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Title: CONTAMINANT CONCENTRATIONS IN BURNED CONIFER TREE BARK COLLECTED WITHIN THE LOS ALAMOS NATIONAL LABORATORY

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Contaminant Concentrations in Burned Conifer Tree Bark
Collected Within the Los Alamos National Laboratory

G.J. Gonzales and P.R. Fresquez

Abstract

Immediately after the Cerro Grande Fire of 2000, ponderosa pine (*Pinus ponderosa)* bark ash and surface ash were sampled at three of the 12 stations that are sampled for soils on an annual basis as part of the Environmental Surveillance Program. The three stations were at TA-06 (Two-mile Mesa), TA-15 (R-Site Road East), and TA-16 (S-Site) and were the only routine sampling stations impacted by the fire for which pre-fire data exists. The primary intent was to infer whether conifer trees within the southwest area of the Los Alamos National Laboratory (LANL) might have contributed more contaminants (especially uranium isotopes) to ash than offsite areas. Data are also compared to results from several other similar sampling efforts. Mean onsite concentrations of ^{234}U, ^{235}U, ^{238}U, ^{239}Pu, and ^{241}Am in bark ash were above background (reference) concentrations and mean onsite concentrations of ^{90}Sr and ^{137}Cs were below background concentrations. The relative differences were consistent with duplicate sample analysis by the New Mexico Environment Department. Metal and non-metal trace elements concentrations in bark ash were also relatively low although the TA-16 sample had slightly higher levels of B, Ba, Al, Cr, Cu, Fe, Ni, Sr, Ti, and Zn than the reference sample. There were no detections of organochlorine pesticides nor aroclors in bark ash. In surface ash, the analytes for which onsite concentrations exceeded background concentrations were 1,2,3,4,6,7,8-HpCDD, OCDD, Total HxCDD, and Total HpCDD. This was generally consistent with the analytical results for soil samples taken from the same locations after the fire. No detections of 2,3,7,8-TCDD, the most toxic of the dioxins, were made in any of the samples.

Introduction

The Cerro Grande Fire in May 2000 burned approximately 50,000 acres of conifer forest in New Mexico including about 7,500 acres of forest at the Los Alamos National Laboratory (LANL) (Figure 1). The general public had concerns over the possibility of contaminant transport from windborne ash from LANL during and after the fire. In the weeks shortly after the fire, we measured radioactivity, metals, non-metal trace elements, and organics concentrations in three samples of ponderosa pine bark ash from three mesa-top locations where the fire intensity was severe and where overstory and understory vegetation was collected in 1998 (Gonzales and Fresquez 2000). We also measured metal, non-metal trace element, and organics concentrations in surface ash that accumulated on the ground during the fire. Presumably this ash would represent plant

overstory and understory as well as litter, but it could also have small amounts of soil in it.

Some of the burned areas were known to contain trace amounts of radionuclides and chemicals in soils (Fresquez and Gonzales 2000) and plants (Gonzales et al. 2000). A concern expressed by the general public was that contamination potentially contained in trees and vegetation was released with wind-blown ash that resulted from the burning of these plants. Although samples of airborne particulate were taken during the fire and analyzed for radioactivity from some radionuclides (Kraig et al. 2001), other potential contaminants were not analyzed. We also were interested in knowing how the contaminant levels in the bark ash and surface ash compared to samples taken elsewhere on LANL after the fire or how they compared to other media. The physical forces of a convective fire itself as well as many types of impacts on soil from human activities (the use of bull dozers and other heavy equipment, digging and trenching, walking on soils devoid of vegetation, etc.) during the fire likely loosened soil and subjected it to the forces of wind. This soil would have settled on ground surfaces along with deposited ash. While some of this same soil imbeds in the crevices of the sampled bark when winds are high enough to suspend soil particles, the amount of soil contributing to contamination in tree bark is likely to be much lower than the soil that deposits on ash that lies on the ground surface. While the importance of this is minimal in the larger question of how overall contamination levels may have changed resulting from the fire, the distinction is necessary to address the particular stated concern of radionuclides and radioactivity in the wind-blown ash coming from trees.

