribed burning since such burns are classified as low intensity and low severity fires (Carter and Foster, 2003). Dense, organic ground fuels, such as soil (i.e. Oi, Oe, and Oa horizons in soil taxonomy), burn in the smoldering phase of consumption and can result in a long-term release of pollutant emissions and tree damage or mortality from prolonged cambial heating (Phillips et al., 2000).

HISTORICAL RADIONUCLIDE RELEASES BY MEANS OF FOREST FIRE

Natural and man-made processes contribute to radionuclide deposition in the environment, leading to accumulations in soil, concentration in soluble ash and uptake in plant material that can be released during forest wild fires and prescribed fires (Amiro et al., 1996). Radiation accumulated on and in vegetation over time can be released into the air upon combustion (Malilay, 1998). Several studies look at the redistribution of radionuclides from wildfires occurring on contaminated land (Gürer and Georgopoulos, 2001; Malilay, 1998; Yoschenko et al., 2006a, 2006b). For example, the decay of radon in the atmosphere to ^{214}Bi and ^{214}Pb can result in deposition in surface dead litter and organic materials that can be released during fires, such as during the May 2000 Cerro Grande fire in New Mexico (Whicker et al., 2006). Described below are past nuclear events where reported air or soil measurements were collected concerning radionuclide release from forest fire occurring on contaminated sites.

Chernobyl

A study quantifying the resuspension, transport, and deposition of radionuclides, ^{90}Sr, ^{238}Pu, and $^{239,240}Pu$, during grassland and forest fires in the Chernobyl exclusion zone, concluded that the fire only impacted a small area downwind of the burn of which airborne concentration of radionuclides increased several orders of magnitude compared to background levels (Yoschenko et al., 2006a). Yoschenko et al. (2006) concluded that wildland fire occurrence contributed negligible to the redistribution of radioactivity within and outside of the Chernobyl zone.

Another study characterizing radioactive aerosol resuspension and exposure of wildland firefighters in territory contaminated by Chernobyl accident showed that while burning a dry grass site, 2-5% of the ^{137}Cs of grass was released, amounting to one millionth of all the deposition in the soil (Kashparov et al., 2000). It was also found that during active burning, ^{137}Cs concentration in lower air layer increased by several hundred times, tens of times during smoldering phase, and several times during post-fired period compared to background levels (Kashparov et al., 2000).

Los Alamos

In early May 2000, a prescribed burn administered on Cerro Grande, New Mexico grew out of control and soon reached Los Alamos National Laboratory (LANL), burning approximately 50,000 acres within and adjacent to the site's grounds (Fresquez et al., 2000). LANL land suffers past radionuclide and chemical contamination (Gonzales et al., 2000). Soil samples were taken within LANL after the Cerro Grande fire, and analyzed for radionuclide activity and heavy metals. Results showed that resuspension of radionuclides post fire occurrence was minimal and the impact to regional areas from smoke/fallout ash was also minimal. However, it should be noted that the Cerro Grande fire was classified as a crowning

fire which may contribute to such results (Volkerding, 2003). Surface fire would be expected to release higher amounts of ^{137}Cs, due to high concentration in forest floor material like litter and duff, as opposed to crowning fires which would release radionuclides

Hanford

July 2000, major brush fires occurred on the Hanford Reservation in the state of Washington. The fires burned approximately 200,000 acres. Handford Reservation was established in 1943 as part of the Manhattan Project and is known as one of the largest nuclear waste storage areas in the United States. Past nuclear weaponry production has contaminated over 130 million cubic yards of soil, along with billions of gallons of contaminated water (USEPA, 2011b).

Air samples were taken immediately following the fires and analyzed for radionuclides. United States Environmental Protection Agency (USEPA) studies showed that most samples came within range of normal national background levels with few samples being slightly elevated but within or below USEPA's protective risk range for human health and the environment (USEPA, 2011a).

SAVANNAH RIVER SITE

History

Located in the Southeastern United States, near Aiken, South Carolina, the United States Department of Energy's (DOE), Savannah River Site (SRS), is a secured facility operated by Savannah River Nuclear Solutions, LLC. (USEPA, 2011d). Opening in 1952, SRS's past facility operations were used for national defense, space program initiatives, nuclear-related research and production (USEPA, 2011d). Since the cease of nuclear production for defense program purposes in 1988, SRS is in progress for cleanup from past disposal practices of nuclear

materials. Frequently identified contaminants of concern include uranium, arsenic, mercury, cesium, radium, thorium, benzo(a)pyrene, cobalt, lead, chromium, and potassium (USEPA, 2011d).

Prescribed Burns

SRS has also been established as a National Environmental Research Park where approximately 90% of the total area (~310 square miles), is forested and managed for various operational objectives (USEPA, 2011d). The United States Department of Agriculture (USDA) Forest Service performs land management operations on site; Prescribed burning is routinely conducted at SRS to sustain and enhance habitat for the endangered red-cockaded woodpecker (*Piciodes borealis*) and ecological communities associated with longleaf fire savannahs, and to reduce hazardous fuel accumulation and associated wildfire potential (Kilgo and Blake, 2005; Parresol et al., 2006). Forest types include loblolly and slash pine, long leaf pine, mixed pine and hardwood, and upland hardwood (Parresol, 2007). Previous studies show that consumption of forest surface fuels (i.e. litter and duff) are major contributors to fuel consumption subsequent prescribed burning (Kilgo and Blake, 2005). Prescribed burns at SRS are characterized as relatively low intensity and low severity fires, ideal conditions for litter and duff consumption (Cole et al., 1992).

KRIGING

Spatial distribution is a valuable component of risk assessment which is useful for the characterization of environmental level of contaminants (Cattle et al., 2002). Spatial statistical methods, such as kriging, are used to interpolate environmental levels of contaminants across an area from measurements collected from a limited number of locations within the area. It is also

used to estimate the probability that ascribed values will exceed a given threshold at a particular location (Cattle et al., 2002).

OBJECTIVES OF RESEARCH

A potential concern regarding fire on land and forested areas contaminated with radionuclide isotopes is the incorporation of such constituents into smoke columns following consumption. This research seeks to identify and understand radiological concentrations present in primary surface fuels that may consume either during prescribed burns or wildfire occurrences on SRS.

The objectives of this research are as follows: (1) to characterize and quantify the radionuclide constituents in forest surface fuels (i.e. litter and duff) from selected areas within SRS; (2) to identify any spatial distributions of radionuclide concentrations found in surface fuels across SRS by means of ordinary kriging.

Although soil studies have been conducted in the past, few studies characterize radionuclide concentrations in litter and duff material. This research provides preliminary data for future referential purposes regarding radionuclide activity concentrations found in surface fuels at SRS. This research also provides spatial distributional maps of forest surface fuel radioactivity levels distributed within SRS, which has not previously existed to date.

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CHAPTER 3

RADIONUCLIDE CONCENTRATIONS IN FOREST SURFACE FUELS AT THE SAVANNAH RIVER SITE[1]

[1] Hejl, A.M., Ottmar, R.D., Jannik, G.T., Eddy, T.P., Rathbun, S.L., Commodore, A.D., Pearce, J.L., and Naeher, L.P., Submitted to *Journal of Environmental Management*, 10/7/2011.

ABSTRACT

Background/Objective: A study was undertaken at the United States Department of Energy's Savannah River Site (SRS), Aiken, South Carolina to investigate radiological concentrations in litter and duff from select areas at SRS. Litter (i.e. vegetative debris) and duff (i.e. highly decomposed vegetative debris) can often be the major fuels consumed during prescribed fires and have potential to release radiological contaminants into the environment.

Methods: Repeated samples from 97 locations were collected systematically across SRS and analyzed for radiological activity. Gamma spectroscopy analysis was used for radionuclide characterization of the samples. Sign tests were used to compare litter and duff radioactivity differences. As spatial trends were of interest, continuous surface maps for each radionuclide were created using ordinary kriging to explore spatial distributions in litter and duff radionuclide activity levels across SRS. Spatial correlation tests were also performed to identify if significant spatial dependency existed in the data.

Results: ^{7}Be, ^{40}K, and ^{137}Cs showed statistically significant proportional differences between litter and duff samples. Duff sample concentrations for ^{137}Cs ($p<0.0001$) and ^{40}K ($p=0.0015$) were statistically higher compared to litter samples. ^{7}Be activity concentrations were statistically higher in litter as compared to duff ($p<0.0001$). For ^{40}K litter and duff samples, spatial correlation tests were found to be insignificant ($p=0.6611$ and $p=0.9644$, respectively) and the maps did not indicate any apparent high concentrations centered near possible radionuclide sources (i.e. SRS facilities). For ^{7}Be litter samples, significant spatial correlation was calculated ($p=0.0085$) whilst the map indicated increased concentrations in the northeast and west portions of SRS. No spatial correlation was evident in the ^{7}Be duff samples ($p=1.0000$) due to small sample size (n=7).

Conclusions: ^{137}Cs, is the primary radionuclide of concern, with the highest number of samples reported above minimum detectable concentration (MDC) in litter (51.4% above MDC [n=171 out of 333 litter samples]) and duff samples (83.2% above MDC [n=198 out of 238 duff samples]). ^{137}Cs litter and duff samples showed significant spatial correlations (p<0.0001 and p<0.0001, respectively); however, the ^{137}Cs litter and duff spatial trends in the maps generated from the kriging parameters do not appear to directly link the areas with higher activity concentrations with SRS facilities.

INTRODUCTION

The Savannah River Site (SRS), a National Environmental Research Park, is located in the upper coastal plain of South Carolina near Aiken, South Carolina and shares a border with the Savannah River for approximately 44 kilometers (Jannik, 1999). At approximately 800 square kilometers (310 square miles) (Garten et al., 2000), the forested area of SRS is primarily made up of about 31% hardwood or mixed pine hardwood and 69% pine (Kilgo and Blake, 2005). Approximately 12% of the SRS has been used or is currently used for nuclear processing purposes (ATSDR, 2007). The majority of the remaining portion of the SRS is forested and managed (i.e. prescribed fires) for a variety of operational objectives (ATSDR, 2007; USFS-SR, 2005).

The United States Department of Energy (DOE) established SRS for production of special nuclear materials. Construction started at SRS in 1951 with some facilities becoming operational in 1952 (Garten et al., 2000). From 1952 to 1988, SRS' mission was dedicated to the production of nuclear materials, primarily tritium and ^{239}Pu, used in fabrication of nuclear weapons (Cummins, 1994; Dai et al., 2002). Production of nuclear materials discontinued in 1988 and SRS cleanup of contaminated ground water, surface water, sediment, sludge, solid waste, and soil remains in progress (USEPA, 2010). Throughout the years, releases of over 50 radionuclides and various non-radiological contaminants into the atmosphere, onsite streams and seepage basins occurred as a result of various operations at SRS (Cummins et al., 1991). At SRS, nuclear facility releases have resulted in the emission and consequently deposition of radionuclides into surface soils (Ellickson et al., 2002).

Previous studies indicate that radionuclides deposited years ago and incorporated into uncultivated soils, floodplains, and surface and ground water can be transported via biological

and physical processes into forest floor and woodland vegetation—from root to aboveground tissue—growing on contaminated areas (Adriano and Pinder, 1977; Gürer and Georgopoulos, 2001; McLendon et al., 1976; Pinder et al., 1984; Whicker et al., 1999; Yoschenko et al., 2006a, 2006b; Zhu and Smolders, 2000). Contaminants can incorporate into needles, bark, and leaves that fall and become litter (freshly fallen needles/leaves) (Adriano et al., 1981). Litter can act as highly absorptive mulch, thereby accumulating contaminants (Adriano et al., 1981).

A fire occurring on contaminated vegetation has potential to release non-radiological and radiological contaminants into the atmosphere, which thereby may be transported downwind and deposited at various locations distant to the burn (Gürer and Georgopoulos, 2001; Malilay, 1998; Yoschenko et al., 2006a, 2006b). Sampling distance from point sources contribute in determining measured radionuclide concentrations present in ground fuels. A previous soil study conducted at SRS in 1972 found ^{238,239}Pu and ^{240}Pu decreased with soil depth and sampling distance from point source (McLendon et al., 1976), indicating aerial dispersal of radionuclides (Adriano and Pinder, 1977).

Several global studies investigated release of radionuclides during forest fires in areas contaminated by nuclear material, including areas contaminated by the Chernobyl Nuclear Power Plant accident (Kashparov et al., 2000; Pazukhin et al., 2004; Yoschenko et al., 2006a, 2006b) and areas near the Los Alamos National Laboratory in the May 2000 Cerro Grande Fire (Johansen et al., 2003; Volkerding, 2004). The radionuclides of greatest concern following Chernobyl were ^{137}Cs, ^{90}Sr, and ^{238,239,240}Pu; however, results showed wildland fires contribute negligibly to the redistribution of radioactivity compared to the whole zone contamination at Chernobyl (Yoschenko et al., 2006a). Radiological emissions released from recent wildfires at Los Alamos, NM showed smoke samples containing naturally occurring elements—those of

which are decay products of radon (^{214}Bi and ^{214}Pb) in the atmosphere (Jacobson, 2001; Whicker et al., 2006).

Prescribed burning is conducted routinely at SRS to primarily sustain and improve habitat for the endangered Red-Cockaded Woodpecker (*Piciodes borealis*) and to reduce hazardous fuel accumulation and associated wildfire potential (Kilgo and Blake, 2005). SRS' prescribed fire program pursues a goal of burning approximately 9,300 hectares per year (22,500 acres per year). Previous studies at SRS determined that total forest floor litter and duff (partially decomposed litter) often contributes to a majority of the fuel consumed during prescribed burns (Goodrick et al., 2010).

Due to increased surface area and persistent foliage throughout the year for pine species, airborne particulates are intercepted on the needles (Copplestone et al., 1999). When the needles fall due to senescence, the litter and duff layers accumulate radioactive materials which have potential to become airborne once more during fires (Malilay, 1998). The biogeochemical cycle of each element as well as the generation and decay processes make an assessment of potential exposure complex. Radionuclides can also be taken up from soil by trees and recycled through foliage drop. ^{137}Cs, a common and widely distributed product of nuclear testing and processing, is easily taken up by vegetation as an analogue of potassium (Simonoff et al., 2007) and can be volatilized or re-suspended in fires, concentrated in ash (Adriano et al., 1981; Amiro et al., 1996), and redistributed by runoff (Johansen et al., 2003).

A concern with prescribed burning on land with radionuclide isotopes present in the primary ground fuels, litter and duff, is the incorporation of such elements into the smoke column following consumption. The primary objective of this study was to characterize and quantify the radionuclide constituents in litter and duff samples from randomly selected areas

within SRS. To date, few studies characterize radionuclide concentrations in litter and duff material. Two previous studies showed elevated concentrations of ^{137}Cs near reprocessing plants in both soil and litter samples, indicating long-term impact of the reprocessing operations on SRS (Adriano and Pinder, 1977; Adriano et al., 1981). Additionally, pine and hardwood litter collected on SRS in 1977 had total plutonium concentrations of 2.92×10^3 pCi/kg and 1.51×10^3 pCi/kg, respectively (Adriano et al., 1981). A second objective was to understand specific spatial trends of radionuclide concentrations and where high activity concentrations are located across SRS. Naturally occurring radionuclide concentrations in litter and duff are expected to lack spatial correlation within SRS, with no apparent high concentrations near nuclear reactors or major production facilities; while it is hypothesized that anthropogenic radionuclide concentrations will be slightly elevated around nuclear reactors, production facilities, and areas that were affected by global nuclear weapons testing fallout from Trinity Site and Nevada Test Site in the 1950's and early 1960's (Adriano et al., 1981; Marter, 1986).

