ASSESSMENT OF POLYCHLORINATED DIBENZODIOXINS AND POLYCHLORINATED DIBENZOFURANS (PCDD/F) AND TITLE 22 METALS CONTAMINATION ON AGRICULTURAL LAND: REVIEW AND ANALYSIS OF A SAMPLING PLAN

A Project

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by

Kevin Cordes

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ABSTRACT

ASSESSMENT OF POLYCHLORINATED DIBENZODIOXINS AND POLYCHLORINATED DIBENZOFURANS (PCDD/F) AND TITLE 22 METALS CONTAMINATION ON AGRICULTURAL LAND: REVIEW AND ANALYSIS OF A SAMPLING PLAN

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This project paper covers the scientific methods and the regulations related to the proposed work plan, including the scope of work and technical procedures needed to obtain samples from the subject property. The work plan was informed by preliminary sampling conducted in 2009 by Chico Environmental staff along with a District Attorney Special Investigator and representatives of the Regional Water Quality Control Board. Following the preliminary sampling, fly ash from a biomass-fueled power plant was tilled into the soil and corn was planted on the subject property. A work plan (Appendix A) was written to outline the assessment of the property to determine the presence and/or the extent of contamination of polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/F) and Title 22 metals. According to the

work plan, fifteen samples (six soil samples, three corn samples, three corn roots samples, and three corn stock samples) will be collected at three discrete sample locations on the property. The samples will be analyzed for PCDD/Fs, Title 22 metals, and pH based on laboratory standards outlined in the Environmental Protection Agency's "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," also referred to as SW-846. Analytical results will be compared to a variety of regulatory standards and guidelines established by both federal and California government agencies. Based on the site conditions and sample results, Chico Environmental Science and Planning will recommend to the Department of Toxic Substances Control and the District Attorney's Office appropriate actions to be taken which may include further sampling or removal of contaminated soil.

CHAPTER I

INTRODUCTION

Biomass-fueled energy production is meant to be a relatively clean, renewable energy alternative to more environmentally detrimental power plants. The term biomass refers to biological material such as grassy and woody plants, food crops, agriculture or forestry residues, algae, organic material from municipal and industrial wastes, and methane from landfills (National Renewable Energy Laboratory, 2012a). Most biomass power plants burn organic material to create steam which drives turbines and generates electricity (National Renewable Energy Laboratory, 2010). Biomass power generation was the second largest contributor to renewable energy generation in the United States as of 1999, generating about 11 billion kilowatts per year (National Renewable Energy Laboratory, 2012b).

There are, however, drawbacks to this energy source. One of which is the potential toxicity of a biomass power plant's fly ash byproducts—a problem exacerbated by the combustion of dangerous fuels and poor power plant quality control measures (Ernsting, 2012). Fly ash is produced during the biomass combustion process; it consists of fine particles that are captured and collected from flue gases. It is the lightest and smallest type of ash produced from biomass combustion with its average size at around 200 micrometers (Pitman, 2006). It usually contains higher levels of heavy metals and polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/Fs) than other types of ash byproducts (Pitman, 2006). Open burning of biomass is estimated to contribute up to 68% of the total PCDD/F emissions in some countries (Fiedler, 2007).

Fly ash from biomass power plants can contain naturally occurring elements that are also found in soil. Application of fly ash to agricultural land can improve the soils concentration of micronutrients and beneficially alter soil texture, improving water retention capacity and microporosity (Mittra et al., 2003). However, according to Pitman (2006), heavy metals are commonly concentrated in fly ash compared to other combustion residues and should not be used as a soil amendment.

A biomass power plant in California – which is undisclosed because of its involvement in a criminal case – generates on average about 8,000 tons of fly ash yearly (Lane, 2010). This fly ash was disposed at various locations across three counties (Lane, 2010). Multiple sampling events were conducted by Chico Environmental and the District Attorney at the power plant and fly ash disposal locations. The fly ash contained significantly toxic levels of polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/Fs), pH, and various heavy metals (Lane, 2010).

In a preliminary assessment in 2009, Chico Environmental Science and Planning, an environmental consulting company, was hired by the District Attorney to investigate the subject property that received this power plant’s fly ash. The property owner planned to use the fly ash as a soil amendment; he spread the ash into 95 linear piles across his agricultural field (Lane, 2009). The property location and property owner’s name also will not be disclosed because of the same criminal investigation. Preliminary sampling and analysis of the ash piles indicated levels of arsenic, cobalt, copper, lead, molybdenum, vanadium, and zinc that exceeded one or more regulatory guidelines (Lane, 2009). Furthermore, lead concentration in the ash exceeded hazardous waste levels (Lane, 2009). Despite the elevated levels of contaminants of concern and advice from the Department of Toxic Substances Control (DTSC) to remove or contain the contamination, the property owner tilled the fly ash into his soil and planted corn in the fly ash-amended soil.

In the fall of 2012, Chico Environmental was hired again by the District Attorney to assess the extent of contamination on the subject property. Chico Environmental and the DTSC were assigned to sample soil and corn plants on the subject property to determine the concentration of PCDD/Fs, Title 22 metals, and pH.

Developing a project work plan is a balance between regulatory authority, risk to the environment as determined by the regulatory agency, and the ability to reach a mutually agreeable clean-up plan between the parties that meets the legal requirements. In this case, the parties are the owners of the biomass power plant, the subject property owner, the DTSC, and the District Attorney.

The purpose of this project paper is to describe the content and rationale behind proposed actions to be taken according to the Work Plan for Soil, Corn Roots, Corn Stocks, and Corn Sampling (Appendix A). This project paper introduces and validates the contents of the Work Plan with focus mainly on the reasoning for the scientific methods proposed and deeper explanation of the regulations that support them. The literature review in the following section presents relevant background information about the physical characteristics, the human and environmental health risks, and the regulation of PCDD/Fs, pH, and Title 22 metals. The sampling methodology of the work plan will subsequently be discussed, followed by derived conclusions and recommendations.

Definition of Terms

- 2,3,7,8 TCDD = Tetrachlorodibenzodioxin
- ATSDR = Agency for Toxic Substances and Disease Registry, Federal agency for Toxic Substances and Disease Registry
- CCR = California Code of Regulations
- CERCLA = Comprehensive Environmental Response, Compensation, and Liability Act
- CFR = Code of Federal Regulations
- CHHSL = California Human Health Screening Levels
- DTSC = California Department of Toxic Substances Control
- EPA = Federal Environmental Protection Agency
- ESL = Environmental Screening Levels
- mg/kg = milligrams per kilogram; parts per million
- mg/kg/day = milligrams per kilogram per day; parts per million per day
- mg/m^3 = milligrams per cubic meter
- MRL = Minimal Risk Level
- PCDD/F = polychlorinated dibenzodioxins and polychlorinated dibenzofurans
- pg/g = picograms per gram; parts per trillion
- pg/mL = pictograms per milliliter
- pg/kg/day = picograms per kilogram per day = parts per quadrillion per day