Methods

In early June, 2000, ponderosa pine (*Pinus ponderosa)* bark ash and surface ash were sampled at three of the 12 sites that are sampled for soils on an annual basis as part of the Environmental Surveillance Program. The three sites were TA-06 (Two-mile Mesa), TA-15 (R-Site Road East), and TA-16 (S-Site). The sampling sites were most affected by the fire and they are in the vicinity of firing sites at TAs-11, -15, and -36 where munitions are exploded. A background (reference) sample was obtained approximately 3.5 miles upwind and upslope of LANL off of NM State Road 4.

Bark Ash

At each sampling location, subsamples were obtained from four directions (N, S, E, W) radiating outward from the central sampling location that corresponded to long-term soil sampling locations. That is, from the central sampling location we walked north, south, east, and west in a linear direction to the nearest group of ponderosa pine trees. At each of these radial points, we randomly selected five trees for sampling. At breast height, equal amounts of burnt bark was scraped into sterilized beakers using sterile scrapers while wearing polypropylene gloves. A total of 20 subsamples were composited from each site to constitute a sample. Samples were ashed to a consistent weight and submitted for analysis at LANL's Analytical Chemistry Group.

Ash was analyzed for ^{90}Sr using liquid scintillation. Total uranium was analyzed by kinetic phosphorescence analysis. The radionuclides ^{238}Pu, ^{239}Pu, ^{234}U, ^{235}U, ^{238}U, and ^{241}Am were analyzed by alpha spectrometry. ^{137}Cs was analyzed by gamma spectroscopy. Gross alpha (α), beta (β), and gamma (γ) radioactivity were also

analyzed. Silver (Ag), aluminium (Al), arsenic (As), boron (B), barium (Ba), beryllium (Be), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), mercury (Hg), manganese (Mn), molybdenum (Mo) nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), tin (Sn), strontium (Sr), titanium (Ti), thallium (Tl), vanadium (V), Zinc (Zn), and cyanide (CN) were prepared and analyzed following Environmental Protection Agency (EPA) Method SW-846 using cold vapor atomic absorption or trace inductively coupled plasma analysis. Organics (organochlorine pesticides and polychlorinated biphenyls [PCBs]) were analyzed by EPA Method SW8081.

Surface Ash

At each sampling location, relatively deep sources of ground surface ash were identified for sampling. Dioxins and furans were analyzed in a composite sample of surface ash that consisted of equal amounts of ash from the same onsite locations (TA-06 Two-mile Mesa, TA-15 R-Site Road East, and TA-16 S-Site) as the bark ash. A total of 125 individual and total dioxins and furans were analyzed using EPA Method 8290.

Results and Discussion

Bark Ash

Table 1 shows the results of the bark ash analyses for radionuclides at the three onsite and one reference site sampling locations. Concentrations are per unit of ash. Most radionuclides were detected (measured values were above three times the total propagated uncertainty) in both the onsite and offsite samples. ^{238}Pu was not detected in any of the samples. Although mean onsite concentrations of ^{234}U, ^{235}U, ^{238}U, ^{239}Pu, and ^{241}Am were consistently between two and two-and-one-half times higher than the background (reference) sample, similar or higher concentrations in another study (Gonzales et al. 2001) resulted in extremely low doses to humans in a postulated scenario of burning woody material in air curtain destructors resulting in airborne emissions. Mean onsite concentrations of ^{90}Sr and ^{137}Cs were slightly lower than the background concentration. Forty-three of 45 gamma-emitting radionuclides were nondetectable and the two detectable gamma-emitters, ^{7}Be and ^{212}Pb (data not presented), are naturally occurring.