METHODS

Sample Collection

Forest floor organic material consists of two basic layers known as litter and duff. Litter refers to the surface layer of the forest, shrub or grassland that has undergone little to no decomposition, with the entire original plant structures still recognizable. It typically consists of leaves, needles, twigs, bark fragments and other organic material. The litter layer (also referred to L-layer/Oi soil horizon) is found above the duff layer and mineral soil. Duff (F and H-layer/Oe and Oa soil horizon) refers to the layer located beneath the litter layer and above the mineral soil and consists of a well compacted layer composed of moderately to highly decomposed leaves, needles, fine twigs, and other organic material. Forest floor samples were

collected at 97 randomly selected Forest Inventory (FI) sample sites at SRS during the late winter and early spring of 2004 in four major forest types (loblolly/slash pine, longleaf pine, mixed pine and hardwood, and upland hardwood) (Ottmar et al., 2007, Fig. 3.1). Within each sample site, 4 sub-samples were collected to establish litter and duff loadings across a range of forest conditions.

For each FI sample site, a subplot was designated and marked as the plot center and then located using a combination of GPS coordinates and bearing tree information. Four sampling locations were established 10 meters (33 feet) from the plot center at each of the four cardinal directions (Fig. 3.2). If the sampling point proved unrepresentative of the surrounding forest floor (live tree/stump, mineral soil/rocks, downed bole, topographic barriers such as streams/ravines, etc.), 3 additional meters (10 feet) were added to the original end point until a suitable sample point was located. A 30.48 centimeters (12 inch) beveled steel square was used to systematically collect and quantify the litter and duff layers. The left corner and left edge of the square was aligned parallel with the cardinal directions and placed on top of the forest floor.

Twelve nails were positioned in a grid pattern within the square, each tapped downwards until the nail was flush with the top of the litter layer. The litter was carefully removed and placed within a labeled bag (FI plot identification, sample type, sub-sample direction, and date). The nails were again tapped down flush with the top of the duff layer. The same procedures from litter collection were administered for duff layer collection. A thorough description of the study design and materials may be found in the congruent study focused on forest floor bulk density evaluation at SRS (Maier et al., 2004).

After collection, all litter and duff samples were initially oven dried for 48 hours to determine dry mass: Litter samples at 70 degrees Celsius and duff samples at 100 degrees

Celsius. Dried litter (n = 333) and duff (n = 238) samples were then analyzed for radiological activity. The samples were analyzed by the SRS Environmental and Bioassay Laboratory (EBL) during the months of June and July of 2004. At the EBL, samples were again placed in a drying oven and allowed to dry overnight or for several hours to assure samples were desiccated before radioanalysis.

Analytical Techniques

Gamma Spectrometric Analysis

Exploratory analysis was performed using gamma spectroscopy for characterization of the majority of radionuclides suspected to be present in the samples. Radionuclides identified hence are all gamma emitting.

The vegetation was kept in a Secador Auto-Dessicator to maintain a relative humidity of 25-40% until sample counting and then placed into a calibrated 130G Marenelli beaker or 500 mL low density polyethylene bottle geometry for analysis. The gamma spectroscopy analyses were performed using a Canberra ®/Nuclear Data Genie High Purity Germanium Gamma analysis system with either a Canberra ® Model GC4019 coaxial germanium detector with a relative efficiency of 40% or a Canberra ® Model GC2518 detector with a relative efficiency of 26.7%. Samples were counted for 5,000 or 10,000 seconds and the concentrations of gamma-emitting radioisotopes were determined using the Genie^{TM} applications software. The Genie^{TM} software applies the ANSI N42.14 (ANSI, 1999) standard in calculating the quantity of radioactivity in a sample. The radionuclide concentration results were decay-corrected to their respective sampling dates.

Radiological activity was determined to be significant if the activity was above the minimum detectable concentration (MDC; units in pCi/kg) for each radioisotope within each

litter or duff subsample. At SRS, the MDCs are calculated at the 95% confidence level using the Curie MDC application (Currie, 1968). MDCs take into account factors such as count time, efficiency of detector, quantity of material analyzed, and background levels measured for a given day. Individual MDC values are not typically reported with the analytical results. The reported "yes" or "no" significance of each result is determined automatically by the analytical software package. Representative MDCs for the soil and vegetation radiological analyses performed at the SRS lab in 2004 are reported in the SRS Environmental Report (2004). MDCs are provided in pCi/g units.

In compliance with EBL protocols, all activity values, significant (above MDC) and non-significant (below MDC) radioactivity concentrations were reported for ^{40}K, ^{60}Co, and ^{137}Cs. Only significant activity concentrations were reported for the remaining radionuclide isotopes.

Statistical Procedures

Descriptive Statistics and Sign Tests

Descriptive statistics include mean concentration per radionuclide, standard deviation, 95% confidence interval (CI), range, and number and percent above minimal detectable concentration (MDC) for litter and duff samples (Tables 3.1 and 3.2, respectively). Data were screened to identify paired samples to perform sign tests.

Litter and duff data results for each isotope were paired by location within each FI sample site. Isotope data results were heavily censored with many values falling below their MDC. Therefore, a sign test was used to compare litter and duff activity levels. The sign test is based on the frequency X_1 at which duff activities exceed litter activities and the frequency X_2 at which litter activities exceed duff activities among paired samples. When duff activity exceeds the MDC but the paired litter does not, duff activity level is taken to exceed that of the litter.

Conversely, when the litter activity exceeds the MDC but the paired duff does not, litter activity level is taken to exceed that of the duff. When neither duff nor litter activities exceed the MDC, the paired sample provides no information regarding which fuel type had the higher activity, so such paired samples were dropped. Similarly, those samples that were not paired were disregarded. Under the null hypothesis that litter and duff activities are equal, the frequencies X_1 and X_2 are expected to be equal. The proportion of paired samples where duff activity exceeds litter activity is

$$\hat{p} = X_1/(X_1 + X_2). \quad (1)$$

Under the null hypothesis, the test statistic

$$z = \frac{\hat{p} - 0.5}{\sqrt{1/4n}} \quad (2)$$

has a standard normal distribution. Comparisons were carried out only for those radionuclides with greater than 20 paired samples. Radionuclides with small sample sizes are addressed in the descriptive statistics only.

Spatial Analysis

With no previous spatial data to date, this data allows for the exploration of natural and man-made radionuclide distributions found in litter and duff samples across SRS. The spatial objectives were: i) to identify if radionuclide concentrations in litter and duff samples exhibit spatial trends, and; ii) to determine if high radionuclide activities appear to be located near what we refer to in this paper as SRS facilities (see Fig. 3.1), which are identified as major nuclear production facilities and reactors at SRS (ATSDR, 2007). These SRS facilities are defined as areas that have released and/or had the potential to release radionuclides (ATSDR, 2007; Carlton, 1999). As spatial trends were of interest, continuous surface maps for each radionuclide were created using ordinary kriging to explore spatial distributions in litter and duff radionuclide

activity levels. Spatial correlation tests were also performed to identify if significant spatial dependency existed in the data.

The data used in this study included the spatial coordinates for each field sample (collected using global positioning systems (GPS)), the locations of SRS facilities, forest management compartments, and the SRS administrative boundary which was provided by the United States Forest Service-Savannah River (USFS-SR). All geographic data used in this study were spatially referenced using 1927 North American Datum and then projected using the Universal Transverse Mercator (UTM) zone 17N coordinate system.

It is important to note that as individual MDC values were not provided in the lab reported results (exempt ^{40}K, ^{60}Co, and ^{137}Cs), a soil/sediment generic MDC of 285 pCi/kg (retrieved from SRS Environmental Report, 2004 – Table 2: Representative Minimum Detectable Concentrations for Radiological Analyses) was used for spatial locations that were below the limit of detection (in the case for ^{7}Be).

After this was complete, the spatial analysis was conducted in two stages. First, spatial covariance for each data set was modeled (Table 3.4) using an exponential variogram constructed by restricted maximum likelihood (REML) in the *PROC MIXED* procedure of SAS (Littell et al., 1996) version 9.2 (Cary, N.C.). Spatial dependence among observations was described by fitting the exponential variogram to the data,

$$2\gamma(d) = c_0 + c_1(1-\exp\{- d / \alpha\}) \qquad (3)$$

where γ is the theoretical variogram,
d is the distance between data points,
c_0 is the nugget effect,
c_1 is the partial sill,
and α is the range parameter.

The variogram assumes that the strength of spatial dependence depend only on the distance d between a pair of sites. The nugget effect, c_0, describes the small-scale spatial variation, variation at scales shorter than the distances between neighboring sites. The sill, $c_0 + c_1$, is equal to twice the population variance of the data, and the range, α, is the distance at which the difference between the variogram the sill becomes negligible. Pairs of sites further than distance 3α apart are negligibly correlated.

Second, ordinary kriging (Webster and Oliver, 2001) (based on the previously described spatial models) was used to interpolate radionuclide concentrations across a grid constrained by the point sample locations. Ordinary kriging was performed using the *krigconv* function in the 'geoR' package and final maps were created using the 'map' and 'maptools' packages in R (R Development Core Team, 2010).

RESULTS

Radionuclide Concentrations

To characterize radionuclide concentrations in forest fuel bed material at SRS, litter (n = 333) and duff (n = 238) samples were collected and analyzed in 2004 for dry mass and radiological activity. The mean, standard deviation, 95%CI, sample sizes, and minimum and maximum observed specific activity of all identified radionuclides are reported in Tables 3.1 and 3.2 for the litter and duff samples, respectively.

^{208}Tl, ^{212}Pb, ^{214}Pb, ^{212}Bi, and ^{214}Bi were detected in a majority of the litter and duff samples (Tables 3.1 and 3.2). However, these radionuclides are short-lived decay products of radon, an inert gas, found naturally in the environment. Due to their short half-lives and because of the long delay between sampling and analyses, the radionuclide concentrations reported are not indicative of what is in the sample and therefore are not included in the summary statistics.

In addition, ^{228}Ac, ^{224}Ra, ^{231}Th, ^{234}Th, and ^{234m}Pa, were reported in the original data set, but these radionuclides are short-lived progeny which only exist in secular equilibrium with their parent radionuclide, they do not exist on their own. Therefore, for this analysis herein, ^{228}Ac was reported as ^{228}Ra, ^{224}Ra as ^{228}Th, ^{231}Th as ^{235}U, and ^{234}Th and ^{234m}Pa were reported as ^{238}U. Although, progeny of ^{238}U were detected, they were detected in minimal samples (3 samples in litter [Table 3.1] and 2 samples in duff [Table 3.2]), so data for them were not considered for further statistical analysis. Gamma spectroscopy results did not indicate the presence of unusual levels of natural radionuclides in the samples. However, for completeness and future comparative references, concentrations for all radionuclides measured in litter and duff during 2004 are provided in Tables 3.1 and 3.2, respectively. Thereafter, proportional comparison results are only displayed for the following radionuclides—^{7}Be, ^{60}Co, ^{40}K, and ^{137}Cs (Table 3.3). Three of the four radionuclides—^{7}Be, ^{40}K, and ^{137}Cs—showed statistically significant proportional differences between litter and duff samples (Table 3.3).

Litter and duff mean radiological activities ^{7}Be, ^{40}K, and ^{137}Cs are displayed in Fig. 3.3. ^{137}Cs (p<0.0001) and ^{40}K (p=0.0015), had statistically higher activity concentrations in duff compared to litter samples (Table 3.3). The mean ^{137}Cs activity in the litter was 2.67 x 10^2 pCi/kg (95%CI: 2.43 x 10^2, 2.90 x 10^2 pCi/kg) and 6.36 x 10^2 pCi/kg (95%CI: 5.82 x 10^2, 6.91 x 10^2 pCi/kg) for the duff (Fig. 3.3). The mean ^{40}K activity found in litter and duff were 6.57 x 10^2 pCi/kg (95% CI: 4.59 x 10^2, 8.55 x 10^2 pCi/kg) and 1.14 x 10^3 pCi/kg (95%CI: 8.79 x 10^2, 1.41 x 10^3 pCi/kg), respectively (Fig. 3.3). ^{7}Be activity concentrations were, however, statistically higher in litter samples verses duff (p<0.0001; Table 3.3). Mean activity concentration for ^{7}Be in litter was 3.05 x 10^3 pCi/kg (95%CI: 2.76 x 10^3, 3.34 x 10^3 pCi/kg) and 1.92 x 10^3 pCi/kg

(95%CI: 9.37 x 10^2, 2.91 x 10^3 pCi/kg) in duff (Fig. 3.3). ^{60}Co did not show significant differences between litter and duff samples (p=0.0569; Table 3.3).

The number of litter and duff samples reported above MDC along with corresponding percentage of litter and duff samples above MDC are presented in Tables 3.1 and 3.2, respectively. Collectively, the number of litter and duff samples reported at significant activity concentrations ranged from 0 in both litter and duff (0% above MDC for ^{60}Co [Tables 3.1 and 3.2]) to 171 (51.4% above MDC for ^{137}Cs in litter [Table 3.1]) and 198 (83.2% above MDC for ^{137}Cs in duff [Table 3.2]).

Spatial Distributions

Kriging parameters and corresponding mean concentrations, standard error, degrees of freedom, p-values, and chi-squared values are provided in Table 3.4. Significant spatial correlation existed in ^{7}Be litter samples (p=0.0085, n=104) and in both ^{137}Cs litter and duff samples (p<0.0001, n=333 and p<0.0001, n=238, respectively) (Table 3.4). No significant spatial correlation was found in ^{40}K litter or duff samples (p=0.6611, n=333 and p=0.9644, n=238 respectively) or in ^{7}Be samples duff (p=1.0000, n=7) (Table 3.4). Fig. 3.4 presents the final continuous surface maps for the litter and duff samples of ^{7}Be, ^{40}K, and ^{137}Cs.

Although ^{60}Co is a concern at DOE sites due to its longer half-life of about 5.3 years and external hazardous gamma rays during its radioactive decay process (Peterson et al., 2007), all litter and duff ^{60}Co concentrations were below MDC (Tables 3.1 and 3.2) and could not be included in spatial analyses. SRS soil and vegetative data for ^{60}Co activity concentrations are available for 2004 (SRS Environmental Report, 2004). Given the limited sample size for the remaining radionuclides, kriging models could not be generated.

DISCUSSION

This study investigated radionuclide concentrations and spatial distributions of radionuclides in litter and duff across SRS. Primary focus for discussion is the comparison of anthropogenic verses natural radionuclides. Continuous surface maps are discussed identifying any spatial correlations and are visually assessed to address whether high activity concentrations are relative to potential sources (i.e. SRS facilities). Due to the relative lack of litter and duff data in the literature, much of the referential data presented within this article comes from soil radiological activity concentrations. The radionuclides ^{137}Cs, ^{40}K, and ^{7}Be are discussed because of results and levels found in litter and duff samples across SRS in 2004.

Anthropogenic Radionuclide

Cesium-137

Varying amounts of ^{137}Cs are found in the environment from nuclear weapons tests that occurred decades ago and from nuclear reactor accidents (CDC, 2004; Peterson et al., 2007). With a half life of 30.17 years and due to its chemical nature, it is one of the radioisotopes of major concern at Chernobyl and other nuclear processing facilities like SRS. After Chernobyl, the accepted standard for contaminated firewood utilization in Russia was established as < 2.03 x 10^4 pCi/kg (750 Bq/kg; Note: 27.02 pCi unit conversion was used for 1Bq) (Lujaniene et al., 2007). ^{137}Cs is a man-made radionuclide and is the most abundant radiological soil contaminant at SRS. Results of a previous study show that the average activity concentration is approximately 30 pCi/kg in SRS soil samples (n=38) and is consistent with local background levels (Kubilius, 2004). The SRS Environmental Report provides soil ^{137}Cs activity concentrations, taken during the Savannah River Swamp Surveys, ranging from nondetectable to 5.00 x 10^4 pCi/kg (n=39) (SRS Environmental Report, 2004). Our results showed litter (2.67 x

10^2 pCi/kg [95%CI: 2.43 x 10^2, 2.90 x 10^2 pCi/kg]) and duff (6.36 x 10^2 pCi/kg [95%CI: 5.82 x 10^2, 6.91 x 10^2 pCi/kg]) (Tables 3.1 and 3.2, respectively) average activity concentrations were both higher than Kubilius, 2004 ^{137}Cs soil sample average reported, but were within range of the Savannah River Swamp Survey soil samples.