- RCRA = Resource Conservation and Recovery Act
- RSL = Regional Screening Levels
- STLC = Soluble Threshold Limit Concentration
- TEF = Toxic Equivalency Factors
- TEQ = Toxic Equivalent
- TTLC = Total Threshold Limit Concentration
- WHO = World Health Organization

CHAPTER II

REVIEW OF RELATED LITERATURE

Polychlorinated Dibenzodioxin and Polychlorinated Dibenzofuran Characteristics

One of the major contaminants of concern to be investigated in the attached work plan is commonly referred to as “dioxins.” The term “dioxins” refers to 75 different polychlorinated dibenzodioxin compounds; seven of these compounds are considered to have harmful effects. Dioxins can be divided into eight distinct groups—mono-chlorinated dioxins through octa-chlorinated dioxins—based on the amount of chlorine atoms in the compound; these compounds can be further divided into different stereoisomers based on the position of the chlorine atom or atoms (Agency for Toxic Substances and Disease Registry [ATSDR], 1998). Figure 1 outlines the shape and numbering pattern for chlorinated dibenzodioxins.

Dibenzofurans are a type of polycyclic aromatic hydrocarbon and are the most structurally related compound to polychlorinated dibenzodioxins (ATSDR, 1998). Ten of its congeners are considered to be hazardous (Van den Berg et al., 2006). Figure 2 shows the structural formula of polychlorinated dibenzofuran:

Polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/Fs) are nonpolar, making them hydrophobic and lipophilic. Because PCDD/Fs are stable and durable compounds that easily dissolve in fatty tissue, they are considered

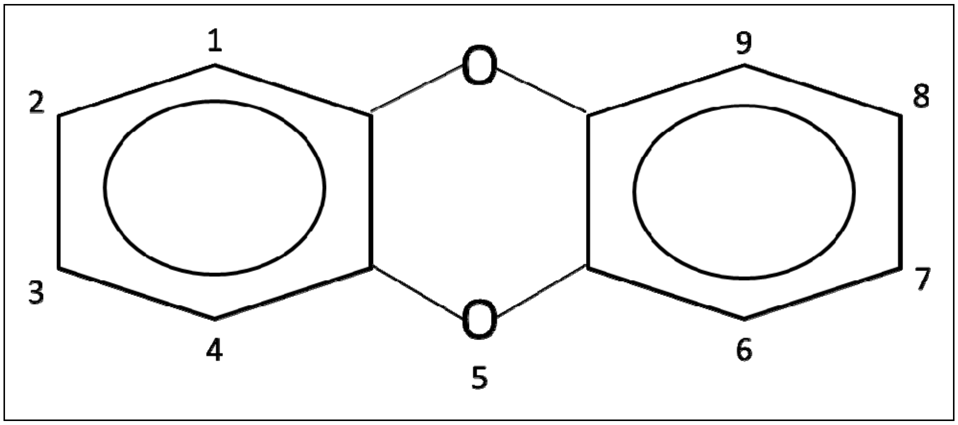

Figure 1. General Structure of Polychlorinated Dibenzodioxin. The circles inside of the two benzene rings represent the resonance of the three double bonds in each ring. The numbers represent the location of either hydrogen atoms or chlorine atoms. As an example, 2,3,7,8 Tetrachlorodibenzodioxin (2,3,7,8 TCDD) will have chlorine atoms located at the 2, 3, 7, and 8 positions in the Figure 1; Hydrogen atoms will be located at positions 1, 4, 6, and 9.

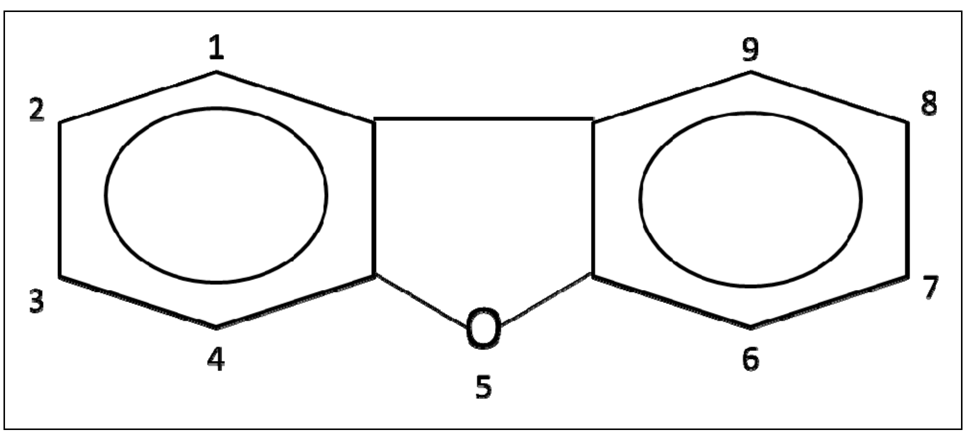

Figure 2. General Structure of Polychlorinated Dibenzofuran. The structure of Polychlorinated dibenzofurans are similar to polychlorinated dibenzodioxins. The same system of numbering chlorine atoms on the benzene rings applies.

to be persistent organic pollutants (National Academy of Sciences, 2006). Persistent organic pollutants are often halogenated with chlorine; in general, the more chlorine groups that a compound has, the longer it will take for the compound to break down over time (Ritter et al., n.d.). The general structure of PCDD/F compounds make them resistant to chemical breakdown through oxidation-reduction, acid-base reaction, and hydrolysis (Ministry of Environment and Forests, Indian Central Pollution Control Board, 2004). Thermal decomposition will only occur at temperatures exceeding 750 degrees Celsius (Ministry of Environment and Forests, Indian Central Pollution Control Board, 2004).

There are a combined total of 17 polychlorinated dibenzodioxins and dibenzofurans (PCDD/F) that are considered hazardous substances. The World Health Organization (WHO) created toxic equivalency factors (TEF) for these compounds in 1994. Revisions to the TEF values were made in 1998 and again in 2005. These factors compare the toxic equivalency of the 17 compounds to 2, 3, 7, 8 Tetrachlorinated dibenzodioxin (2,3,7,8-TCDD) which is the most toxic – and most widely studied – type of PCDD/F (Ministry of Environment and Forests, Indian Central Pollution Control Board, 2004; Van den Berg et al., 2006). The most current TEF values are shown in Table 1.