There are several sets of data from other studies (LANL and non-LANL) that can be compared to the results of this study. Some are directly comparable and others less comparable because of differences in sampling method and/or media. One set of comparable data reported by the New Mexico Environment Department consisted of data from duplicate samples of bark taken from our samples from two of the onsite locations (TA-06 and -16). One difference in methods was that they dried the samples of burnt bark whereas we ashed our samples to a stable weight. We do this primarily to concentrate the radionuclides so that they can be more easily detected and to get better confidence in the quantification of activity levels. Ashing our samples also allowed us to compare radioactivity levels to previous studies of radioactivity in vegetation. When comparing the mean for the two sites in common (TA-06 and -16), our results, as expected, were higher for most of the radionuclides when compared to the NMED data (^{90}Sr–0.30 pCi/g, ^{137}Cs–0.17 pCi/g, ^{234}U–0.39 pCi/g, ^{235}U–0.038 pCi/g, ^{238}U–0.69 pCi/g, ^{238}Pu–0.005 pCi/g, ^{239}Pu–0.034 pCi/g, and ^{241}Am–0.025 pCi/g) (NMED 2001), but the

higher values are likely due to greater concentration of the radionuclides in the ashed samples. LANL's Environmental Restoration (ER) Project collected ash and "muck" samples from background canyon locations west of LANL. The primary differences in these samples is that the ER samples include sediment, were collected in canyons as compared to our mesa top samples, and ER samples were dried whereas ours were ashed. Aside from the differences, since the ER samples are background samples they're most comparable to our reference samples. The ER sample means for the radionuclides that we detected (^{90}Sr–2.08, ^{137}Cs–4.39-, ^{234}U–1.38, ^{235}U–0.129, ^{238}U–1.84, ^{238}Pu–0.029, ^{239}Pu–0.037, and ^{241}Am–0.12 pCi/g) (LANL 2000), are all higher than our reference site values, but are in good agreement considering the differences in media. [Note: All radioactivity values except for ^{238}Pu in our reference site sample were "detections".] The ER values for ^{90}Sr, ^{137}Cs, and ^{241}Am were slightly higher than our reference site values and the ER values for ^{234}U, ^{235}U, ^{238}U, ^{238}Pu, and ^{239}Pu were about one order of magnitude higher than our reference site values. In addition to differences caused by different sample preparation, the presence of sediment in the ER samples also likely contributed to the differences.

In late June, 2000, after the fire, samples of burnt bark were taken from three trees in a preliminary study in Mortandad Canyon. Those results were reported in a report on doses that could result from burning Mortandad Canyon bark and wood (Gonzales et al. 2001). Based on differences in radioactivity in soil and sediment between the two sites, it was expected that higher concentrations of the actinides and ^{90}Sr and ^{137}Cs would occur in the Mortandad Canyon samples and that U-isotope radioactivity might be higher in the mesa-top samples (TA-06, TA-15, and TA-16) if affected by the release of depleted uranium from research conducted by DX Division. Considering net (LANL minus background) radioactivity for the two different sets of samples, ^{90}Sr and ^{241}Am were one to two orders of magnitude lower in post-fire mesa-top bark than in the Mortandad Canyon post-fire bark samples, but there were generally no differences in the U isotopes indicating no notable influence by the firing sites on the near-by mesa-top samples.

Also for comparison, in 1998 radioactivity was measured in ashed shoot tips of ponderosa pine at the same three sampling locations (Gonzales et al. 2000), however, most radionuclides were not detected in those samples. For the few samples that had detections, there basically was no difference in net (LANL minus background) radioactivity between the post-fire burned-bark values and the pre-fire (1998) shoot tip values.

Table 2 shows the results of the burned bark analyses for metals and nonmetal trace elements at the onsite and reference site sampling locations. Many of the analytes were not detected. Two of the three onsite Ba concentrations were lower than in the reference sample but the TA-16 sample had higher Ba than the reference site sample. The TA-16 sample also had slightly higher levels of B, Al, Cr, Cu, Fe, Ni, Sr, Ti, and Zn than the reference sample and where mean onsite concentrations exceeded the reference sample concentration – Al, Cr, Cu, Ni, and Ti – it was often the TA-16 value that increase the onsite mean above the reference sample value. The NMED duplicate bark sample values generally agreed with the LANL onsite values, but were slightly higher for six metals – Al, Ba, Cu, Fe, Mn, and Pb (NMED 2001)