Our study found ^{137}Cs activity concentrations higher in the duff samples compared to the litter (p<0.0001) (Table 3.3, Fig. 3.3). Out of 238 duff samples, 198 samples (83.2% above MDC: Table 3.2) contained significant ^{137}Cs activity while 171 out of 333 litter samples (51.4% above MDC: Table 3.1) were found to have significant ^{137}Cs activity. A possible explanation of this finding could be attributed to lignin: the higher the lignin content of plants, the higher the concentration of ^{137}Cs as it can accumulate in lignin upon plant uptake by as much as 90% in hardwood (Andolina and Guillitte, 1990; Rafferty et al., 1997). Though not measured, the duff layer may have had more lignin than the litter layer at SRS. Rafferty et al. (1997) found that ^{137}Cs retention is higher in more humified litter (decomposed litter, in this case duff [Berg and McClaugherty, 2008; Ottmar et al., 2007]). When litter decomposes, it has been shown that lignin content increases in decomposed organic material (Coûteaux et al., 1995).

The concentration of ^{137}Cs in surface soil from global fallout events ranges from approximately 1.00 x 10^2 pCi/kg to 1.00 x 10^3 pCi/kg (Peterson et al., 2007). SRS litter and duff ^{137}Cs average concentrations fall within range in soil surfaces from global fallout. Cesium preferentially adheres to soil, particularly sandy soil, and clay and is generally one of the less mobile radioactive elements within the environment (Peterson et al., 2007). The maximum ^{137}Cs activity, 3.03 x 10^3 pCi/kg (Table 3.2), was found in the duff (more than 3 times the higher end of what is usually found in soils from global fallout events). In an earlier study looking at ^{137}Cs contamination in and around swamp areas at SRS, a range of ^{137}Cs concentrations varying from

1.35 x 10^2 pCi/kg to 6.49 x 10^4 pCi/kg (5 Bq/kg to 2.4 x 10^3 Bq/kg) was detected in soil samples (Fledderman et al., 2007) and consequently the maximum concentration found in the 2004 duff samples is within range of previous soil measurements collected from SRS.

Spatial correlation tests found significant spatial correlations in ^{137}Cs litter and duff samples (p<0.0001 and p<0.0001, respectively [Table 3.4]); however, the ^{137}Cs litter and duff spatial trends in the maps generated from the kriging parameters do not appear to directly link the areas with higher activity concentrations with SRS facilities (Fig. 3.4 (e) (f)). Concentrations found in duff samples showed that higher concentrations appeared near the center, northern, and southerly regions of the SRS with a number of samples with highest activity values being present in the northeastern portion of the map (Fig. 3.4 (e)). Higher ^{137}Cs concentrations in litter samples appear near the center and northeastern regions of the SRS (Fig. 3.4 (f)). Such an occurrence may be due to previous fallout from nuclear weapons testing in past years and possible contamination from SRS sources (Corey et al., 1982). In the past, atmospheric emissions from reactors and other processing stacks (located near the center region of SRS [Fig. 3.1]) released radionuclides onto surface soils at SRS (Ellickson et al., 2002). Auspiciously, SRS releases have been reduced greatly since the end of the cold war in 1991 and global fallout has decreased greatly on the SRS (as throughout the U.S.) since weapons testing ending in the 1960's (SRS Environmental Report, 2008). Additionally, with time, ^{137}Cs levels are expected to decrease due to radioactive decay.

Naturally Occurring Radionuclides

Potassium-40

^{40}K is a primordial, naturally occurring radionuclide, comprising only a small fraction of naturally occurring potassium and contributing to only about 0.012% of potassium (Peterson et

al., 2007). It has a long half life of 1.3 billion years (Peterson et al., 2007). Man-made processes such as mining fossil fuels (i.e. coal) can also release natural radionuclides like ^{40}K. Coal contains natural radionuclides such as ^{40}K (1.4×10^3 pCi/kg), ^{238}U, and ^{232}Th (Cooper et al., 2003; McBride et al., 1978). These natural radionuclides can be released to the environment during combustion (Cooper et al., 2003). For instance, D-Area, once as a heavy water reprocessing area at SRS, has had an operating coal-burning power plant since its construction in 1952 and is planned to be shut down in 2011 (ATSDR, 2007; USEPA, 2011). Since the early 1950's, there are also coal storage and disposal piles within SRS facilities such as P-Area (also housing a coal-burning power plant) and A-Area (USEPA, 2011). Such processes may have elevated ^{40}K levels found at SRS.

The natural activity concentrations usually found in soil range from 1.00×10^3 to 3.00×10^4 pCi/kg (HPSUM, 2005). The maximum concentration of ^{40}K that was found at SRS was 1.59×10^4 pCi/kg in duff (Table 3.2), falling within such natural activity soil range. SRS available soil data has ^{40}K average activity of 1.22×10^3 pCi/kg (Range: -3.17×10^2, 1.22×10^4 pCi/kg) and vegetative data of 1.27×10^4 pCi/kg (Range: 1.72×10^3, 3.33×10^4 pCi/kg) (SRNS, 2011); average ^{40}K litter and duff concentrations (Tables 3.1 and 3.2) are lower than soil and vegetative data and fall within the range of normal soil global concentrations (HPSUM, 2005; UNSCEAR, 2000). ^{40}K mean concentrations were statistically higher (p=0.0015) in duff compared to litter samples across SRS (Table 3.3; Fig. 3.3). This phenomenon is plausible because ^{40}K assimilates into the tissues of living organisms and plants and readily adheres to soil particles, behaving in the environment like other potassium isotopes (Peterson et al., 2007). Duff material more closely resembles soil particle composition—comprised of dense, well-compacted,

moderately to highly decomposed organic material—when compared to litter, which is comprised of little to no decomposed material, with its original plant structures still recognizable.

Spatial correlation tests found no significant spatial correlations for ^{40}K litter and duff samples (p=0.6611 and p=0.9644, respectively [Table 3.4]). Lack of spatial correlation in the distribution at SRS was to be expected due to natural occurrence of ^{40}K in the environment. Based on visual assessment, continuous surface maps generated from the kriging parameters do not appear to directly link the areas with higher activity concentrations with SRS facilities (Fig. 3.4 (c) (d)). Contours indicate that higher concentrations found in duff samples appear to be localized near the southeastern region of the SRS (Fig. 3.4 (c)). Higher ^{40}K activity concentrations in litter samples appear near the west and northwestern regions of the SRS (Fig. 3.4 (d)).

Beryllium-7

^{7}Be is a naturally occurring radionuclide, produced by cosmic-ray interactions with atmospheric constituents (Matisoff et al., 2002). ^{7}Be is relatively short lived, with a half-life of 53.28 days and natural activity levels of 0.27 pCi/kg (0.01 Bq/kg) (HPSUM, 2005). Our results had average litter and duff ^{7}Be activities higher (Tables 3.1 and 3.2) than natural activity levels, and may be an indication of stratospheric origin, where higher production of ^{7}Be is exhibited (Zanis et al., 1999).

Historical SRS soil data did not have any samples above MDC, while vegetative data shows average ^{7}Be levels at 4.34 x 10^{3} pCi/kg (Range: 7.13 x 10^{2}, 1.90 x 10^{4} pCi/kg) (SRNS, 2011). Average litter and duff ^{7}Be activity levels are slightly lower (Tables 3.1 and 3.2) than vegetative values. Higher concentrations were often found in litter samples compared to duff (Table 3.3). This result could be expected due to ^{7}Be fallout from the atmosphere; litter is the

first point of contact (Adriano et al., 1981; Copplestone et al., 1999). Due to its shorter half-life, ^{7}Be may decay prior to the litter decomposing into duff.

Due to small sample size (n=7), no significant spatial correlations exists in the ^{7}Be duff samples (p=1.0000 [Table 3.4]). No visual assessment can be concluded for ^{7}Be duff map since few duff samples (n=7) had reported ^{7}Be detections above MDC. Higher ^{7}Be concentrations found in the duff appear intermittently dispersed within SRS (Fig. 3.4 (a)). However, the litter map shows a significant spatial correlation (p=0.0085 [Table 3.4]). Based on visual assessment, spatial trends in the ^{7}Be litter continuous surface map generated from the kriging parameters do not appear to link areas that have higher activity concentrations with SRS facilities (Fig. 3.4 (b)). ^{7}Be concentrations found in litter samples appear to be concentrated in the west, southwest and north, northeastern regions of the SRS with a few high values intermittently dispersed within the SRS (Fig. 3.4 (b)). It is difficult to conclude an explanation of this finding because ^{7}Be is a naturally occurring radionuclide of cosmogenic origin. Therefore, man-made emissions or deposition could not have been responsible for the spatial variation that was observed. Levels would be due to upper solar winds distribution (Papastefanou and Ioannidou, 2004).

Limitations

Gross alpha and gross beta measurements in litter and duff samples were not measured and so quantitative levels of radionuclides expected to contribute to gross alpha and beta measurements could not be determined. Used as baseline, gross alpha and beta measurements can help decipher atypical radionuclide activity concentrations found in a select area (Hernández et al., 2005).

The spatial analysis performed was intended to provide a broad overview of radionuclide concentrations across the SRS. Therefore, results are limited to examine trends across the entire

SRS (i.e. global) and not trends that may exist at small scale (i.e. local) around individual SRS facilities; nevertheless, the litter and duff data can be used to make inferences in this regard. However, more specialized spatial analysis is needed to determine if significant localized spatial trends exist around individual SRS facilities.

Furthermore, no control locations were measured to compare litter and duff radiological activity concentrations elsewhere in states near the Atlantic Coastal Plain or other regions of the southeastern United States. Future areas of interest include further exploration in the release, fate, and transport of radionuclides—such as tritium, gross alpha, and gross beta emitting radionuclides—found in concurrent soil, litter, and duff material at SRS. Future research may lead to better trapping technology and more accurate predictive modeling of environmental deposition of radionuclides (Engelmann et al., 2009).

CONCLUSION

Key findings show that across SRS, ^{137}Cs, is the primary radionuclide of concern, with the highest number of samples reported above MDC in litter (51.4% above MDC) and duff samples (83.2% above MDC). Naturally occurring radionuclides ^{40}K and ^{7}Be (except ^{7}Be litter samples) showed no significant spatial correlations across the collection area; whereas anthropogenic ^{137}Cs showed significant spatial correlations in litter and duff samples across SRS. However, the ^{137}Cs litter and duff spatial trends in the maps generated from the kriging parameters do not appear to directly link the areas with higher activity concentrations with SRS facilities.

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Table 3.1. Descriptive Statistics for Litter Samples.

Litter Radionuclide Activity						
Radionuclide Isotope	**Mean Activity (pCi/kg)**	**St Dev (pCi/kg)[a]**	**95% CI (pCi/kg)**	**Min, Max (pCi/kg)**	**Number of Samples above MDC[b]**	**% Above MDC[b]**
^{7}Be	3.05×10^{3}	1.53×10^{3}	$(2.76 \times 10^{3}, 3.34 \times 10^{3})$	$(9.73 \times 10^{2}, 8.88 \times 10^{3})$	104	31.2%
^{40}K	6.57×10^{2}	1.84×10^{3}	$(4.59 \times 10^{2}, 8.55 \times 10^{2})$	$(-6.83 \times 10^{3}, 9.52 \times 10^{3})$	26	7.8%
^{60}Co	1.45×10^{1}	7.38×10^{1}	$(6.58 \times 10^{0}, 2.24 \times 10^{1})$	$(-2.89 \times 10^{2}, 4.70 \times 10^{2})$	0	0.0%
^{137}Cs	2.67×10^{2}	2.20×10^{2}	$(2.43 \times 10^{2}, 2.90 \times 10^{2})$	$(-3.11 \times 10^{2}, 1.38 \times 10^{3})$	171	51.4%
^{208}Tl	2.31×10^{2}	9.63×10^{1}	$(1.88 \times 10^{2}, 2.75 \times 10^{2})$	$(6.03 \times 10^{1}, 4.25 \times 10^{2})$	19	5.7%
^{212}Pb	5.06×10^{2}	2.29×10^{2}	$(4.30 \times 10^{2}, 5.83 \times 10^{2})$	$(1.43 \times 10^{2}, 9.51 \times 10^{2})$	34	10.2%
^{214}Pb	7.47×10^{2}	3.90×10^{2}	$(6.05 \times 10^{2}, 8.89 \times 10^{2})$	$(1.82 \times 10^{2}, 2.03 \times 10^{3})$	29	8.7%
^{212}Bi	2.10×10^{3}	6.42×10^{2}	$(1.54 \times 10^{3}, 2.67 \times 10^{3})$	$(1.23 \times 10^{3}, 2.90 \times 10^{3})$	5	1.5%
^{214}Bi	6.91×10^{2}	3.46×10^{2}	$(5.61 \times 10^{2}, 8.23 \times 10^{2})$	$(1.32 \times 10^{2}, 1.41 \times 10^{3})$	27	8.1%
^{226}Ra	5.29×10^{3}	2.03×10^{3}	$(3.31 \times 10^{3}, 7.28 \times 10^{3})$	$(3.41 \times 10^{3}, 7.47 \times 10^{3})$	4	1.2%
^{228}Ra	1.45×10^{3}	-	-	1.45×10^{3}	1	0.3%
^{228}Th	1.06×10^{4}	2.40×10^{3}	$(7.28 \times 10^{3}, 1.38 \times 10^{4})$	$(8.91 \times 10^{3}, 1.23 \times 10^{4})$	2	0.6%
^{235}U	-	-	-	-	-	-
^{238}U	7.01×10^{3}	8.39×10^{3}	$(-2.49 \times 10^{3}, 1.65 \times 10^{4})$	$(2.12 \times 10^{3}, 1.67 \times 10^{4})$	3	0.9%

[a] Based on number of samples above MDC, except in the case of ^{40}K, ^{60}Co, and ^{137}Cs, n=333 was used.
[b] Minimum Detectable Concentration.

Table 3.2. Descriptive Statistics for Duff Samples.