The relative effect potency listed above as TEF values compares the toxic or biological effects relative to 2,3,7,8 TCDD, the reference compound. These relative effect potencies from all of the 17 congeners allow for the toxic equivalent (TEQ) of 2,3,7,8 TCDD to be used as standard reference values. The different TEF values listed above are from a consensus-based WHO expert panel; they are based on consideration of

TABLE 1. WHO 2005 TOXIC EQUIVALENCY FACTORS FOR PCDD/FS

Compound (dioxins)	TEF	Compound (furans)	TEF
2,3,7,8-TCDD	1	2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDD	1	1,2,3,7,8-PeCDF	0.03
1,2,3,4,7,8-HxCDD	0.1	2,3,4,7,8-PeCDF	0.3
1,2,3,6,7,8-HxCDD	0.1	1,2,3,4,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDD	0.1	1,2,3,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDD	0.01	2,3,4,6,7,8-HxCDF	0.1
OCDD	0.0003	1,2,3,7,8,9-HxCDF	0.1
		1,2,3,4,6,7,8-HpCDF	0.01
		1,2,3,4,7,8,9-HpCDF	0.01
		OCDF	0.0003

Note: Table 1 represents Toxic Equivalency Factors for polychlorinated dibenzodioxins and polychlorinated dibenzofurans. Values of each congener are multiplied by TEF values and summed to determine the Toxic Equivalent to 2,3,7,8 TCDD (Van den Berg et al., 2006).

previously published TEFs (WHO 1996; van den Berg et al., 2006). The sum of the calculated TEF values for each sample is the TEQ of 2,3,7,8 TCDD, which is the most toxic PCDD/F congener. 2,3,7,8 TCDD is also the most widely studied congener; most toxicity studies are in reference to 2,3,7,8 TCDD.

PCDD/Fs are created as by-products of human activities such as fossil fuel combustion, industrial processes, or waste destruction (Ministry of Environment and Forests, Indian Central Pollution Control Board, 2004). They can also be found in certain herbicides and pesticides (Chang et al., 2012). It is widely recognized that combustion processes are a major source of PCDD/Fs when occurring in the presence of metals and chlorine (Chang et al., 2012).

The most common distribution pathway for PCDD/Fs is through emissions. The specific composition of the PCDD/F is influenced by different factors such as atmospheric loss processes and selective transport of different congeners (Lohmann and

Jones, 1998). The migration of PCDD/F congeners from fly ash has also been shown to occur in multiple studies (Sakai et al., 1997; Hsing-Cheng and Tsung-Hsien, 2006; Hsing-Cheng et al., 2008). The leachability of PCDD/Fs from solid waste material such as fly ash is generally considered to be low, yet variable. The leachability of PCDD/Fs depends on the type of material and quantity (ATSDR, 1998). The type of solvent also has an effect on the mobility and leachability of PCDD/Fs (Sakai et al., 1997).

PCDD/Fs are toxic to certain animals, especially in the early stages of development.

There is a range of adverse effects on a widespread number of animals; each studied animal has different responses to PCDD/F exposure. A variety of harmful developmental effects such as weakened immune responses in rats (Holladay, 1999) and fish (Spitsbergen et al., 1986) has been observed. Behavior changes and reproductive impairment in a wide range of species have also been described (Fiedler, 2003).

Plants do not generally absorb PCDD/Fs. A study was conducted by Lahkwinder et al. in 2008 to determine the uptake of PCDD/Fs by corn grown in soil that was treated annually with PCDD/F-contaminated biosolids. The study found that while PCDD/F levels were increased in the soil, PCDD/F uptake in corn was negligible. However, PCDD/Fs will stick to organic matter such as ash, soil, and plants (Lahkwinder et al., 2008). Animals or people can obtain PCDD/Fs by eating plants that are externally contaminated with PCDD/F contaminated soil or dust (ASTDR, 1998). PCDD/Fs can become a serious concern as biomagnification and bioaccumulation occur throughout the affected food chain when contaminated vegetation is consumed.

Biomagnification and bioaccumulation of PCDD/Fs refer to the buildup of PCDD/Fs in various organisms through a food chain. The inherent lipid solubility of PCDD/Fs allows for the passage of PCDD/F congeners through phospholipid membranes where they will remain and bioaccumulate in fatty tissue (Ritter et al., n.d.). PCDD/Fs will be at greater concentration in organisms of higher trophic levels such as primary and secondary consumers. Because PCDD/Fs are widely spread in low concentrations and are persistent pollutants, most people have detectable levels of it in their bodies, specifically in fatty tissue. These levels will persist for years (Fiedler, 2003). The half-life of PCDD/Fs in human fatty tissue ranges from 4.9 to 13.1 years (Milbrath et al., 2009)

Short-term exposure to high levels of PCDD/Fs in humans can result in altered liver function, skin lesions, and chloracne. Long-term exposure to PCDD/Fs can cause harm to the endocrine system, reproductive functions, the immune system and the nervous system in early stages of development (ATSDR, 1998). Due to the bioaccumulative characteristics of PCDD/Fs, all people have a certain level of exposure to dioxins; however, average background exposure is generally not likely to negatively affect human health. The Agency for Toxic Substances and Disease Registry (ATSDR) and the United States Environmental Protection Agency (EPA) have set the Minimal Risk Levels (MRL) of tolerable intake of the 2,3,7,8 TCDD TEQ (ATSDR, 1998) as listed in Table 2.

The ATSDR and the EPA are required by the Comprehensive Environmental Response, Compensation, and Liability Act under Title 42 of the United States Code to create a list of the most commonly found hazardous substances (42 U.S.C., 2012b). They are also required to prepare toxicological profiles and MRLs for each listed

TABLE 2. ATSDR MINIMAL RISK LEVELS FOR HAZARDOUS SUBSTANCES

Oral intake of 2,3,7,8 TCDD		
Exposure duration	MRL	units
Acute	0.2	pg/kg/day
Intermediate	0.02	pg/kg/day
Chronic	0.001	pg/kg/day

Note: Table 2 is based on ATSDR MRLs for 2,3,7,8 TCDD. Acute duration spans from 1 to 14 days; Intermediate duration ranges from 15 to 364 days; Chronic duration represents one year or longer. These MRLs were assigned in December, 1998.

hazardous substance. Minimal Risk Levels are estimates of the largest concentration of a substance that is not considered to have the risk of detrimental non-cancer health effects. Minimal Risk Levels are meant to serve as initial screening levels at hazardous waste sites and are only derived when ATSDR staff determines that sufficient data exist to accurately identify health risks after a thorough review process (ATSDR, 1998). The Minimal Risk Levels are based on acute, intermediate, and chronic exposure to the substance.

Title 22 Metals

The California Code of Regulations Title 22, Chapter 11 (22 Cal. Code Reg. § 66261.10, 1991) identifies seventeen metals as hazardous at varying concentrations, often referred to as Title 22 Metals. Hazardous waste is defined in this section as a waste that can “cause, or significantly contribute to, an increase in mortality or an increase in serious irreversible, or incapacitating reversible, illness; or pose a substantial present or potential hazard to human health or the environment when it is improperly treated, stored, transported, disposed of or otherwise managed” (22 Cal. Code Reg. § 66261.10, 1991).

Heavy metal contamination in soils is prevalent in the U.S. and other parts of the world. Since heavy metals do not break down like organic compounds, they are often moved to a safe location, buried, covered, recycled, or changed into a less toxic form during a site cleanup. The leaching and migration of different metals in soil and fly ash vary depending on the type of metal and the environmental conditions (Meima and Comens, 1998). The leachability of metals can be dependent on the pH levels of the soil or fly ash. Generally, metals' leaching is more likely to occur when the pH is greater than 4 pH units (Meima and Comens, 1998). The EPA and ATSDR define Minimum Risk Levels for these metals (Table 3 and Table 4).