Surface Ash

The analytical results for dioxins and furans in LANL onsite and offsite samples are shown in Table 3. The analytes for which onsite concentrations exceeded background concentrations in surface ash were 1,2,3,4,6,7,8-heptachlorodibenzodioxin (HpCDD), 1,2,3,4,6,7,8-octachlorodibenzodioxin (OCDD), total hexachlorodibenzodioxin (HxCDD), and total heptachlorodibenzodioxin (HpCDD). This was consistent with the analytical results for soil samples (Fresquez et al. 2000) taken from the same locations. No detections of 2,3,7,8-tetrachlorodibenzodioxin (TCDD), the most toxic of the dioxins, were made in the surface ash. Although one onsite detection of total TCDD was made in the surface ash, the level measured (1.53 ppt), was less than the background concentration (3.46 ppt). Dioxins and furans were analyzed in the ER background samples of ash and muck. Comparing values for analytes that were detected in our samples, total TCDD and total tetrachlorodibenzofuran (TCDF) were about the same and the ER mean background values for 1,2,3,4,6,7,8-HpCDD, 1,2,3,4,6,7,8-OCDD, and total HpCDD were about an order of magnitude higher than in our reference sample.

Dioxin is the common name for a group of 75 related organic compounds. They have never been intentionally manufactured; they are an unwanted byproduct of the manufacture of other chemicals such as PCBs, wood preservatives (e.g. pentachlorophenol), and herbicides (e.g. 2,4-D), and of the combustion of organic matter (e.g. municipal or industrial waste). Consequently anywhere these other constituents and/or processes exist dioxins usually also are present. Combustion of organic matter is the largest source of dioxins in the environment. Dioxins can be emitted in gaseous form or as particulates.

Although many dioxin compounds are toxic, the most toxic to humans is 2,3,7,8-TCDD, sometimes referred to as the most toxic human-made chemical known. It is also quite toxic to non-human organisms, with a minimum (lowest or most stringent) ecological screening level (ESL) of 1.8 ng TCDD/kg soil (dry) (ppt) (based on the shrew). ESLs for various organisms for this dioxin range from 1.8 ppt to 5 ppm. Chronic effects from dioxins are a subject of controversy. Animal studies have shown that chronic exposure can result in reproductive dysfunction, birth defects, and cancer. Little is known about the environmental effects of dioxin. TCDD is known to be persistent in the environment, and may last in excess of 10 years in soils. Like PCBs, the toxicity and persistence of dioxins likely increases with an increasing number of chlorine atoms. Also like PCBs, dioxins are poorly soluble in water but have a high affinity and solubility for lipids and fats. As a result, dioxins tend to bioaccumulate and biomagnify, at times resulting in their detection in animal life when they could not be detected in soil, sediment, or water.

Acknowledgments

Rick Velasquez and Louie Naranjo, Jr. supported sample collection and processed the samples. Hector Hinojosa performed the editing and Carolyn Hedrick compiled the final document.

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Table 1. Radioactivity (pCi/g ash ±1 s total propagated uncertainty) in bark ash collected from trees at three locatic reference site, both within the Cerro Grande Fire area.

Sample	^{90}Sr	^{137}Cs	^{234}U	^{235}U	^{238}U	^{238}Pu	^{239}Pu	^{241}Am	Gr Al
TA-06 (Two-Mile Mesa)	0.46±0.12	3.53±0.44	1.07±0.04	0.048±0.007	1.69±0.06	0.001±0.001	0.014±0.002	0.036±0.005	19.2
TA-15 (R-Site Road East)	1.75±0.24	3.43±0.59	1.47±0.05	0.084±0.009	2.41±0.08	0.006±0.002	0.092±0.007	0.021±0.004	33.7
TA-16 (S-Site)	1.57±0.20	2.22±0.36	0.88±0.03	0.041±0.007	1.24±0.05	0.003±0.001	0.025±0.003	0.010±0.004	17.2
Mean (Std. Dev.)	1.26 (0.70)	3.06 (0.73)	1.14 (0.3)	0.058 (0.02)	1.78 (0.59)	0.003 (0.003)	0.044 (0.042)	0.022 (0.013)	2 (9
Reference Site	2.43±0.35	4.02±0.50	0.58±0.03	0.028±0.006	0.69±0.03	-0.001±0.001	0.022±0.003	0.009±0.002	10.9

Table 2. Total recoverable metals and nonmetal trace elements (μg/g) in burned bark collected from LANL and an offsite reference location.