Duff Radionuclide Activity						
Radionuclide Isotope	**Mean Activity (pCi/kg)**	**St Dev (pCi/kg)[a]**	**95% CI (pCi/kg)**	**Min, Max (pCi/kg)**	**Number of Samples above MDC[b]**	**% Above MDC[b]**
^{7}Be	1.92×10^{3}	1.33×10^{3}	$(9.37 \times 10^{2}, 2.91 \times 10^{3})$	$(4.87 \times 10^{2}, 4.71 \times 10^{3})$	7	2.9%
^{40}K	1.14×10^{3}	2.07×10^{3}	$(8.79 \times 10^{2}, 1.41 \times 10^{3})$	$(-9.14 \times 10^{3}, 1.59 \times 10^{4})$	40	16.8%
^{60}Co	2.95×10^{1}	1.17×10^{2}	$(1.47 \times 10^{1}, 4.43 \times 10^{1})$	$(-3.51 \times 10^{2}, 8.35 \times 10^{2})$	0	0.0%
^{137}Cs	6.36×10^{2}	4.32×10^{2}	$(5.82 \times 10^{2}, 6.91 \times 10^{2})$	$(-1.29 \times 10^{1}, 3.03 \times 10^{3})$	198	83.2%
^{208}Tl	2.00×10^{2}	1.60×10^{2}	$(2.44 \times 10^{2}, 1.55 \times 10^{2})$	$(3.57 \times 10^{1}, 9.39 \times 10^{2})$	50	21.0%
^{212}Pb	4.34×10^{2}	2.72×10^{2}	$(3.83 \times 10^{2}, 4.84 \times 10^{2})$	$(7.20 \times 10^{1}, 1.58 \times 10^{3})$	111	46.6%
^{214}Pb	4.87×10^{2}	3.45×10^{2}	$(4.20 \times 10^{2}, 5.55 \times 10^{2})$	$(1.01 \times 10^{2}, 1.91 \times 10^{3})$	101	42.4%
^{212}Bi	1.28×10^{3}	1.18×10^{3}	$(5.07 \times 10^{2}, 2.04 \times 10^{3})$	$(5.52 \times 10^{2}, 4.29 \times 10^{3})$	9	3.8%
^{214}Bi	4.94×10^{2}	3.14×10^{2}	$(4.17 \times 10^{2}, 5.71 \times 10^{2})$	$(1.32 \times 10^{2}, 1.86 \times 10^{3})$	64	26.9%
^{226}Ra	3.31×10^{3}	2.59×10^{3}	$(1.24 \times 10^{3}, 5.39 \times 10^{3})$	$(1.14 \times 10^{3}, 8.18 \times 10^{3})$	6	2.5%
^{228}Ra	5.42×10^{2}	2.72×10^{2}	$(3.88 \times 10^{2}, 6.96 \times 10^{2})$	$(2.27 \times 10^{2}, 9.51 \times 10^{2})$	12	5.0%
^{228}Th	2.51×10^{3}	-	-	2.51×10^{3}	1	0.4%
^{235}U	5.44×10^{2}	4.12×10^{2}	$(-2.78 \times 10^{1}, 1.11 \times 10^{3})$	$(2.52 \times 10^{2}, 8.35 \times 10^{2})$	2	0.8%
^{238}U	9.01×10^{3}	9.89×10^{3}	$(-4.70 \times 10^{3}, 2.27 \times 10^{4})$	$(2.01 \times 10^{3}, 1.60 \times 10^{4})$	2	0.8%

[a] Based on number of samples above MDC, except in the case of ^{40}K, ^{60}Co, and ^{137}Cs, n=238 was used.
[b] Minimum Detectable Concentration.

Table 3.3. Sign Test Table for ^{7}Be, ^{60}Co, ^{40}K, and ^{137}Cs.

Radionuclide	Litter (X_1)[a]	Duff (X_2)[b]	$\hat{p}$ [c]	Z statistic[d]	p-value[e]
^{7}Be	62	2	0.97	13.29	**<0.0001**
^{60}Co	87	144	0.43	-1.90	0.0569
^{40}K	78	123	0.39	-3.17	**0.0015**
^{137}Cs	18	183	0.09	-11.64	**<0.0001**

[a] Frequency at which duff activities exceed litter activities among paired samples.
[b] Frequency at which litter activities exceed duff activities among paired samples.
[c] Proportion of paired samples where duff activity exceeds litter activity.
[d] Test statistic under the null hypothesis.
[e] p-value < 0.05 is significant.

Table 3.4. Kriging Parameters and Corresponding Mean Concentrations, Standard Error of the Mean, Degrees of Freedom, *p*-Values, and Chi-Squared Values for ^{7}Be, ^{40}K, and ^{137}Cs Litter and Duff Samples.

Parameter	Radionuclide (Litter, Duff)[a]		
	^{7}Be[b]	^{40}K	^{137}Cs
Range (km)	5.92×10^{0}, 5.69×10^{-1}	6.57×10^{1}, 3.33×10^{4}	2.00×10^{0}, 1.63×10^{0}
Nugget (pCi/g)^2	2.08×10^{0}, 1.2×10^{-1}	3.38×10^{0}, 4.32×10^{0}	2.44×10^{-2}, 1.15×10^{-1}
Partial Sill (pCi/g)^2	3.06×10^{-1}, 0	1.26×10^{-1}, 1.34×10^{1}	2.58×10^{-2}, 8.04×10^{-2}
Mean (pCi/kg)	1.11×10^{3}, 3.34×10^{2}	7.17×10^{2}, 1.15×10^{3}	2.66×10^{2}, 6.45×10^{2}
SE (pCi/kg)	1.33×10^{2}, 2.28×10^{1}	2.80×10^{2}, 3.66×10^{3}	2.06×10^{1}, 4.03×10^{1}
Degrees of Freedom	2, 1	2, 2	2, 2
X^2	9.53, 0	0.83, 0.07	82.35, 25.11
***p* -value**	**0.0085**, 1.0000	0.6611, 0.9644	**<0.0001**, **<0.0001**

Note: *Range (α)*: distance beyond which there is little or no correlation. *Nugget (c_0)*: independent error or microscale variation at spatial scales too fine to detect. *Partial sill (c_1)*: difference between the nugget and the sill. *p-value* < 0.05 is significant.

[a] Litter values are represented first while duff values are presented second.

[b] As individual MDC values were not provided in the lab reported results, a soil/sediment generic MDC of 285 pCi/kg (retrieved from SRS Environmental Report, 2004) was used for spatial correlation calculations for all below detect values (in the case of ^{7}Be).

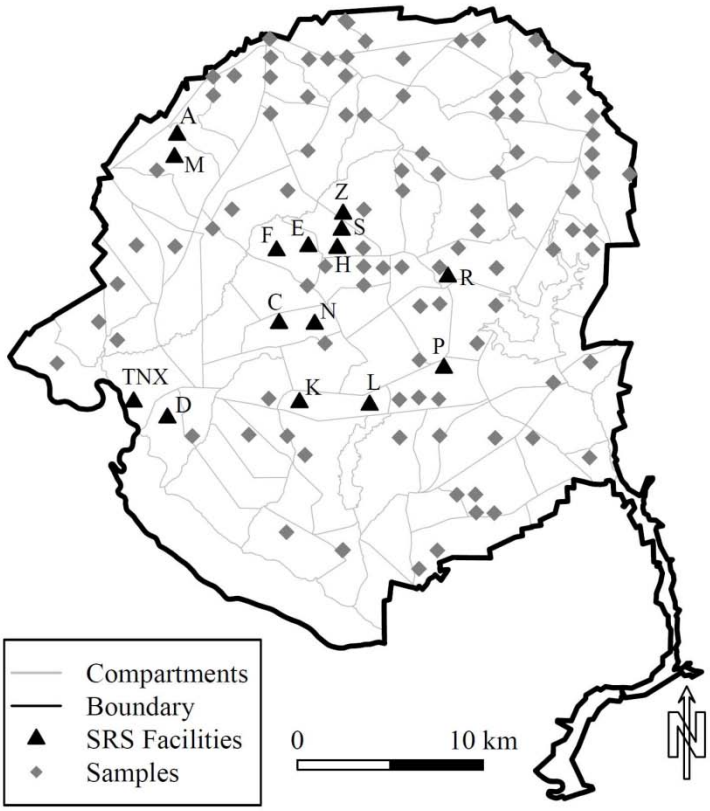

Fig. 3.1. Litter and Duff Samples (Forest Inventory Sample Sites) across Savannah River Site with Plotted SRS Facilities. *Compartments* refer to forest management partitions across SRS. *Boundary* refers to the SRS administrative perimeter. *SRS facilities* refer to areas that have released and/or had the potential to release radionuclides (ATSDR, 2007; Carlton, 1999) and thus are identified as major nuclear production facilities and reactors at SRS (ATSDR, 2007), hence:

- C, K, L, P and R—areas with past operating nuclear reactors;
  - P-Area also houses a coal-fired power plant along with coal storage and disposal piles (USEPA, 2011)
- F and H—nuclear processing and separation areas;
- A and M—fuel fabrication areas;
  - A-Area also consists of coal storage and disposal piles (USEPA, 2011)
- E, S and Z—general separation and waste management areas;
- N—storage of construction materials area;
- D—past heavy water reprocessing area, also houses a coal-fired power plant since its construction in 1952 (ATSDR, 2007; USEPA, 2011), and;
- TNX—radionuclide recovery area.

Samples refer to Forest Inventory sample sites where litter and duff were collected.

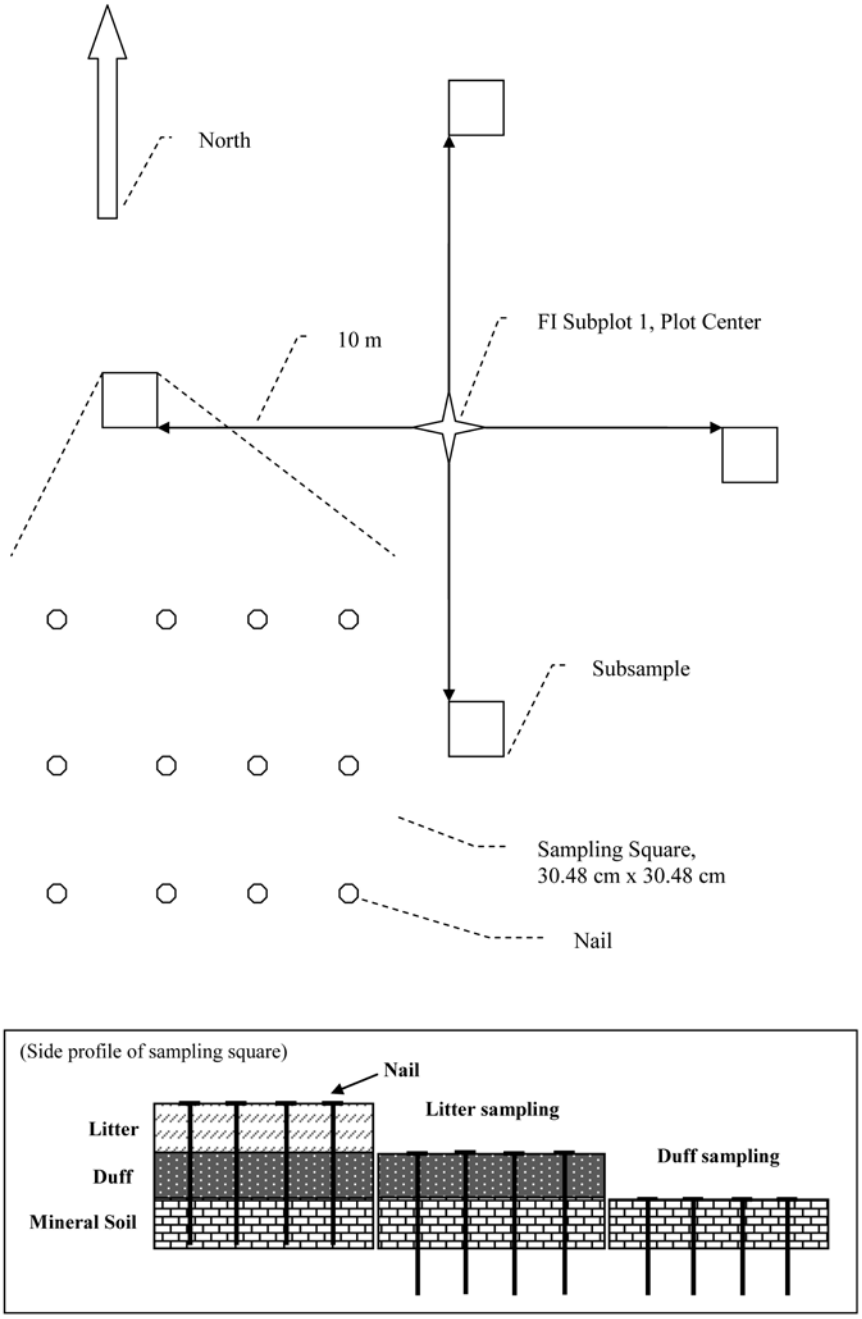

Fig. 3.2. Typical Sample Point Layout.[a]

[a] Adopted and modified from Maier et al., 2004.

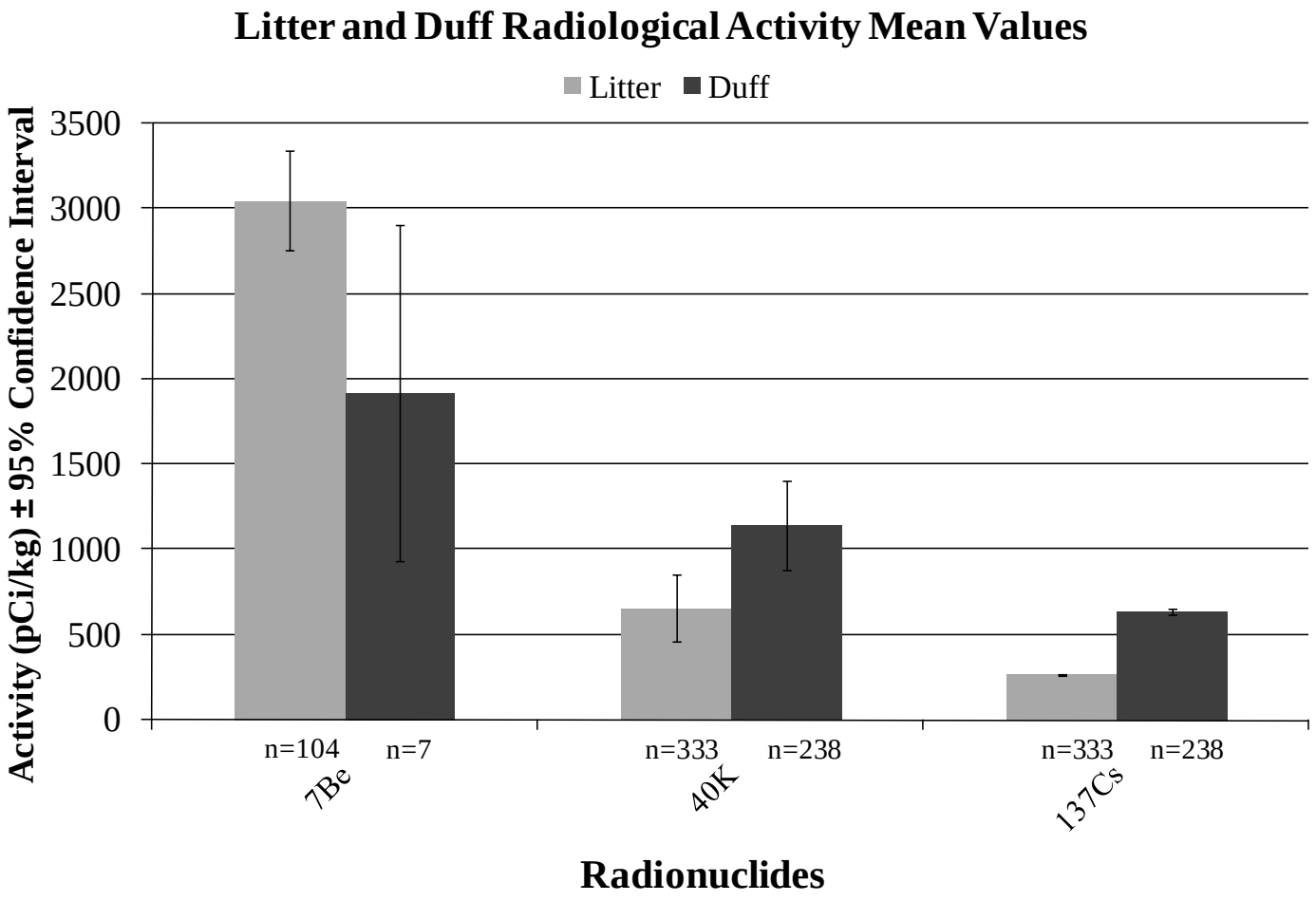

Fig. 3.3. Litter and Duff Mean Radiological Activities for ^{7}Be, ^{40}K, and ^{137}Cs.