TABLE 3. ATSDR MINIMAL RISK LEVELS: ORAL EXPOSURE TITLE 22 METALS

Metal	Route	MRL	Duration	units
Arsenic	oral	0.00500	Acute	mg/kg/day
	oral	0.00030	Chronic	mg/kg/day
Barium	oral	0.20000	Intermediate	mg/kg/day
	oral	0.20000	Chronic	mg/kg/day
Beryllium	oral	0.00200	Chronic	mg/kg/day
Cadmium	oral	0.00050	Intermediate	mg/kg/day
	oral	0.00010	Chronic	mg/kg/day
Cobalt	oral	0.01000	Intermediate	mg/kg/day
Copper	oral	0.01000	Acute	mg/kg/day
	oral	0.01000	Intermediate	mg/kg/day
Selenium	oral	0.00050	Chronic	mg/kg/day
Vanadium	oral	0.01000	Intermediate	mg/kg/day
Zinc	oral	0.30000	Intermediate	mg/kg/day
	oral	0.30000	Chronic	mg/kg/day

Note: Agency for Toxic Substances and Disease Registry MRLs for Title 22 Metals. Acute duration spans from 1 to 14 days; Intermediate duration ranges from 15 to 364 days; Chronic duration represents one year or longer. Standards represent oral intake of hazardous constituents measured in parts per million per day. Not all Title 22 Metals have been assigned Minimal Risk Levels.

TABLE 4. ATSDR MINIMAL RISK LEVELS: INHALATION TITLE 22 METALS

Metal	Route	MRL	duration	units
Cadmium	Inhalation	0.00003	acute	mg/m^3
	Inhalation	0.00001	chronic	mg/m^3
Chromium III	Inhalation	0.00010	intermediate	mg/m^3
Cobalt	Inhalation	0.00010	chronic	mg/m^3
Mercury	Inhalation	0.00020	chronic	mg/m^3
Nickel	Inhalation	0.00020	intermediate	mg/m^3
	Inhalation	0.00009	chronic	mg/m^3
Vanadium	Inhalation	0.00080	acute	mg/m^3
	Inhalation	0.00010	chronic	mg/m^3

Note: Agency for Toxic Substances and Disease Registry MRLs for Title 22 Metals. Acute duration spans from 1 to 14 days; Intermediate duration ranges from 15 to 364 days; Chronic duration represents one year or longer. Standards represent the inhalation of hazardous constituents measured in milligrams per cubic meter per day. As with Table 3, not all Title 22 Metals have been assigned Minimal Risk Levels.

The preliminary sampling event at the subject property in 2009 tested for the presence of Title 22 metals and chromium VI – PCDD/Fs were not tested due to budgetary restrictions. Seven of these metals - Arsenic, Cobalt, Copper, Lead, Molybdenum, Vanadium, and Zinc –found in the fly ash samples from the 2009 preliminary sampling event exceeded some regulatory standard listed in Table 6. Lead was the most toxic metal with levels above the STLC hazardous waste standard (Lane, 2009).

Lead accumulates in the environment, and can be retained in topsoil for many years. It is toxic to the heart, intestines, kidneys, bones, and reproductive and nervous systems, and it interferes with a variety of body processes (ATSDR, 2007). Severe cases of lead poisoning can cause seizures, coma, and death. It can also cause permanent learning and behavior disorders to children. (ATSDR, 2007) It is likely that lead will be taken up by corn plant root systems and will be transported throughout the plant if lead is available to a corn plant (Malone et al., 1974).

Hazardous concentrations of heavy metals on agricultural land are a recognized potential contaminant because of ensuing human health effects and potential effect on ecosystems (McLaughlin et al., 1999; Qishlaqi and Moore, 2007). Fly ash can be utilized as a soil amendment since it can potentially enhance soil quality by increasing the amount of micronutrient metals in the soil. Because the concentration of an element in plant tissue is generally thought to increase in proportion to its concentration in soils (Chen et al., 2008), there is a growing public health concern with the risks involved with the increasing amount of Arsenic, Cadmium, and Lead in cropland soils that have resulted from the use of fly ash as a soil amendment (De Meeurs et al., 2002).

To decide whether contaminants in soil amendments may pose unacceptable risks to the environment or to human health, the EPA is currently assessing the types of wastes that are being used in soil amendments and their composition with regards to potentially hazardous constituents such as metals and PCDD/Fs (United States EPA, 1997). They are also assessing the potential for human health and environmental risks, as well as crop damage incidents (United States EPA, 1997). Currently, national and international regulations for fertilizer and soil amendment composition vary. The EPA will review regulations and collected information with support from the U.S. Department of Agriculture and individual states to determine regulatory requirements to protect both human health and agricultural products (United States EPA, 1997).

pH

A material's pH level is a measure of its acidity or alkalinity. The pH levels in the samples can be used to determine the apparent toxicity of the site. Extreme acidity or alkalinity can have a wide variety of environmental effects including crop tolerance, nutrient availability, and soil microbe activity (McCauley et al., 2009). The amount of nutrients available for plant uptake is dependent on soil pH levels; the availability of nutrients can be hindered in highly alkaline soils, and highly acidic soils increases the likelihood of leaching of nutrients (McCauley et al., 2009).

Non-aqueous sampled material is considered to be hazardous waste if it has a pH that is less than 2 pH units or greater than 12.5 pH units when it is mixed with an equivalent weight of water (22 Cal. Code Reg. § 66261.22, 1998a). Exposure to extreme pH values can cause irritation of the skin, eyes, and mucous membranes (WHO, 1996). High pH values have been associated with increased aggravation of skin disorders (WHO, 1996).

Regulations and Guidelines

A decisive way to regulate waste containing metals and PCDD/Fs is to compare it to the California Code of Regulations (CCR) and/or the United States Code of Federal Regulations (CFR) hazardous waste levels (40 C.F.R., 2012b; 22 Cal. Code Reg. § 66261.10, 1991). Material is deemed to be hazardous if it causes an increase in mortality or serious incapacitating illness that is either reversible or irreversible (22 Cal. Code Reg. § 66261.10, 1991). It is also considered hazardous waste if it is a substantial hazard to the environment or human health when it is improperly managed (22 Cal. Code

Reg. § 66261.10, 1991). The material needs to be measured by a standardized test method which is practical for waste generators or private sector labs to perform (40 C.F.R., 2012b; 22 Cal. Code Reg. § 66261.10, 1991).

Several protocols can be used to determine hazardous waste levels of substances as defined by the California Code of Regulations, Title 22, Chapter 11, Article 3. First, a totals test can be performed on sampled material to determine the PCDD/F or Title 22 metals levels relative to the regulatory level total threshold limit concentration (TTLC). A wet extraction test, or a leaching test, can then be performed to determine the leached amount of PCDD/Fs or Title 22 metals from the sampled material. The leached value is compared to the Soluble Threshold Limit Concentration (STLC). If either PCDD/F or Title 22 metals value is greater than the TTLC or STLC regulatory limits, then the material is considered hazardous waste (22 Cal. Code Reg. § 66261.24, 1998b). These regulatory levels are listed in Table 5.