Location	Ag	Al	As	B	Ba	Be	Cd	Co	Cr	Cu	Fe	Hg
TA-06	<2.0	160	<0.50	16	17	<0.20	<0.40	<1.0	1.0	4.1	100	<0.05
TA-15	<2.0	300	<0.50	14	17	0.37	<0.40	<1.0	1.2	12.0	150	<0.05
TA-16	<2.0	850	<0.50	20	51	<0.20	<0.40	1.4	2.0	6.5	560	<0.05
Mean	<2.0	437	<0.50	16.7	28	0.37	<0.50	1.4	1.4	7.5	270	<0.05
Offsite Reference	<2.0	370	<0.5	17	43	<0.2	<0.4	1.4	0.52	2.1	190	<0.05

Table 2 (continued). Total recoverable metals and nonmetal trace elements (μg/g) in burned bark collected from LANL and offsite.

Location	Mn	Mo	Ni	Pb	Sb	Se	Sn	Sr	Ti	Tl	V	Zn	CN
TA-06	31	<5.0	<2.0	0.9	<0.20	1.00	<5.0	24	4.4	<0.20	<0.30	25	2.4
TA-15	33	<5.0	<2.0	0.6	<0.20	1.00	5.8	21	7.1	<0.20	0.40	24	2.2
TA-16	55	<5.0	4.6	1.6	<0.20	0.90	<5.0	52	34.0	<0.20	<0.30	46	0.6
Mean	40	<5.0	4.6	1.0	<0.20	0.97	5.8	32	15.2	<0.20	0.40	32	1.7
Offsite Reference	55	<5.0	<2.0	3.6	0.30	0.90	7.1	39	7.6	<0.20	<0.30	26	5.8

Table 2. Concentration (ng/kg) of dioxins and furans in a composited sample of surface ash collected from three locations (TA-06, TA-15, and TA-16) at LANL and a reference site, both within the Cerro Grande Fire area.

Analyte	Onsite	IDL[a]	Qualifiers[b]	Offsite (Reference Site)	IDL	Qualifiers
2,3,7,8-TCDD	0	0.164		0	0.159	
1,2,3,7,8-PeCDD	0	0.3		0	0.146	
1,2,3,4,7,8-HxCDD	0	0.246		0	0.159	
1,2,3,6,7,8-HxCDD	0.545	0	A	0	0.185	
1,2,3,7,8,9-HxCDD	0.486	0	A	0	0.161	
1,2,3,4,6,7,8-HpCDD	7.44	0		0.372	0	A
OCDD	28.1	0		1.72	0	A
2,3,7,8-TCDF	0	0.0901		0	0.0802	
1,2,3,7,8-PeCDF	0	0.121		0	0.132	
2,3,4,7,8-PeCDF	0	0.129		0	0.148	
1,2,3,4,7,8-HxCDF	0	0.278		0	0.104	
1,2,3,6,7,8-HxCDF	0	0.191		0	0.0862	
2,3,4,6,7,8-HxCDF	0	0.287		0	0.101	
1,2,3,7,8,9-HxCDF	0	0.514		0	0.175	
1,2,3,4,6,7,8-HpCDF	0.702	0	A	0	0.117	
1,2,3,4,7,8,9-HpCDF	0	0.166		0	0.191	
OCDF	1.49	0	A	0	0.362	
Total TCDD	1.53	0		3.46	0	
Total PeCDD	0	0.3		0	0.146	
Total HxCDD	5.62	0		0	0.168	
Total HpCDD	16	0		0.825	0	
Total TCDF	0.489	0	A	1.35	0	
Total PeCDF	0	0.125		0	0.139	
Total HxCDF	0	0.285		0	0.111	
Total HpCDF	1.57	0	A	0	0.149	

[a]IDL = Instrument detection level.
[b]A = Analyte detected but was below the reporting limit.