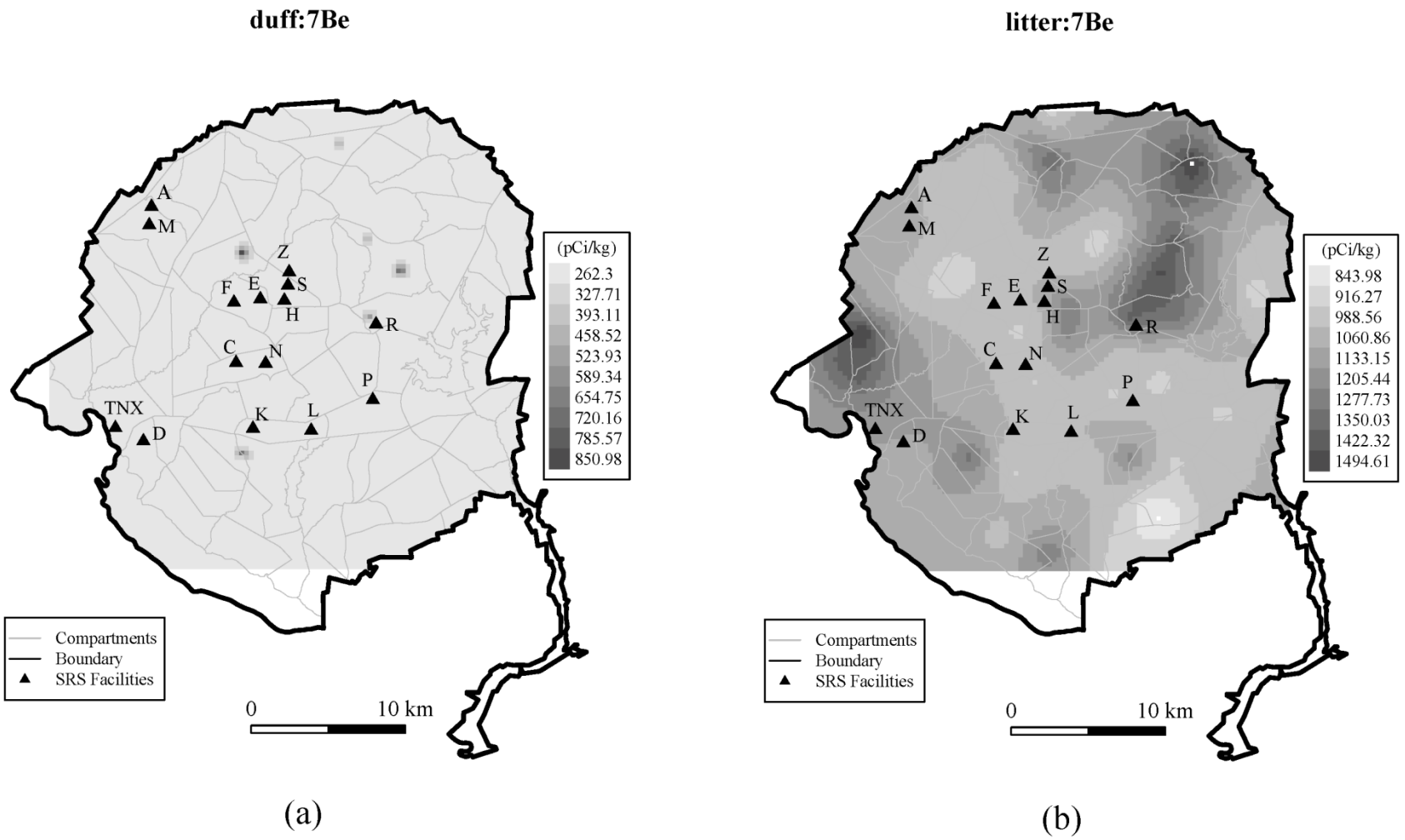

Fig. 3.4. Continuous Surface Maps of Radionuclides (^{7}Be, ^{40}K, ^{137}Cs) Generated using Ordinary Kriging.
Note: Maps are derived based on litter and duff sampling locations (Forest Inventory sample sites [Fig. 1] : ◆) and not *SRS facilities*. The 15 plotted *SRS facilities* (A, C, D, E, F, H, K, L, M, N, P, R, S, TNX, and Z) are defined in Fig. 1. Map contours are displayed using 10 equal intervals a cross final model predictions. Contour intervals were taken from the minimum and maximum values of the data for each radionuclide (^{7}Be, ^{40}K, and ^{137}Cs). **(a) ^{7}Be Duff Map.** No significant spatial correlation exists (p=1.000; n=7) due to small sample size above minimum detectable concentration. **(b) ^{7}Be Litter Map.** Spatial correlation is significant (p=0.0085; n=104).

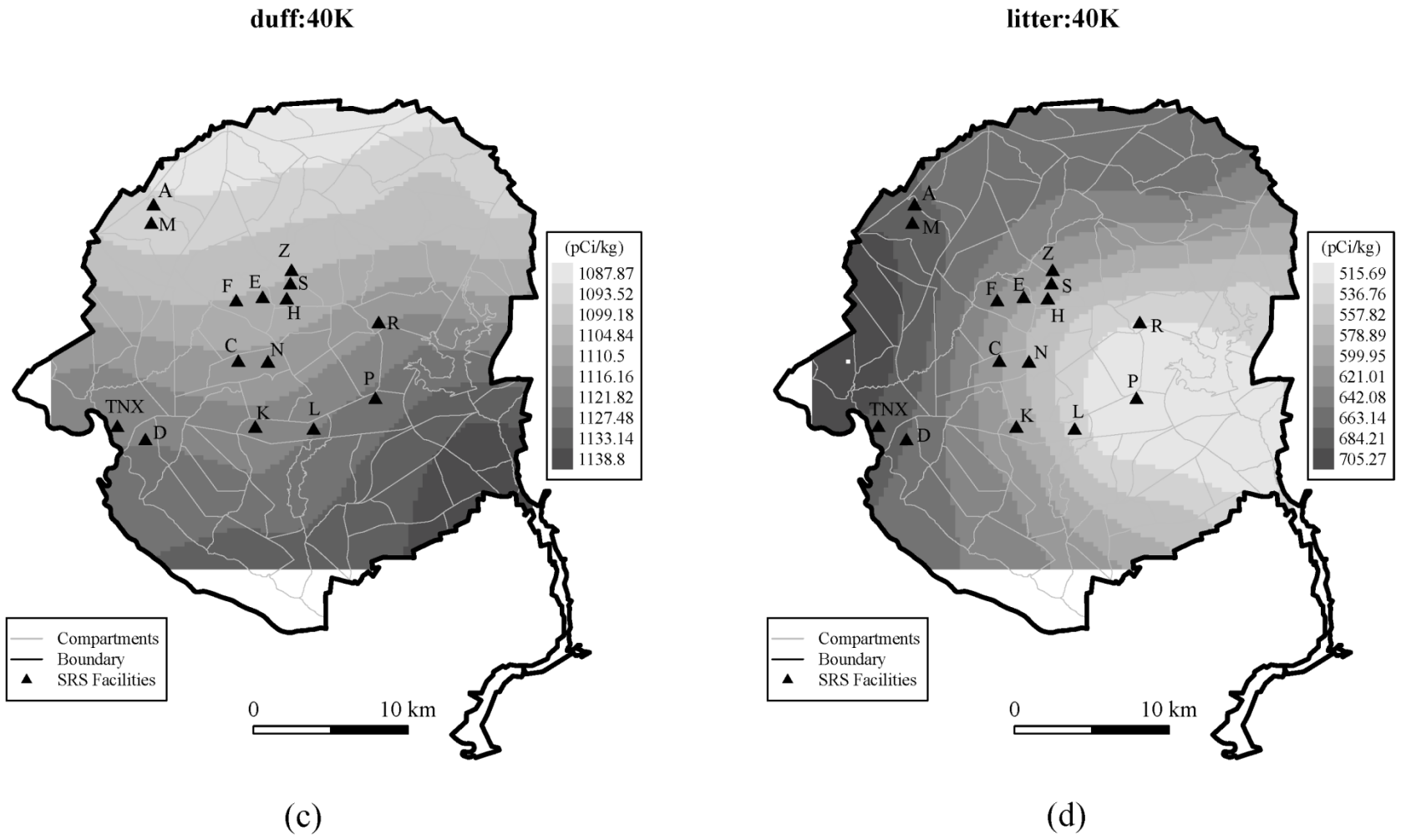

Fig. 3.4. (Cont'd) Continuous Surface Maps of Radionuclides (^{7}Be, ^{40}K, ^{137}Cs) Generated using Ordinary Kriging.
(c) ^{40}K Duff Map. Spatial correlation is insignificant (p=0.9644; n=238). **(d) ^{40}K Litter Map.** Spatial correlation is insignificant (p=0.6611; n=333).

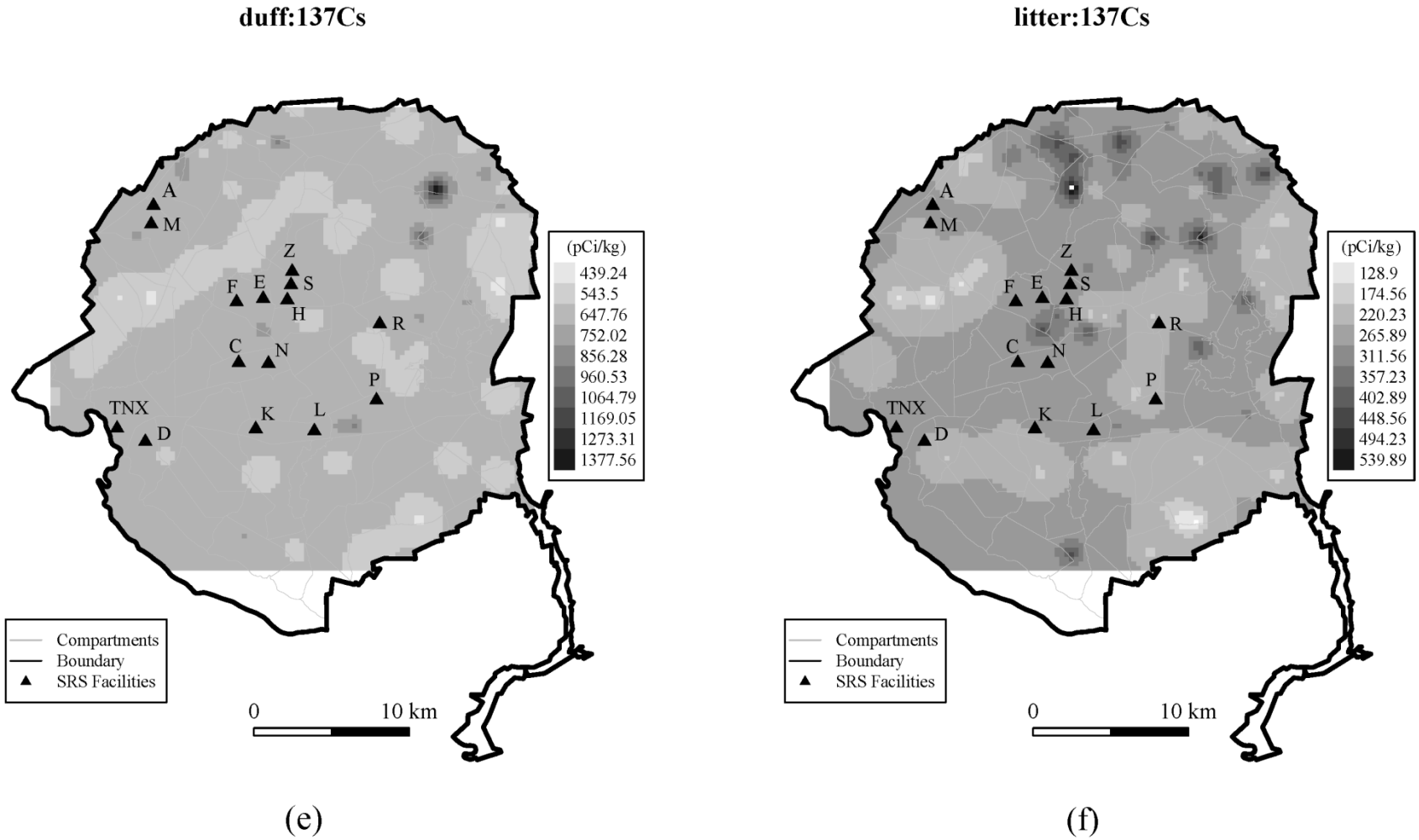

Fig. 3.4. (Cont'd) Continuous Surface Maps of Radionuclides (^{7}Be, ^{40}K, ^{137}Cs) Generated using Ordinary Kriging.
(e) ^{137}Cs Duff Map. A significant spatial correlation exists (p<0.0001; n=238). **(f) ^{137}Cs Litter Map**. A significant spatial correlation exists (p<0.0001; n=333).

PART 2

PRELIMINARY STUDY OF INFLAMMATORY EFFECTS OF WOOD SMOKE EXPOSURE AMONGST WILDLAND FIREFIGHTERS

CHAPTER 4

LITERATURE REVIEW FOR PART 2

WOOD SMOKE EXPOSURE AND OVERVIEW OF ASSOCIATED HEALTH EFFECTS

Several hundred individual compounds including many health damaging pollutants have been detected in wood smoke of which include carbon monoxide, aldehydes, polycyclic aromatic hydrocarbons (PAH), monoaromatics, methoxyphenols, quinones, trace metals, respirable particulate matter and highly reactive free radicals (Larson and Koenig 1994; Naeher et al. 2007). Particulate matter (PM) and carbon monoxide (CO) are shown to be the primary inhalation hazard components of wood smoke (Adetona et al., 2011; Reinhardt et al. 2000). Within the literature, there has been various documented adverse health outcomes related to wood smoke exposure. Briefly, PM exposure has been shown to cause increased respiratory symptoms in subjects (irritation of the airways, coughing, or difficulty breathing), inflammation, decreased lung function, aggravated asthma, development of chronic bronchitis, irregular heartbeat, nonfatal heart attacks, and even premature death in people with heart or lung disease (Moore et al. 2006; Naeher et al. 2007). CO is known to cause hypoxia in the body tissue and in acute exposure instances can cause causes headache, fatigue, nausea, dizziness, neurological effects, hypotension, lethal arrhythmias, and electrocardiographic changes (Raub et al. 2000).

A review on previous studies shows direct adverse health outcomes to PM and CO exposure in population based human and chamber studies (Dockery and Pope, 1994). Epidemiology studies have linked exposure to ambient air pollution and ambient wood smoke to increased pulmonary diseases and mortality in the general population (Dockery et al., 1993;

Moore et al., 2006; Sastry, N. 2002; Schwartz J. 1990). For instance, a population based study found a relationship between increases in wildfire occurrences in British Columbia with increases in physician visits for respiratory diseases in nearby cities (Moore et al. 2006). $PM_{2.5}$ and PM_{10} peak levels, six days after initial fire occurrence, were 200 $ug \cdot m^{-3}$ and 250 $ug \cdot m^{-3}$, respectively (Moore et al. 2006). After severe forest fires in Southeast Asia 1997, all cause mortality increased by 19% in highly polluted areas (Sastry, N. 2002). Smoke haze from the fires lasted from July to December 1997, and reached a peak ambient air pollution concentration of 930 $ug \cdot m^{-3}$ (Sastry, N. 2002). In a study investigating the effects of air pollution on mortality in several metropolitan cities in the United States, mortality was associated with fine particulates where the adjusted mortality-rate ratio for most polluted cities compared to least polluted was 1.26 (95% Confidence Levels [CL]: 1.08, 1.47) (Dockery et al., 1993).

OCCUPATIONAL WOOD SMOKE EXPOSURE

Wildland firefighters around the United States can be exposed to high levels of wood smoke and associated pollutants due to the nature of their job and extended exposure periods throughout the year (Reinhardt and Ottmar, 2004). Frequency of exposure is inadvertently high and workdays may last well over the normal 8-hour work shift (Reinhardt and Ottmar, 2004). Self-contained breathing apparatuses are typically not regularly worn nor are they feasible during wildland firefighting because of the high physical demand and nature of work (Naeher et al. 2007).