Other PCDD/F guidelines have been created by various government agencies for contaminated site clean-ups or investigations. These values do not have as much legal influence as the California Code of Regulations (CCR) hazardous waste levels in Table 3. The standards, however, do represent safe levels of contaminant concentration.

Environmental Screening Levels (ESLs) were established by the San Francisco Bay Regional Water Quality Control Board. They are intended to aid the identification of potential environmental pollutants at sites with previously identified contamination, and to expedite the evaluation of possible cleanup process. These values are based on a target cancer risk of 1/1,000,000 (California Regional Water Quality Control Board: San Francisco Bay Region, 2007).

TABLE 5. CALIFORNIA CODE OF REGULATIONS HAZARDOUS WASTE LEVELS

Constituent	STLC (mg/L)	TTLC (mg/kg)
Antimony	15	500
Silver	5	500
Arsenic	5	500
Barium	100	10000
Beryllium	0.75	75
Cadmium	1	100
Chromium III	5	2500
Cobalt	80	8000
Copper	25	2500
Lead	5	1000
Molybdenum	350	3500
Nickel	20	2000
Selenium	1	100
Thallium	7	700
Vanadium	24	2400
Zinc	250	5000
Mercury	0.2	20
2,3,7,8 TCDD	0.001	0.01

Note: STLC = Soluble Threshold Limit Concentration; TTLC = Total Threshold Limit Concentration. Values are defined in Title 22 of the California Code of Regulations (22 Cal. Code Reg. § 66261.24, 1998b).

The California Human Health Screening Levels (CHHSLs) come from the Office of Environmental Health Hazard Assessment. The values are based on 1/1,000,000 target cancer risk. CHHSLs are not intended to establish policy or regulation. Nor are they meant to be used to determine if the soil is hazardous under federal regulations. Like the Environmental Screening Levels, they are simply a guidance tool, or recommendation, for safe environmental conditions (California Environmental Protection Agency, 2005).

Regional Screening Levels (RSLs) were developed by the EPA. The Regional Screening Levels are risk-based tools for evaluating the clean up of contaminated sites that fall in the EPA designated Region 9. This region includes California, Arizona, Nevada, Hawaii, and the Pacific Islands. They are meant to be used to standardize the risk decision-making process for certain contaminants. Regional Screening Levels combine standard exposure factors with human health toxicity values relevant to the toxin to estimate contaminant concentrations in soil, air, and water. The set values are considered by the EPA to be at levels that are protective of human exposures over a lifetime, and are derived from the 1/1,000,000 cancer risk for each contaminant. Chemical concentrations that are above these levels do not automatically designate a site as unsafe, but exceeding these values suggests that a more extensive evaluation of the potential health and environmental risks is appropriate (United States EPA, 2012).

PCDD/F levels above the guidelines shown in Table 6 may have detrimental effects on humans and/or animals.

TABLE 6. STANDARDS FOR 2,3,7,8 TCDD TEQ (DIOXINS AND FURANS)

	residential	commercial/ industrial	units
ESL: shallow soil, source of drinking water	4.49	18.37	pg/g
ESL: shallow soil, not drinking water	4.49	18.37	pg/g
ESL: deep soil, source of drinking water	227.14	227.14	pg/g
ESL: deep soil, not drinking water	227.14	227.14	pg/g
ESL: direct exposure	4.49	18.37	pg/g
CHHSL	4.6	19	pg/g
RSL	4.5	18	pg/g

Note: Table data adapted from: RSL = EPA’s Regional Screening Levels (United States EPA, 2012); ESL = Environmental Screening Levels from the California Regional Water Quality Control Board: San Francisco Bay Region (2007); CHHSL = California Human Health Screening Levels from the Office of Environmental Health and Hazard Assessment (California Environmental Protection Agency, 2005).

Table 7 highlights the TTLC, STLC, CHHSL, RSL, and ESL standards and guidelines for Title 22 metals.

TABLE 7. REGULATORY GUIDELINES: CCR TITLE 22 METALS (MG/KG)

	CHHSL		RSL		ESL shallow soil / potential drinking water	
Type of Metal	Residential	Industrial	Residential	Industrial	Residential	Commercial
Antimony	30	380	31	410	6.3	40
Silver	380	4800	390	5100	20	40
Arsenic	0.07	0.24	0.39	1.6	0.39	1.6
Barium	5200	63000	15000	190000	750	1500
Beryllium	150	1700	160	2000	4	8
Cadmium	1.7	7.5	70	800	1.7	7.4
Chromium III	100000	100000	120000	1500000	750	750
Cobalt	660	3200	23	300	40	80
Copper	3000	38000	3100	41000	230	230
Lead	150	3500	400	800	200	750
Molybdenum	380	4800	390	5100	40	40
Nickel	1600	16000	1500	20000	150	150
Selenium	380	4800	390	5100	10	10
Thallium	5	63	0.78	10	1.3	16
Vanadium	530	6700	390	5200	16	200
Zinc	23000	100000	23000	310000	600	600
Mercury	18	180	10	43	1.3	10

Note: Table data adapted from: RSL = EPA's Regional Screening Levels (United States EPA, 2012); ESL = Environmental Screening Levels from the California Water Quality Control Board (California Regional Water Quality Control Board: San Francisco Bay Region, 2007); CHHSL = California Human Health Screening Levels from the Office of Environmental Health and Hazard Assessment (California Environmental Protection Agency, 2005).

CHAPTER III

METHODOLOGY

Judgmental sampling will occur at three locations along a transect at the subject property. Samples of soil, corn, corn roots, and corn stocks will be collected from the site. Samples will be collected by employees from the Department of Toxic Substances Control, a District Attorney Special Investigator, and staff from Chico Environmental. The exact sample locations will be determined once on site based on visual observations of fly ash residue in the soil. In total, 15 samples (6 soil samples, 3 corn samples, 3 corn root samples, and 3 corn stock samples) will be collected from three distinct locations. Two soil samples, one corn sample, one corn roots sample, and one corn stocks sample will be collected at each sample location; the corn roots, corn stocks, and corn will be collected from the same corn plant at each of the three locations.

The first sample location will be near the west end of the cornfield at the subject property where a high concentration of ash was dumped. The second sample location will be east of the first sample location, near the eastern end of the dumped ash piles. The third sample location will be located east of sample location 2 where there is no evidence of ash piles. One soil sample at each of the three sample locations will be analyzed by the Department of Toxic Substances Control laboratory. The second soil sample from each location as well as all corn roots, corn stocks, and corn samples will be analyzed by the Department of Public Health. Neither of the two laboratories is EPA certified.