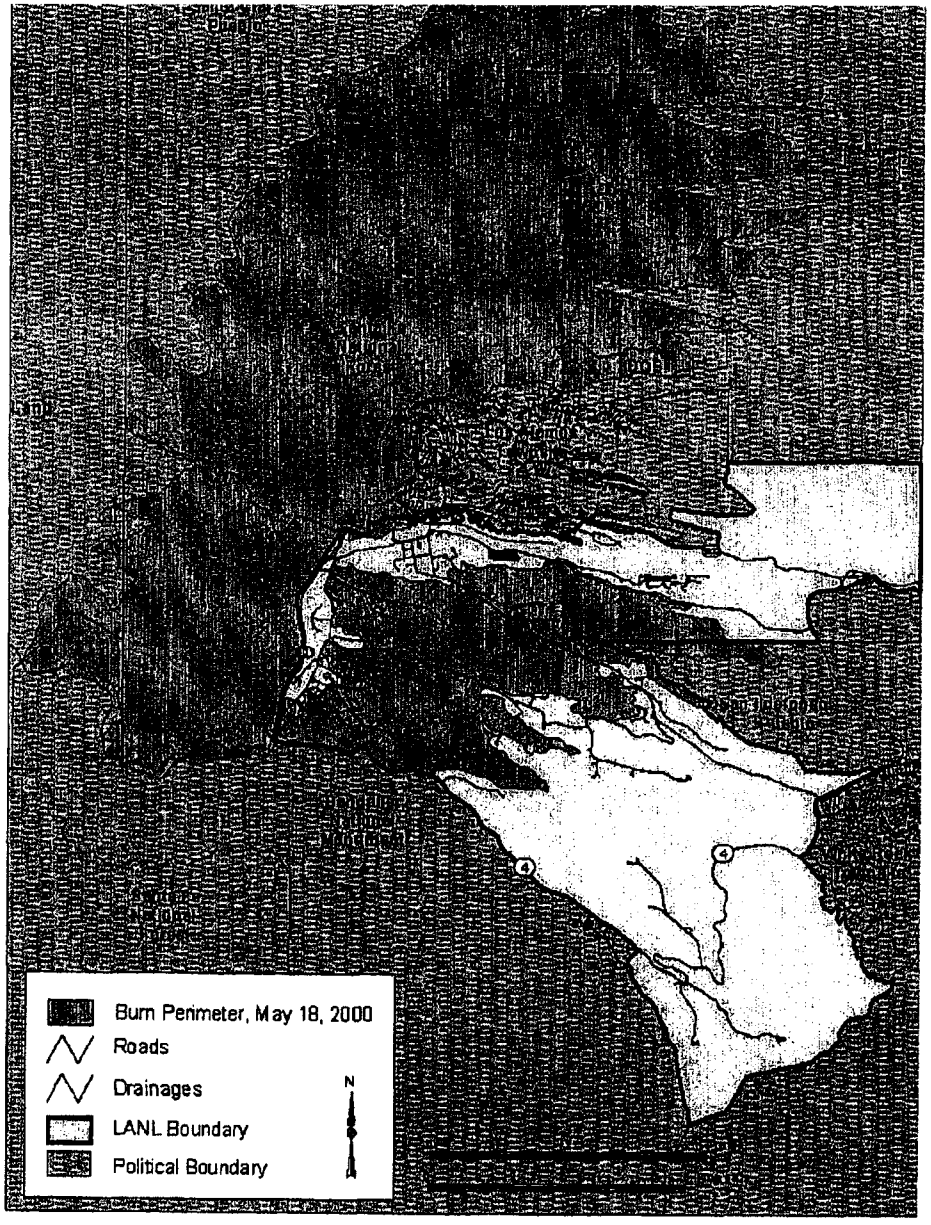

Figure 1. Cerro Grande Fire, total area burned.