Both respirable particulates, $PM_{3.5}$ (particles with a median aerodynamic diameter of 3.5 or 4 micrometers), and CO have been measured at levels above recommended occupational standards to wood smoke in wildland firefighter studies (Reinhardt and Ottmar, 2004). Reinhardt and Ottmar (2004) monitored firefighters for wood smoke exposure during wildfires and firefighters working at prescribed burns (intentionally lit fires) in Washington, Oregon, Idaho, California, and Montana. With work shifts averaging 11 hours, mean cross-shift $PM_{3.5}$

exposure was 500 $\mu g \cdot m^{-3}$ (Standard deviation [SD]: 2,000 $\mu g \cdot m^{-3}$) and 630 $\mu g \cdot m^{-3}$ (SD: 1,700 $\mu g \cdot m^{-3}$) at wildfires and prescribed burns, respectively (Reinhardt and Ottmar, 2004). It should be noted that the United States Environmental Protection Agency national ambient air quality standard gives an allotted 35 $\mu g \cdot m^{-3}$ for $PM_{2.5}$ and 9 ppm during a twenty-four hour period (USEPA, 2008). Although Occupational Safety and Health Administration's (OSHA) 8-hour occupational permissible exposure limits (PEL) are 5000 $\mu g \cdot m^{-3}$ and 50 ppm for respirable particulates for CO, respectively, Reinhardt and Ottmar (2004) found that firefighters' peak exposure can reach above these standards.

Similar levels to wood smoke exposure have been seen in indoor environments in developing countries where primary sources of fuel for cooking and heating is wood and biomass (Fullerton et al., 2008; Bruce et al, 2000). Inadequate ventilation systems and prolonged cooking over open fires indoors create ideal conditions for high levels of wood smoke exposure (Bruce et al, 2000). Such exposure may increase the risk of developing chronic obstructive pulmonary disease (COPD) or acute respiratory infections (Bruce et al., 2000).

WOOD SMOKE EXPOSURE AND INFLAMMATION

Inflammation can be an adverse health outcome due to wood smoke exposure. Studies have suggested that wood smoke exposure leads to acute airway inflammation (Nordenhall et al., 2000; Swiston et al., 2008). Specific acute responses to particulate matter are thought to induce inflammation (Swiston et al, 2008) of which is a likely key component in mediating adverse effects on the cardiovascular system (Donaldson et al. 2005). Inflammation in the lung (local) could lead to systemic inflammation (Greven et al., 2011; Donaldson et al, 2005). Local and systemic inflammation are both identifiers with patients who have COPD (van Eeden et al., 2008). Inflammation may be a key player in the associations found between particulate air pollution and

coronary events (Ruckerl et al., 2006). Additionally, in-vitro studies show that wood smoke particles can have influential effects on inflammatory biomarkers like TNF-α and other cytokines (Myatt et al., 2011; Kocbach et al. 2008). In a study looking at markers of inflammation in rat and human alveolar cells exposed to $PM_{2.5}$ obtained from prescribed burns and urban air, TNF-α released from dendritic cells and alveolar macrophages had increased greatest when exposed to fire-related $PM_{2.5}$ compared to other samples (rural ambient, indoor, and outdoor air samples) (Myatt et al., 2011). Moreover, fire-related $PM_{2.5}$ was highly correlated with increases in TNF-α production (Myatt et al., 2011).

Inflammatory Biomarkers

Multiple cytokines and related immunological proteins are involved in the inflammatory response in the body. Chemokines (i.e. Interleukin-8 [IL-8]) and cytokines (i.e. interleukin-6 [IL-6], interleukin1β [IL-1β], and Tumor Necrosis Factor-α [TNF-α]) are both responsible for the cell-to-cell communication during an inflammatory response. At the tissue site, these proteins recruit leukocytes to which were initiated by cytokine-induced expression of adhesion molecules (Serhan et al., 2010). IL-6, IL-8, IL-1β, and TNF-α are commonly studied circulating biomarkers of inflammation (Swiston et al., 2008; Greven et al., 2011; van Eeden et al., 2005). Several studies have looked at inflammatory Reponses in relationship to wood smoke exposure. For instance, after wood smoke exposure (as measured with CO as a surrogate of PM) IL-6 increased in wildland firefighter blood samples collected via peripheral venopuncture (Swiston et al., 2008). Another study observed that perceived wood smoke exposure was positively associated with a change in IL-8 concentrations (Graven et al., 2011).

Cellular adhesion molecules (Inter-Cellular Adhesion Molecule 1 [ICAM-1] and Vascular Cell Adhesion Molecule-1 [VCAM-1]) have also been studied biomarkers of

inflammation (van Eeden et al., 2005). They are involved in the binding with other cells or extracellular matrix during cell adhesion. Cellular adhesion molecules can be significantly increased in the presence of cytokines (i.e. TNF-α, IL-6, IL-1β) (Hubbard and Rothlein, 2000; Yatera et al., 2008). Research has shown possible associations between cellular adhesion molecules and wood smoke exposure. A study chamber study using Watanabe rabbits, observed that ICAM-1 and VCAM-1 expression increased after exposure to PM_{10} (ambient particulates < 10 μm in diameter) (Yatera et al., 2008).

Furthermore, acute phase proteins such as C-reactive protein (CRP) and Serum Amyloid A (SAA) have been used to measure inflammation in the body (Skogstrand et al, 2008; Badolato et al., 1994). Acute phase proteins are proteins whose plasma concentrations either increase or decrease in response to an inflammatory response and are downstream of cytokine production (Gabay and Kushner, 1999). CRP is a commonly measured biomarker of systemic inflammation and is one of the most studied in relation to cardiovascular disease (van Eeden and Sin, 2008).

DRIED BLOOD SPOT

Dried blood spot (DBS) technique has been used to be an effective method to measure circulating concentrations of IL-6 and IL-8 and other inflammatory cytokines (Parker and Cubitt, 1999; Skogstrand et al., 2008). Benefits of using DBS include the efficiency and ease of sample collection, transportation, storage, and minimal costs. DBS has been used in previous epidemiological studies (Parker and Cubitt, 1999; Skogstrand et al. 2008) and is less invasive than other blood collection techniques (i.e. venopuncture). When compared with serum or plasma collected using venopuncture (via intravenous processes), inflammatory biomarker concentrations tend to be lower on average (Brindle et al., 2010). For instance, Brindle et al. (2010) observed CRP in collected serum was on average 1.6 times (SD: 0.37) higher than in DBS

samples. Nonetheless, DBS may be used as a relevant technique to decipher cross-work shift changes (pre-work shift compared to post-work shift) within a study population. This research seeks to utilize a cost-effective approach to collect repeated blood measurements, where methods such as venopuncture may be very discomforting for the subject.

STUDY LOCATION: SAVANNAH RIVER SITE

Within its 800 square kilometers border, Savannah River Site (SRS), a National Environmental Research Park located near Aiken, South Carolina, comprises of forested land and other operational facilities. Due to high profile operational facilities and because most of the SRS is forested (approximately 80%), the United States Fire Service routinely conducts prescribed burns onsite to control for any natural wildfire occurrences and for ecological benefits (Kilgo and Blake, 2005; Reinhardt et al., 2000). Prescribed burning is the intentional application of fire to land or forested areas under particular forest fuel and weather conditions (Carter and Foster, 2003). In a comprehensive study looking at firefighters working at prescribed burns versus wildland firefighting in Western United States, higher levels of exposure to wood smoke were seen amongst firefighters performing prescribed burning compared to wildland firefighting excursions (Reinhardt and Ottmar, 2004). As previously mentioned, firefighters at wildland firefighting excursions had a mean cross-shift $PM_{3.5}$ exposure of 500 $\mu g \cdot m^{-3}$ (SD: 2,000 $\mu g \cdot m^{-3}$) while those firefighters working at prescribed burns had 630 $\mu g \cdot m^{-3}$ (SD: 1,700 $\mu g \cdot m^{-3}$) (Reinhardt and Ottmar, 2004).

OBJECTIVES OF RESEARCH

In order to gain further insight on wood smoke exposure on inflammation, a study was conducted to investigate changes in multiple cytokines in a healthy occupationally exposed population. With an eye towards reducing exposure to wood smoke to attenuate possible health

consequences, there is still much to be learned about the possible short and long-term health effects of wood smoke.

The objective of this research is to further characterize wood smoke exposure and associated adverse health outcomes by identifying inflammatory responses, using DBS technique, in wildland firefighters working at prescribed burns from Southeastern region of the United States at SRS, Aiken, South Carolina during the spring of 2011. It is hypothesized that wildland firefighters will have higher concentrations of circulating inflammatory biomarkers (i.e. cytokines) post occupational exposure to wood smoke compared to pre exposure to wood smoke during prescribed firefighting. This research provides preliminary data on inflammatory biomarker concentrations collected using DBS technique in a field setting where venopuncture is impractical.

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CHAPTER 5

PRELIMINARY STUDY OF INFLAMMATORY EFFECTS OF WOOD SMOKE EXPOSURE AMONGST WILDLAND FIREFIGHTERS[1]

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ABSTRACT

Background/Objective: Wildland firefighters around the United States are occupationally exposed to high levels of wood smoke due to the nature of work. Results from experimental studies show that exposure to wood smoke could induce inflammation. Therefore, a study using dried blood spot (DBS) methodology was conducted to investigate the effect of occupational wood smoke exposure on multiple inflammatory biomarkers in firefighters working at prescribed burns. DBS is a conventional tool for collecting repeated measurements in field studies.

Methods: Twelve United States Forest Service wildland firefighters at the Savannah River Site, South Carolina volunteered to give blood samples at 4 prescribed burns during the months between February to March 2011. Personal real-time and gravimetric $PM_{2.5}$ air sampling and real-time CO monitoring of firefighters was collected alongside 24 paired (pre- and post-work shift) dried blood spot (DBS) samples. Inflammatory biomarker concentrations in DBS samples were measured using the Meso Scale Discovery multi-spot assay system. Linear mixed models were fitted to the data to test whether there were cross-work shift differences in inflammatory markers—IL-1β, IL-8, CRP, SAA, ICAM-1, and VCAM-1.

Results: IL-8 showed a significant cross-work shift difference (p=0.0012; 95% CL: 1.35, 2.13). Concentrations of IL-8, CRP, and ICAM-1 increased in > 50% of samples across work shift. Firefighters who were lighting fires as opposed to other work tasks had the largest cross-work shift increase in IL-8.

Conclusion: A significant cross-work shift increase in IL-8 in DBS was observed in healthy seasonal wildland firefighters working at prescribed burns in the southeastern region of the United States. Further research and collaboration is needed to understand why a dose-response relationship between wood smoke exposure and IL-8 concentrations was not observed.

INTRODUCTION

Wildland firefighters around the United States are occupationally exposed to high levels of wood smoke and associated pollutants due to the nature of work, with oftentimes prolonged occupational exposure to wood smoke due to long work shifts. Typically self-contained breathing apparatuses are neither routinely worn nor feasible during forest firefighting due to the high physical demand. Particulate matter (PM) and carbon monoxide (CO) are the chief inhalation hazards of exposure to wood smoke and occupational exposure to these pollutants is often elevated (Adetona et al., 2011b; Reinhardt et al., 2000). Adverse health effects, including decline in lung function and increased respiratory symptoms have been documented amongst wildland firefighters (Adetona et al., 2011a; Betchley et al., 1997; Jacquin et al., 2011; Liu et al., 1992; Naeher et al., 2007). Wood smoke exposure (specifically PM) induces oxidative stress and systemic inflammation in lung cells (Danielsen et al., 2008; Barregard et al., 2008).

Circulating cytokines (i.e. interleukin-6 [IL-6], interleukin-8 [IL-8], and interleukin-1β [IL-1β]) have been used as biomarkers of inflammation (Greven et al., 2011; Swiston et al., 2008; van Eeden et al., 2005). Serum IL-6 and IL-8 increased after wildland firefighter work shifts that involved firefighting (Swiston et al., 2008). Similarly some acute phase proteins (i.e. C-reactive protein [CRP] and Serum Amyloid A [SAA]) have been shown to increase after initiation of inflammatory responses (Skogstrand et al., 2008; Badolato et al., 1994, respectively). CRP and SAA are produced downstream of the release of cytokines (van Eeden et al., 2005). CRP is a commonly measured biomarker of systemic inflammation. It is one of the most studied biomarkers of inflammation in relation to cardiovascular disease (van Eeden and Sin, 2008) and shown to be a predictor of the development of cardiovascular diseases and events (van Eeden and Sin, 2008). A study in Erfurt, Germany looking at early physiologic reactions

characterized by inflammatory biomarkers showed that CRP levels increased in patients with coronary heart disease after one inter-quartile range increase in ambient air pollution (i.e. PM_{10} and $PM_{2.5}$) (Ruckerl et al., 2006). Furthermore, a study looking at experimental exposure to wood smoke particles in healthy humans showed significant increase in SAA after 4 hour wood smoke exposure to 240-280 $\mu g \cdot m^{-3}$ (Andersson et al., 2006). Cellular adhesion molecules (Inter-Cellular Adhesion Molecule 1 (ICAM-1) and Vascular Cell Adhesion Molecule-1 [VCAM-1]) and Tumor Necrosis Factor-α (TNF-α) have also been studied biomarkers of inflammation (van Eeden et al., 2005).

Specific acute responses to wood smoke such as oxidative stress in lung cells, systemic inflammation, and lipid peroxidation (Swiston et al., 2008) are likely precursors and contributors to adverse health outcomes including cardiovascular and respiratory morbidities (Donaldson et al., 2005). Epidemiology studies have linked exposure to ambient and indoor wood smoke to increased respiratory diseases and mortality in the general population. For instance, it has been observed that increase in wildfire occurrences is associated with adverse respiratory effects as measured by increases in emergency room and doctor visits related to such outcomes (Moore et al., 2006). In 1997, all cause mortality increased by 19% in highly polluted areas after severe forest fires in Southeast Asia (Sastry N., 2002).

In order to investigate the effect of occupational wood smoke exposure on systemic inflammation, we investigated changes in multiple cytokines in dried blood spot (DBS) samples collected from wildland firefighters working at prescribed burns in southeastern United States. Dried blood spot technique has been used in previous epidemiological studies (Parker and Cubitt, 1999), and shown to be a potentially effective method to measure the concentrations of IL-6 and IL-8 and other inflammatory cytokines (Skogstrand et al., 2008). It is less invasive than other blood collection techniques with the efficiency and ease of sample collection, transportation and

storage, and minimal costs (Mcdade et al., 2007). It is hypothesized that wildland firefighters will have higher concentrations of circulating blood inflammatory biomarkers post occupational exposure (post-work shift) to wood smoke compared to pre exposure (pre-work shift).

METHODS

Study Location and Population

Savannah River Site (SRS) is classified as a secured United States Department of Energy facility which comprises of forested land and other operational facilities within its 800 square kilometers border. Tree species consist of loblolly/slash pine, longleaf pine, mixed pin and hardwood, and upland hardwood (Ottmar et al., 2007). The United States Fire Service (USFS) routinely conducts prescribed burns at SRS to reduce the probability of the occurrence of natural wildfires and for ecological benefits (Reinhardt et al., 2000; Kilgo and Blake, 2005).

Twelve wildland firefighters employed by the USFS-Savannah River (USFS-SR) were recruited from February to March, 2011 to participate in a study to characterize wood smoke exposure and investigate associated inflammatory effects. The study was reviewed and approved by the University of Georgia Institutional Review Board for the inclusion of human subjects while informed and signed consent was obtained from each volunteered subject prior to study participation.

Blood Sample Collection

DBS samples were collected from 6 firefighters per prescribed burn for 4 burns and on 1 burn day which was cancelled, hereafter referred to as 1 non-burn day (pre-work shift samples only). DBS samples were collected immediately before (pre-work shift) and after (post-work shift) each burn from each firefighter. Pre-work shift DBS samples were collected in the morning between 7:20AM and 9:47AM while post-work shift samples were collected in the

afternoon/evening between 3:05PM and 7:46PM. DBS samples were taken on burn days occurring after a 3 to 9 day break in the burn schedule.