Samples will be collected using plastic disposable trowels, 16 oz., and 32 oz. glass jars. A clean pair of nitrile gloves will be used during each sample collection. The jars and DTSC-supplied plastic bags will be the sample containers. Each sample container will be labeled prior to collection of the sample. Labels will contain the sample identification number, sample date and time, and the sampler's name. Soil will be excavated with a disposable trowel then scooped into glass jars until it overflows. The contents of the jar will not be compacted. Evidence tape will be placed over the sealed sample containers. After each sample is collected, it will be placed for shipment into a pre-cooled ice chest on ice packs. Proper chain-of-custody procedures will be followed at all times, and photos will be taken during sampling to document the process.

During sampling, it is important that quality control and health and safety protocols are followed. These protocols are based on the EPA's Quality Assurance Program and Quality Control Procedures (United States EPA, 1994). These are meant to ensure that all collected data are scientifically valid to the point that it could withstand legal and scientific challenges. A sampling work plan needs to include both a quality assurance component and a quality control component in order to follow the EPA criteria (United States EPA, 1994). Equipment blanks, field blanks, trip blanks, method blanks, and instrument blanks are quality control tools that can be utilized during sample collection events. These tools can identify the quality of equipment decontamination procedures, sampling procedures, and the presence of cross-contamination in the field, the transport of samples, and in the laboratory (United States EPA, 2009). Field duplicates can help determine the accuracy of laboratory techniques and the homogeneity of sampled material. The Department of Toxic Substances Control employees will determine if the abovementioned blanks and duplicate sampling are going to be included in the sampling event at the subject property.

Laboratory analytical techniques are regulated to assure quality sample results. The samples will be analyzed for PCDD/Fs by EPA Method 8290A, Title 22 Metals by EPA Method 6010B, Mercury by EPA Method 7471B, and pH by EPA Method 9045B as defined by SW-846: Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (United States EPA, 1994). These methods have been approved by the United States EPA as a tool to obtain data that will satisfy the conditions required by the Resource Conservation and Recovery Act (RCRA) and the Code of Federal Regulations (C.F.R.) Parts 122 through 270 (42 U.S.C., 2012a; 40 C.F.R., 2012a). The methods are based on appropriate technologies that have been approved to characterize the substance or substances being tested. Laboratory and in-field quality control procedures and sampling procedures are outlined below, as well as procedures to determine the hazardous characteristics of wastes - toxicity, reactivity, ignitability, and corrosivity – and the amount of the applicable hazardous constituent in the sampled material (United States EPA, 1994).

EPA Method 8290A includes a procedure to analyze a sample for the total presence of PCDD/Fs by high-resolution gas chromatography and high-resolution mass spectrometry. Gas chromatography separates and analyzes constituents that can be vaporized without decomposing. Levels of each constituent can then be measured. Mass spectrometry is a technique that ionizes a compound and separates it with electromagnetic fields. The separated ions are analyzed and the composition of the compound or the constituents of a sample is determined. Congeners of the PCDD/Fs can be detected in the range of parts per trillion and parts per quadrillion by the high-resolution gas chromatography and high-resolution mass spectrometry data system; the detection limit of EPA Method 8290A ranges from 0.04 parts per trillion to 0.25 parts per trillion, differing with each congener analyzed. The precision in the detection limit is important when considering the high toxicity of miniscule doses of PCDD/Fs (United States EPA, 2007c).

In compliance with EPA Method 6010B, inductively coupled plasma-atomic emission spectrometry to determine the presence and concentration of metals—except for Mercury—in solution. Inductively coupled plasma-atomic emission spectrometry can be used on aqueous samples, Toxicity Characteristics Leaching Procedure extracts, soils, sludges, organic wastes, sediments, and other solid wastes. Organic material such as corn can be pulverized and tested with inductively coupled plasma-atomic emission spectrometry following the same procedure (United States EPA, 2007a). The detection limit of this method varies for each metal, ranging from 1.0 mg/kg to 5 mg/kg (United States EPA, 2007a).

EPA Method 7471B is designed to test for mercury in both solids and solutions through the use of amalgamation, thermal decomposition, and atomic absorption spectrophotometry. The detection limit for this method is 0.1 mg/kg (United States EPA, 2007b).

EPA Method 9045B measures the corrosivity of soil by testing its pH. The soil sample is considered to be hazardous waste if it has a pH that is less than or equal to

2, or greater than or equal to 12.5 pH units when mixed with an equal weight of water. This method has a detection limit of 0.1 pH units (United States EPA, 2004).

CHAPTER IV

SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS

This paper has provided a review of PCDD/F and Title 22 metals, their physical properties and characteristics in soil and fly ash, and the regulations relevant to these contaminants. To summarize, PCDD/Fs consist of 17 toxic congeners; the congeners have been assigned toxic equivalency factors which portray each congener's toxicity relative to 2,3,7,8 Tetrachlorodibenzodioxin – the most toxic congener. The toxic equivalency is the sum of the values for these 17 congeners and is the value used when comparing PCDD/F data to PCDD/F regulations and guidelines. Polychlorinated dibenzodioxins and polychlorinated dibenzofurans are highly toxic at relatively miniscule concentrations and pose serious health risks. They are non-polar, so they do not easily dissolve in water. They, however, will bind to fats and bioaccumulate in animals and humans once they have entered into the food chain.

Title 22 metals consist of seventeen types of heavy metals as defined by Title 22 of the California Code of Regulations. Each metal has detrimental effects on human health and the environment. During a preliminary sampling event of the subject property in 2009, fly ash samples were analyzed to determine the presence and/or the concentration of Title 22 metals. Out of these metals, lead exceeded soluble threshold limit concentration as defined in the California Code of Regulations, section 66261.24

and displayed in Table 5. Arsenic, cobalt, copper, molybdenum, vanadium, and zinc were also previously found in fly ash from the preliminary sampling event in 2009; the levels exceeded one or more standards shown in Table 7.

PCDD/F and Title 22 metals regulations and guidelines were listed from government agencies on the federal level including the EPA and the Agency for Toxic Substance Disease Registry. Guidelines from California state-level agencies and regional level agencies were also explored. These agencies include the California Office of Environmental Health Hazard Assessment and the San Francisco Regional Water Quality Control Board. There is a wide range between these standards. Standards between metals and PCDD/Fs vary greatly and each constituent has unique human health and environmental effects. More surprisingly, there is a wide range of standards between agencies for the same constituent.

Finally, the methodology of the sampling plan was outlined. The methodology mainly followed methods of a publication from the EPA entitled “Test Methods for Evaluating Solid Waste, Physical/Chemical Methods” (United States EPA, 1994). This publication outlines protocol for sampling and laboratory analysis that complies with the Resource Conservation and Recovery Act.

The wide range of standards between regulations makes the regulatory aspect of site assessment and remediation subject to interpretation. For example, the EPA’s total toxicity limit concentration for PCDD/Fs is 10,000 parts per trillion. An exceedance of this value deems a constituent to be hazardous waste according to Resource Conservation and Recovery Act. California Human Health Screening Levels considers the same constituent to be potentially hazardous at about 5 parts per trillion. Both standards are meant to quantitatively determine the amount of PCDD/Fs that will pose an environmental or human health risk, yet one value is 2,000 times greater than the other. To add to the perplexity, the RSLs and TTLC standards were both developed by the EPA, yet one is again about 2,000 times greater than the other. In the California Regional Water Quality Control Board: San Francisco Bay Region's "Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater" (2007), it is stated that Total Threshold Limit Concentration (TTLC) and Soluble Threshold Limit Concentrations (STLC) values and criteria were developed mostly in the 1980s; some standards are out of date and only loosely based on environmental and human health considerations.

Furthermore, Minimal Risk Levels are extremely small when compared to TTLC standards. ATSDR recommends that acute exposure to PCDD/F remains below 0.2 parts per quadrillion per day, yet waste material such as fly ash is not deemed as hazardous waste unless it is at least at a concentration of 10,000,000 parts per quadrillion. The likelihood of contamination through various exposure pathways, site use and reuse, and precautionary actions such as the use of protective equipment are examples of factors that would influence the overall risk of exposure and the comparison of minimal risk levels to hazardous waste levels. Despite these uncertainties, it may be unreasonable to believe that, based on the MRL standards, people who are exposed to high—yet nonhazardous—waste levels of PCDD/F are safe from their detrimental effects.

The disclaimers for the CHHSLs, RSLs, and ESLs also obscure legal implications of significant levels of contaminants. Potentially detrimental levels of contaminants are determined, but are stated to only serve as guidelines; they are not meant to be used for or to establish any policy or regulation. The reason for these disclaimers is unclear and contradictory to the overall purpose of creating these guidelines.

Chico Environmental Science and Planning will offer recommendations to the Department of Toxic Substances Control and the District Attorney's Office after reviewing site conditions and sample results. If fly ash is not readily observed on the property and the sample results are below Environmental Screening Levels, Regional Screening Levels, and California Human Health Screening Levels, then Chico Environmental Science and Planning may recommend that no further sampling or regulatory action is necessary. However, if there are any visual observations made that suggest the possibility of environmental and human health risks or if sample results show elevated levels of contamination, a larger sampling event may be recommended. Increasing the amount of samples collected generally increases sample characterization accuracy and would increase the statistical power of the sampling event; it could provide a more thorough understanding of the extent of contamination.

If samples are close to but do not exceed Total Threshold Limit Concentrations, wet extraction tests will be recommended to determine Soluble Threshold Limit Concentrations of the samples. If samples exceed Total Threshold Limit Concentrations or the Soluble Threshold Limit Concentrations, Chico Environmental will develop a sampling plan; the data gathered from the plan would determine the extent of contamination and recommend the removal of contaminated soil. Post clean-up sampling would be required to confirm the removal of the contaminated soil.

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APPENDIX A

WORKPLAN FOR SOIL, CORN ROOTS, CORN STOCKS, and CORN SAMPLING

Prepared for:

Butte County District Attorney

Prepared by:

Chico Environmental Science and Planning
333 Main St. Suite 260
Chico, CA 95928

September, 2012

John Lane
Professional Geologist

WORKPLAN FOR SOIL, CORN ROOTS, CORN STOCKS, and CORN SAMPLING

**The name and location of the property has been omitted from this document*

September, 2012

This Work Plan has been prepared by the staff of Chico Environmental under direction of a State of California Registered Geologist whose seal and/or signature appears hereon.

This Work Plan has been prepared in an objective and unbiased manner and in accord with generally accepted professional practice for this type of work. Chico Environmental believes the results, specifications, conclusions and professional opinions to be accurate and relevant but cannot accept responsibility for the accuracy or completeness of public documentation or possible withholding of information by interviewees or other private parties. **We make no other warranty, either expressed or implied.**

TABLE OF CONTENTS

1.0 INTRODUCTION

This document is the proposed Work Plan for soil, corn roots, corn stocks, and corn sampling for characterization at an undisclosed location in California**.** The location cannot be disclosed in this document because of its involvement in a current criminal investigation. It will be referred to as “the site” throughout the document. The objective of this investigation is to obtain samples of corn, corn roots, corn stocks, and soil to preliminarily characterize the material (hazardous or not) that originated from an undisclosed biomass power plant in California and to determine the levels of California Code of Regulations Title 22 Metals, and polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/F) within the samples. This work plan will outline the process of acquiring several types of information including results of laboratory analysis of collected samples, general research, and opinions/ observations.

2.0 SITE IDENTIFICATION INFORMATION

Site:	*Omitted*
Lead Agency:	Butte County District Attorney Attn: Mr. Hal Thomas
Environmental Services Contractor:	Chico Environmental Science and Planning 333 Main St., Suite 260 Chico, CA 95928 (530) 899-2900
Registrations:	Professional Geologist #7717

3.0 SITE HISTORY

The site is believed to have been exposed to polychlorinated dibenzodioxins and dibenzofurans (PCDD/F) and/or Title 22 Metals from cogenerated fly ash originating from an undisclosed biomass power plant in California. The ash was deposited for use as a soil amendment.

3.1 The biomass power plant

The biomass power plant and its undisclosed owner and operator generate waste-to-energy power. They predominantly use forest slash and orchard trimmings as a fuel source, but the use of other materials is suspected. Documentation procured by the Butte County District Attorney's office shows that the plant has been receiving and incinerating urban waste such as demolished structures. Burnt scrap metal has been found in multiple fly ash piles at various ash disposal locations. Approximately 8,000 tons of ash is generated each year.

The owner and operator has been fined in the past for environmental violations from similar biomass power plants by the Departments of Environmental Protection of Connecticut, Florida, Hawaii, Massachusetts, Pennsylvania and New Jersey. Violations include municipal garbage piled outside buildings, and numerous instances of air quality violations including nickel, soot, carbon monoxide, sulphur dioxide, PCDD/Fs, hydrogen chloride and nitrogen oxide. In 2006 at an east coast facility, nickel emissions were measured at twice the permitted level. In 2007 at a different east coast facility, PCDD/F levels exceeded allowable emissions by 350%.

Ash is known to have been sent to orchards and row crops in three locations to be used as soil amendment. Ash has also been transported to a trucking property, and a landfill. In January, 2010, the District Attorney Special Investigator sampled ash at the landfill that originated from the biomass power plant. The sampling analysis showed that levels of Arsenic, Barium, Cadmium, Cobalt, Copper, Lead, Selenium, Vanadium, and Mercury exceeded one or more regulatory standards. Sampling events were also performed in December, 2011 and June, 2012 at the ash pile deposited at the trucking property. Analysis of the samples from these sampling events showed significant levels of PCDD/Fs and arsenic.

An inspection of the facility was performed in January, 2010 by a representative from the Central Valley Water Board, along with the plant manager, environmental manager, and plant operator. Another investigation was performed in August, 2012 with a District Attorney Special Investigator, the plant manager, and the lead scientist from Chico Environmental Science and Planning. The purpose of these investigations was to determine whether the ash from the facility was properly characterized prior to use as a soil amendment. The results of the testing indicated that one sample exceeded the California Code of Regulations Title 22 hazardous waste criteria for lead in 2010. All samples collected in 2012 exceeded hazardous waste pH levels; PCDD/F and arsenic levels were also notably high, but did not exceed the California Code of Regulations TTLC limits.