Blood samples were collected on Whatman 903 Protein Saver Cards. Single-use, permanently retracting lancet (BD Genie 366582, 1.5 mm blade, 2.0 mm depth) was used to puncture the subject's finger. Puncture was made on the middle or ring finger of the subject, was cleansed with 70% isopropanol wipes and allowed to dry completely before sampling. The first blood drop was wiped off with a sterile cotton ball to eliminate contamination with excess of tissue fluids. Subsequent drops of blood were immediately added until enough blood was collected in the sampling circle. When feasible, all five sampling circles on a card were filled by subjects' blood drops. Care was taken to not touch the subject's finger on the protein saver card.

Blood samples were allowed to dry overnight in a horizontal position. Once dried, the cards were placed in small low gas-permeable Ziploc bags with a least 2 desiccant packets (4280, Tri-sorb, 2G, 3000/pail) and a humidity indicator card (3HIC125 Moisture Indicator cards) per subject DBS sample card. All bags were placed in another large Ziploc bag with extra desiccants and humidity indicator cards and stored in a -20 degree Celsius freezer at SRS offsite lab until transported to UGA and stored at -80 degrees Celsius before analysis. All DBS samples were sub-sequentially shipped to and analyzed in August, 2011 at the Environmental Protection Agency (EPA) Human Studies Facility, Chapel Hill, North Carolina.

Personal Exposure Monitoring

Personal exposure to CO and $PM_{2.5}$ (particulate matter with aerodynamic diameter≤ 2.5 fractions) were also measured during the study. Exposure was concurrently measured during the work shift for firefighters who gave DBS samples. The exposure monitoring protocol has been described elsewhere (See Adetona O., 2011). Briefly, CO was measured in real-time using

Dräger Pac III single gas monitors (Dräger Safety Inc., Pittsburgh, PA). $PM_{2.5}$ was measured both in real-time using SidePak AM510 personal aerosol monitors (TSI Inc., Shoreview, MN) and gravimetrically using BGI Triplex cyclones (BGI, Inc., Waltham, MA) preloaded with a pre-weighed 37 mm Teflon filters with a 2.0 μm pore size attached to AirChek pump (SKC, Inc., Eighty Four, PA) flown at 1.5 L/min. All monitoring equipment was positioned in the breathing zone of the firefighter. The filters were transported and subsequently weighed using the Cahn C-35 microbalance (sensitivity of ±1.0 μg) according to the United States Environmental Protection specifications (USEPA, 1998) at the Department of Environmental Health Science at the University of Georgia, Athens (UGA).

Questionnaires

Baseline questionnaires were administered to each firefighter to collect information on pre-existing health conditions, allergies, current and past smoking history, age, weight, height, sex, etc. Daily symptom and exposure questionnaires were also administered to the subject at the end of each work shift to obtain data relevant to possible confounding exposures and firefighter estimation of the severity of personal wood smoke exposure. Daily time activity diaries were also used by the firefighters to record work tasks conducted during prescribed burns. Detailed field notes were also taken at the fire line by field investigators observing subject firefighter activities throughout the workday. Two work tasks were identified: "Holding" which involves maintaining the fire within pre-established boundaries and "lighting" which involves the ignition of forest understory. Primary work tasks were assigned to a subject for a given day based on the time worked per task: a task was classified based on ≥75% of the time during a work shift. A third category of work, "lighting/other" was created for work shifts when no task occupied at least 75% of the time of a work shift: all the work shift periods in this category were

spent lighting and conducting other miscellaneous fire duties (i.e. mop-up which involves extinguishing actively smoldering areas).

Inflammatory Biomarker Analyses

DBS samples were analyzed for the following inflammatory biomarkers— IL-1β, IL-6, IL-8, TNF-α, CRP, SAA, ICAM-1, and VCAM-1. The Meso Scale Discovery (MSD) multi-spot assay system was administered in two separate kits to measure IL-1b, IL-6, IL-8, TNF-α and CRP, SAA, ICAM-1, VCAM-1, respectively. Samples were punched from the center of each DBS on Whatman 903 Protein Saver cards (Whatman, Inc., GE Healthcare Bio-Sciences Corp., Piscataway, NJ) using a 6.0mm Harris Uni-Core punch (Whatman, Inc., GE Healthcare Bio-Sciences Corp., Piscataway, NJ). All 6.0 mm diameter punches were eluted overnight in 200 ul of 1 x phosphate buffered saline, 0.05% Tween 20, with shaking, at 4°C. Resultant eluents were assayed according to manufacturer's specifications (Vascular Injury Panel II assay and Human ProInflammatory II 4-plex assay ultra-sensitive kit, MSD, Gaithersburg, MD).

Statistical Analyses

First, intercept only linear mixed models were ran for the log transformed inflammatory biomarker—IL-1β, IL-8, CRP, SAA, ICAM-1, and VCAM-1—concentrations to test whether there were cross-work shift differences (changes) amongst subject firefighters. In other words, we tested that log (Post-work shift) - log (Pre-work shift) was significantly different from zero, or when results were back-transformed, that the Post-work shift / Pre-work shift ratio was significantly different from one. The response variables were the individual cross-work shift differences calculated as the differences between the log transformed post-work shift and pre-work shift inflammatory biomarkers concentrations. Random subject and date effects were included in the models to account for longitudinal within-subject correlation among the data.

Secondly, covariates were individually included in the linear mixed model to test whether cross-work shift differences in inflammatory biomarkers were associated with factors such as work shift exposure to $PM_{2.5}$ and CO, gender, number of burns before sampling, work task, age, BMI, illness status, or allergies.

Logistic regression was used to test if the binominal response (yes/no) which was whether a firefighter had experienced respiratory symptoms during the prescribed burn was dependent on a change in the inflammatory biomarkers from pre- to post-work shift. Odds ratios were calculated.

All inflammatory biomarker concentrations were log transformed before inclusion in the models, and concentrations below the lower limit of detection (LOD) (only in the case of 4 of 56 IL-1β sample concentrations; LOD: 0.18 $pg \cdot mL^{-1}$) were substituted with the LOD divided by the square root of two (Hornung and Reed, 1990). All Il-6 and TNF-α concentrations were below the LOD the (0.26 and 0.37 $pg \cdot ml^{-1}$, respectively) and therefore were not statistically analyzed. The LOD is defined as 2.5 times the standard deviation above the background (Meso Scale Discovery, 2010). Linear mixed models were created using the *PROC MIXED* procedure in SAS (Littell et al., 1996). All statistical analyses were performed in SAS version 9.2 (Cary, N.C.). Statistical significance for all analyses was set at $p < 0.05$.

RESULTS

Firefighters did not note having any pre-existing health conditions (i.e. asthma, immune disorders, etc.). Three (27%) firefighters noted having allergies. Two (18%) firefighters had been former smokers. No participating firefighters were current smokers. The average age in years (± standard deviation) was 28.8 ± 5.0 (Range: 22, 41), while the average body mass index

(BMI) was 26.51 (95% Confidence Limit [CL]: 24.5, 28.5). Ten (83%) subjects were male (one baseline questionnaire is not available for one male subject).

Twenty-three paired DBS samples had corresponding personal $PM_{2.5}$ and personal CO exposure data. The corresponding unadjusted $PM_{2.5}$ geometric mean (95%CL) (n) was 650 $\mu g \cdot m^{-3}$ (510, 828) (23) ranging from 288 to 3260 $\mu g \cdot m^{-3}$, while the unadjusted CO geometric mean was 3.64 ppm (2.64, 5.00) (23) ranging from 1.54 to 19.85 ppm. As a subset of the data collected from Adetona (2011), these values fall within the larger sample size ranges: unadjusted geometric mean (95%CL) (n), where the gravimetric $PM_{2.5}$ was 608 $\mu g \cdot m^{-3}$ (481, 767) (41) and CO was 3.9 ppm (3.2, 4.5) (58) (Adetona, 2011).

A total of 24 paired (pre- and post-work shift) DBS samples were collected on 4 burn days and 6 pre-shift samples were collected on 1 non-burn day (hence, n=30 pre-work shift and n=24 post-work shift DBS samples). Descriptive statistics of pre- and post-work shift inflammatory marker concentrations for IL-1b, IL-8, CRP, SAA, ICAM-1, and VCAM-1 are presented in Table 5.1. Concentrations of IL-8, CRP, and ICAM-1 increased in > 50% of samples from pre- to post-work shift (Table 5.1).

Fig. 5.1 displays the linear mixed model derived cross-work shift differences (back-transformed) for the above statistically analyzed inflammatory biomarkers; IL-8 was the only biomarker with Post-work shift / Pre-work shift ratio statistically different from 1 (p=0.0012). The linear mixed model derived geometric Post-work shift / Pre-work shift ratio for IL-8 was 1.70 $pg \cdot mL^{-1}$ (95%CL: 1.35, 2.13).

Work task was associated with IL-8 (p=0.0186) (Fig. 5.2). No other association between the changes in inflammatory biomarker concentrations and covariates including measured exposures were observed. A scatter plot between $PM_{2.5}$ exposure and IL-8 changes across work

shift pictorially displays the lack of association between exposure and inflammatory biomarkers (Fig. 5.3). Firefighters who lighted had the largest cross-work shift increase in IL-8 (Fig. 5.2). There were significant differences between "Holding" vs. "Lighting" (p=0.0122) and "Lighting" vs. "Lighting/Other" (p=0.0431). No significant difference was seen for "Holding" vs. "Lighting/Other" (p=0.8307) (Fig. 5.2).

There was no effect of pre- to post-work shift changes in biomarkers on whether or not a firefighter had any respiratory symptoms. Odds ratios (results not shown) for these relationships were not significantly different from zero.

DISCUSSION

To our knowledge, our study is the first to use dried blood spot technique to measure blood inflammatory biomarker concentrations in wildland firefighters exposed to wood smoke. We propose dried blood spot methodology as a reliable and inexpensive blood collection technique in field project studies where venopuncture collection is not practical or feasible. Our results show lower inflammatory biomarker concentrations compared to other wildland firefighter studies who used venopuncture as the primary means to collect serum or plasma (Swiston et al., 2008; Greven et al., 2011), which is likely due to use of DBS. DBS samples are well known to give lower amounts of circulating inflammatory biomarkers compared to plasma or sera. Brindle et al. (2010) observed CRP in collected serum was on average 1.6 times (standard deviation: 0.37) higher than in DBS samples. Nonetheless, our study found significant elevations observed in IL-8, an acute inflammatory cytokine, post-exposure. Such data is relevant to compare inflammatory endpoint trends in other parallel sample populations.

The observed significant cross-work shift difference in IL-8 is suggestive that such levels of wood smoke exposure induce systemic inflammatory responses and may be consequent upon

pulmonary inflammation among wildand firefighters. Our findings are similar with results from another study that was able to establish baseline measurements and control days (Swiston et al., 2008) and other cross-sectional studies (Greven et al., 2011; Kido et al., 2009) that show that inhalation of wood smoke induces a pulmonary inflammatory response. Swiston et al. (2008) found that cytokine (IL-6 and IL-8) baseline measurements were significantly lower from days when firefighters were exposed to wood smoke. IL-8, a chemokine produced by macrophages and other cell types such as epithelial cells, is a major mediator of the inflammatory response in the lung (Kunkel et al., 1991). It is also highly involved in the recruitment of neutrophils in the lung (Kunkel et al., 1991).

Results show that work task influenced the cross-shift increase observed with IL-8 (Fig. 5.2). Firefighters who lighted had the highest IL-8 response even though their PM and CO exposures were statistically lower than those who performed holding (See Adetona et al., 2011). Firefighters who performed lighting used a flame torch composed of a mixture of lighter fluid (consisting of 3 part diesel and 1 part gasoline) which could have contributed to the larger increase in IL-8 cross-work shift changes compared to those firefighters who performed holding or lighting with miscellaneous work tasks throughout the work day. Acute exposure to diesel exhaust has also been shown to induce increases in IL-8 concentrations (Riedl and Dias-Sanchez, 2005; Salvi et al., 2000).

Cross-work shift change in IL-8 was not associated with exposure. Our findings were consistent with Swiston et al. (2008) as they did not find a relationship between the change in cytokine concentrations and $PM_{2.5}$ as estimated from CO exposure. However, another study found that perceived exposure was positively associated with a change in IL-8 concentrations (Graven et al., 2011). Serum Il-8 levels in municipal firefighters (n=50) were significantly

higher after 24 hours, 1 week and 3 months post-exposure compared to pre-exposure (Greven et al., 2011). However, it should be noted that exposure was estimated by firefighters' self-reported perceived exposure to fire smoke (Greven et al., 2011).

Our results showed no associations between self-reported symptom responses and IL-8 cross-work shift changes. A recent study also observed that acute exposure to fire smoke induces acute neutrophilic airway and long-lasting systemic inflammation in healthy municipal firefighters in the absence of adverse health symptoms such as bronchial hyperresponsiveness (Greven et al., 2011). On the other hand, another study found associations between cytokine changes and symptoms of both upper and lower respiratory tract irritation (Swiston et al., 2008).

We were unable to analyze IL-6 or TNF-α concentrations because all values were below LOD. However, another study using blood serum found significant changes in IL-6 (Swiston et al., 2008). Both IL-6 and TNF-α exhibit diurnal pattern (Liebmann et al., 1998; Sothern et al., 1995) therefore any changes in blood concentrations may likely not be seen until 24 hours post exposure. Our pre and post blood samples were collected within a work shift day, which could explain why all samples were below LOD.

Although no other significant cross-work shift differences were evident in the other measured inflammatory biomarkers, 75% of DBS samples had increase in CRP concentrations from pre to post-work shift and approximately 67% of ICAM-1 post-work shift samples were higher compared to pre-work shift. CRP and SAA are produced downstream from IL-6 production (van Eeden et al., 2005; Uhlar and Whitehead, 1999, respectively), which may explain why no significant change occurred over work shifts. Moreover, previous animal and human experimental chamber studies have found significant blood concentration increases after particulate matter exposure in the following inflammatory biomarkers. CRP and ICAM-1

increased after subjects were exposed to diesel exhaust particles (DEP) (Salvi et al., 1999). While SAA, IL-1β and VCAM-1 also have been shown to increase after exposure to wood smoke (Andersson et al., 2006; van Eeden et al., 2001; van Eeden et al., 2005, respectively).

Limitations

Results herein support the notion that a larger sample size could provide clearer understanding of inflammatory responses observed in wildland firefighters exposed to wood smoke. In addition, to control for diurnal variations in some of the inflammatory markers (such as IL-6), post-work shift samples could be taken the following morning (16 to 24 hours after exposure). In this study firefighters posed as their own controls, however, control days where pre- and post-work shift samples are taken on non-burn days could help establish baseline measurements. No association was calculated between exposure and the change in IL-8 concentrations; hence, there remains further investigation between such relationships.

CONCLUSION

A significant cross-work shift difference in IL-8 in DBS was observed in healthy seasonal wildland firefighters working at prescribed burns in the southeastern region of the United States. Firefighter work task may have influenced the cross-shift increase observed with IL-8, as firefighters who performed lighting had a larger increase in IL-8 cross-work shift differences compared to those firefighters who performed other work tasks. Although there may be a need to validate DBS technique against more established procedures like venopuncture, the detection of cross-work shift difference in IL-8 using DBS, indicate that this procedure could be used cost effectively in field studies where venopuncture may be impractical, or where repeated measurements are collected and venopuncture may be very discomforting for the subject.

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Table 5.1. Descriptive Statistics for Pre- and Post-Work Shift Inflammatory Biomarker Concentrations.