3.2 The site

The site is an agricultural field with corn growing throughout most of the property. In 2009, fly ash disposed at the site was sampled for Title 22 Metals and Chromium VI. A representative of the site owner, two representatives of the Regional Water Quality Control Board, and the Butte County District Attorney's Special Investigator observed the sampling procedures. The sample analysis found that Arsenic, Cobalt, Copper, Lead, Molybdenum, Vanadium, and Zinc exceeded one or more regulatory levels. Lead was determined to be above hazardous waste levels. At the time of sampling, ash materials were observed in approximately 95 discrete linear piles on the agricultural field. The piles were roughly three feet high with flat tops, five to six feet wide at the base, and varied in length from just a few feet to over a hundred feet long. The fly ash was unconsolidated, loose material including nails, screws, rocks up to about 1.5 inches and other unidentifiable materials.

The site is also expected to have been exposed to PCDD/Fs based on results from previous sampling events mentioned above in section 3.1.

4.0 OBJECTIVES AND SCOPE OF WORK

The objective of this Work Plan is to establish the scope of work and technical procedures needed to obtain samples from the sites. The purpose of collecting samples is to initially determine the level of contamination present, and to determine if the materials fall into the classification of Hazardous Waste.

The proposed investigation will consist of collecting material samples from soil, corn, corn roots, and corn from the site. Three distinct sample locations will be identified once on site. The corn, corn, roots, and corn stocks will be collected from the same plant for each sample. Two soil samples will be collected directly adjacent to the plant that is to be sampled. The soil will be analyzed for PCDD/Fs, pH, and Title 22 Metals. The corn, corn roots, and corn stocks will only be analyzed for Title 22 Metals.

In total, 15 samples – 6 soil samples, 3 corn samples, 3 corn root samples, and 3 corn stock samples – will be collected. Samples will be sent to the Department of Public Health's laboratory and to the Department of Toxic Substances Control laboratory for PCDD/F, pH, and Title 22 metals analysis. Due to the unknown nature of the project layout, exact sample location will be determined once on site.

The investigation will be carried out by a qualified contractor under the direct supervision of a state of California Registered Professional Geologist and Environmental Professional. A District Attorney Special Investigator and scientists from the Department of Toxic Substances Control will be present during the sampling event at the sampling site.

The scope of work has been divided into 6 tasks as follows:

Task 1. Project Setup.

Task 2. Soil Sampling.

Task 3. Corn Roots Sampling.

Task 4. Corn Stocks Sampling.

Task 5. Corn Sampling.

Task 6. Chemical Analysis.

Task 7. Preparation of the Technical Report.

Task 1. Project Setup

Upon approval of this Work Plan by BCDA, prior to the initiation of field activities, the following sub-tasks will be undertaken for each sampling location:

1. BCDA Special Investigator will arrange sampling date, time and access.

2. Chico Environmental and the Department of Toxic Substances Control will prepare necessary sampling equipment, containers and shipping materials.

Task 2. Soil Sampling

Samples will be collected using disposable trowels, a 16 oz., and a 32 oz. glass jar. The jars are also the sample containers. Each sample container will be labeled prior to collection of the sample. Soil will be excavated with a disposable trowel then scooped each glass jar until it overflows. The contents of the jar will not be compacted. Debris or rocks that would prevent the closing of the sampling container will be removed. The sample container will be labeled, and evidence tape will be placed over the sealed sample container. A clean pair of nitrile gloves will be used during each sample collection. After the sample is collected, it will be placed for shipment into a pre-cooled ice chest on ice packs at approximately 4°C for transportation to the laboratories. Proper chain-of-custody procedures will be followed at all times.

Task 3. Corn Roots Sampling.

Samples will be collected using gardening scissors and disposable trowels, and placed into plastic bags which will serve as the sample containers. The roots will be removed from the stock and dug up with the disposable trowel. The sample container will be labeled prior to collection of the sample. Evidence tape will be placed over the sealed sample container. The contents of the plastic bag will not be compacted. A clean pair of nitrile gloves will be used during the sample collection. After the sample is collected, it will be placed for shipment into a pre-cooled ice chest on ice packs at approximately 4°C for transportation to the laboratories. Proper chain-of-custody procedures will be followed at all times.

Task 4. Corn Stock Sampling.

Samples will be collected using gardening scissors, and placed into plastic bags which will serve as the sample containers. Two sections of corn stock will be cut at approximately 10" segments and collected. The sample container will be labeled prior to collection of the sample. Evidence tape will be placed over the sealed sample container. The contents of the plastic bag will not be compacted. A clean pair of nitrile gloves will be used during the sample collection. After the sample is collected, it will be placed for shipment into a pre-cooled ice chest on ice packs at approximately 4°C for transportation to the laboratories. Proper chain-of-custody procedures will be followed at all times.

Task 5. Corn Sampling.

Samples will be collected using gardening scissors, and placed into plastic bags which will serve as the sample containers. The sample container will be labeled prior to collection of the sample. Evidence tape will be placed over the sealed sample container. A clean pair of nitrile gloves will be used during the sample collection. After the sample is collected, it will be placed for shipment into a pre-cooled ice chest on ice packs at approximately 4°C for transportation to the laboratories. Proper chain-of-custody procedures will be followed at all times.

Task 6. Sample Analysis.

All samples will be analyzed for the following: polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/F) by EPA method 8290, pH by EPA Method

9045, Mercury by EPA Method 7471, and Title 22 Metals by EPA method 6010B. If elevated levels of Metals are present, a Soluble Threshold Limit Concentration (STLC) analysis will be conducted. Samples will be sent to the Department of Public Health and to the DTSC laboratory for PCDD/F, Title 22 metals, and pH analysis. One soil sample at each of the three sample locations will be sent to the DTSC lab; the rest of the samples will be sent to the Department of Public Health.

Task 7. Preparation of the Technical Report.

Following completion of the tasks listed above and receipt of the results of all chemical analyses a technical report will be prepared by Chico Environmental. The report will be prepared to include the following at a minimum:

1. A description of local and regional geology and hydrogeology.

2. A description of the work performed.

3. Results of chemical analysis.

4. Conclusions and recommendations.

5.0 PARTIES INVOLVED

Chico Environmental, a Butte County District Attorney Special Investigator, and representatives from the Department of Toxic Substances Control will be present during sampling.

6.0 SUMMARY

This Work Plan outlines the investigative procedures necessary to initially determine the level of contamination and potential waste classification of corn, corn roots, corn stocks, and soil at the subject sites. Following results of this investigation, recommendations will be made for additional investigation, remedial actions, and/or site closures.

7.0 QUALIFICATIONS AND SIGNATURE

Signature of Professional Geologist – John Lane, P.G. No. 7717

Signature/Seal of Professional Geologist Date