Inflammatory Biomarker	Pre-Work Shift Concentrations (n=30)			Post-Work Shift Concentrations (n=24)			% (n) Positive [b]
	Arithmetic Mean (95% CLs)[a]	Geometric Mean (95%CLs)[a]	Range	Arithmetic Mean (95% CLs)[a]	Geometric Mean (95%CLs)[a]	Range	
IL-1β (pg·mL^{-1})	0.94 (0.51, 1.38)	0.61 (0.44, 0.84)	(0.13, 5.29)	0.58 (0.30, 0.86)	0.41 (0.29, 0.56)	(0.13, 3.59)	33.3 (8)
IL-8 (pg·mL^{-1})	0.93 (0.81, 1.06)	0.86 (0.74, 1.01)	(0.26, 1.79)	1.67 (1.35, 1.99)	1.49 (1.22, 1.83)	(0.56, 3.70)	91.7 (22)
CRP (ng·mL^{-1})	30.63 (19.72, 41.55)	19.68 (13.61, 28.44)	(2.80, 123.91)	31.63 (19.29, 43.97)	21.07 (14.24, 31.19)	(4.14, 119.36)	75.0 (18)
SAA (ng·mL^{-1})	36.72 (21.17, 52.28)	23.92 (16.85, 33.95)	(4.01, 228.73)	33.92 (22.25, 45.60)	22.71 (14.61, 35.28)	(1.32, 108.56)	33.3 (8)
ICAM-1 (ng·mL^{-1})	6.33 (5.50, 7.15)	5.96 (5.23, 6.79)	(2.87, 12.06)	6.29 (5.56, 7.03)	6.05 (5.36, 6.83)	(3.60, 10.53)	66.7 (16)
VCAM-1 (ng·mL^{-1})	15.16 (13.00, 17.32)	12.99 (9.85, 17.12)	(0.54, 24.92)	14.53 (12.70, 16.36)	13.79 (11.95, 15.92)	(6.91, 23.03)	45.8 (11)

[a] refers to upper and lower 95% confidence limits.
[b] refers to the percentage (number) of samples with higher post-work shift concentrations compared to pre-work shift concentrations.

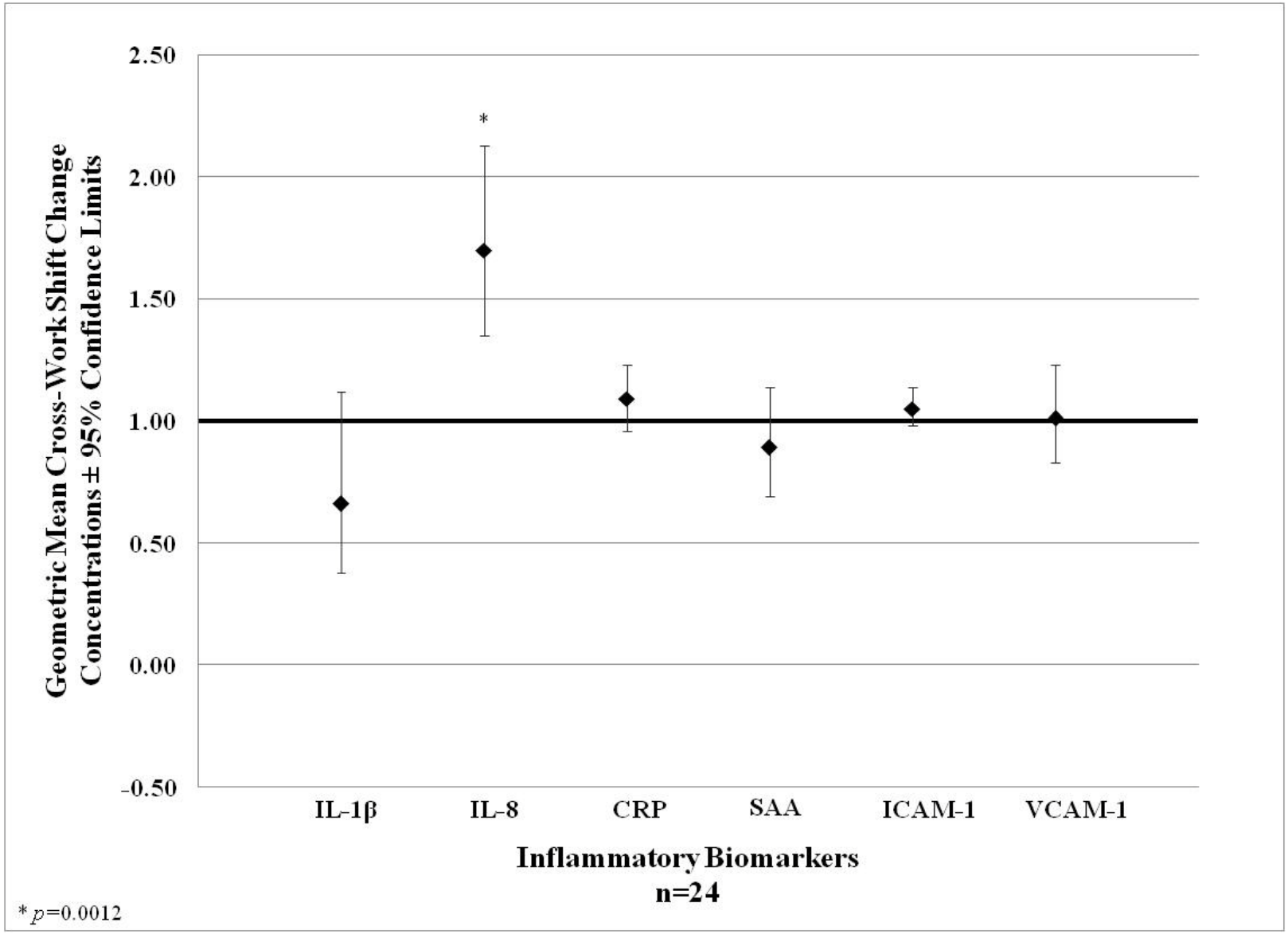

Fig. 5.1. Linear Mixed Model Derived Geometric Mean Cross-Work Shift Changes (Post-Work Shift/Pre-Work Shift Ratios) in Inflammatory Biomarker Concentrations.

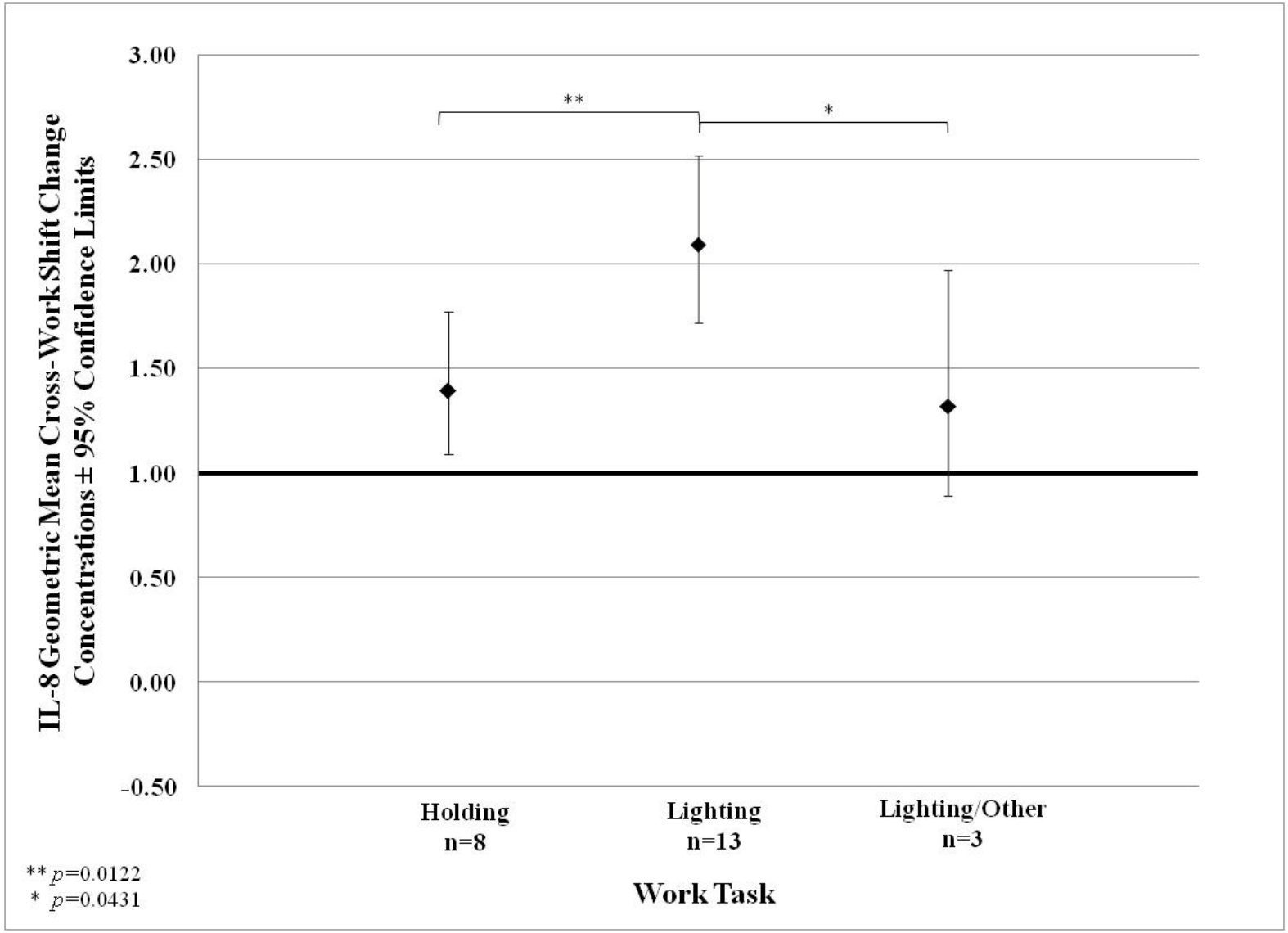

Fig. 5.2. Linear Mixed Model Derived Geometric Mean Cross-Work Shift Changes (Post-Work Shift/Pre-Work Shift Ratios) in IL-8 Concentrations According to Work Task. Note: Work task is defined by ≥ 75% of the time per work shift; Linear mixed model according to work task *p*-value = 0.0186; * refers to test of contrast *p*-values; *p*-value < 0.05 is significant.

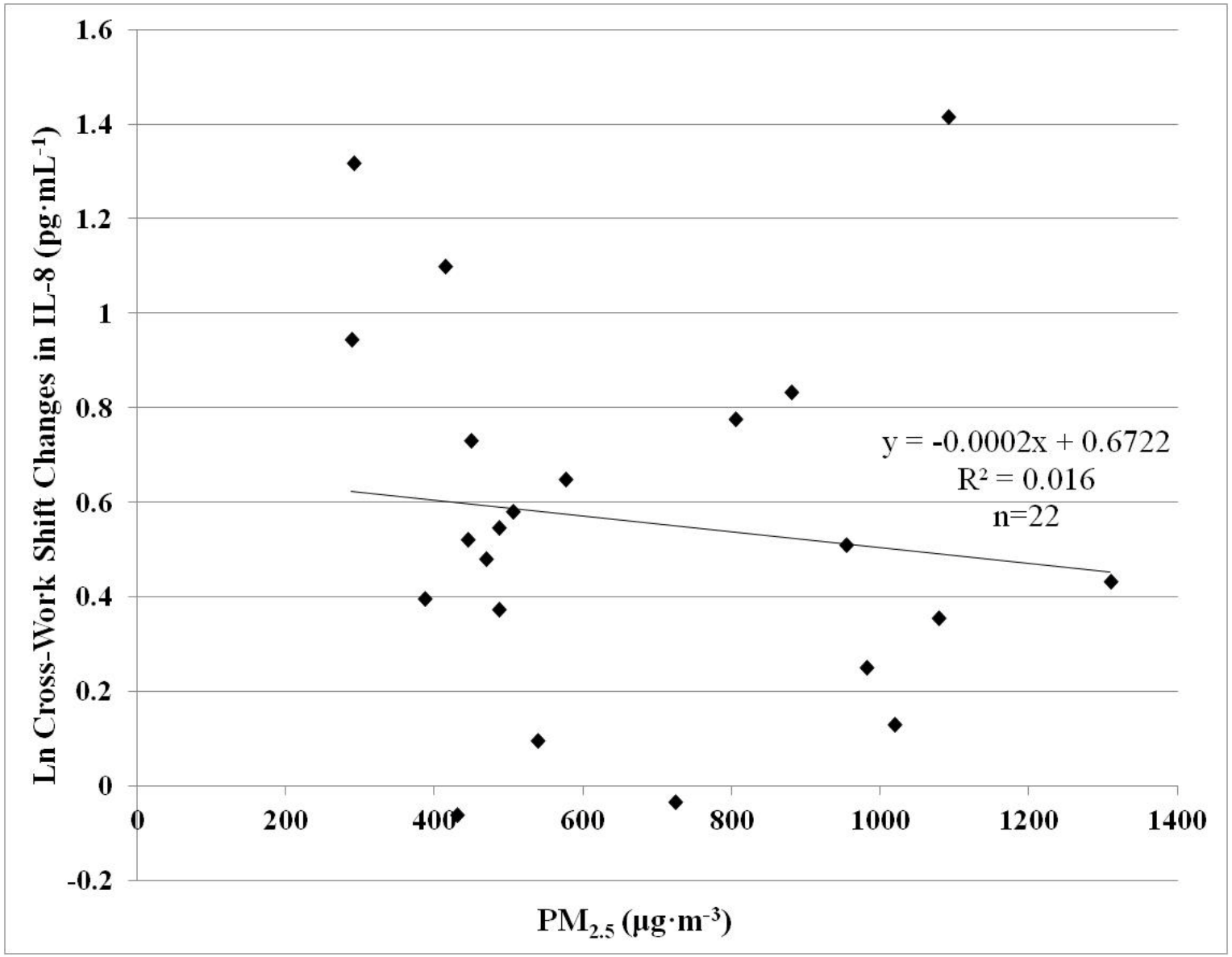

Fig. 5.3. IL-8 Cross-Work Shift Changes Plotted Against $PM_{2.5}$. Note: One potential outlier was removed, hence n=22.

CHAPTER 6

CONCLUSIONS

CLOSING REMARKS FOR PART 1

This study characterized and quantified manmade and natural radionuclide concentrations in forest floor vegetation, litter and duff, at the Savannah River Site (SRS). Spatial analysis via kriging provided a pictorial display of where higher activities were distributed on site. The primary radionuclide of concern, ^{137}Cs, had the highest number of samples reported above minimal detectable concentration in litter and duff samples. Although, ^{137}Cs showed significant spatial correlations in litter and duff samples, spatial trends generated from the kriging parameters do not appear to directly link areas with higher activity concentrations with facilities. These findings supply quantitative and qualitative results to Department of Energy sites which have had past or current radionuclide contamination such as SRS, and thereby may serve as a scientific basis of forest fire prevention on areas where contamination by radionuclides is most high. Future areas of interest include further exploration in the release, fate, and transport of radionuclides found in concurrent soil, litter, and duff material.

CLOSING REMARKS FOR PART 2

This study was a pilot study investigating the effects of occupational wood smoke exposure on inflammatory biomarkers collected via dried blood spot (DBS) technique from wildland firefighters working at prescribed burns. DBS was used to allow for ease of storage and transport, and for collecting repeated measurements from subjects as opposed to the alternative venopuncture technique, which may be upsetting for subjects. A significant cross-

work shift difference in IL-8 in DBS was observed in healthy seasonal wildland firefighters working at prescribed burns in the southeastern region of the United States. Interpretation of this finding is currently unclear because of two overarching limiting factors, i) a dose-response between wood smoke exposure and inflammatory biomarker concentrations was not observed, and ii) no baseline measurements were collected to establish controls for non-exposure days. Collaboration with Environmental Protection Agency's Clinical Research Branch at the Environmental Public Health Division Research Triangle Park, North Carolina is currently underway to understand and best interpret these findings since limited literature is available. Future research includes sampling of personal air monitoring and inflammatory effects of firefighters during similar activity days when firefighters are not exposed to wood smoke constituents in order to establish baseline inflammatory biomarker levels. Next day same time (post 24-hour exposure) blood samples should also be collected in the future to reduce any potential diurnal variations seen in the inflammatory biomarkers.