

Appendix D
Cullinan Ranch Contaminant Sampling Report and Contaminant
Cleanup Report

Contract Number GS-10F-0076K
Order Number 11640-3-M083A

Cullinan Ranch Contaminant Sampling Report

Vallejo, California

November 2003

Prepared for



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ACRONYMS AND ABBREVIATIONS

µg/g	Micrograms per gram
ATSDR	Agency of Toxic Substances and Disease Registry
DDD	Dichlorodiphenyldichloroethane
DDE	Dichlorodiphenyldichloroethene
DDT	Dichlorodiphenyltrichloroethane
DOI	Department of the Interior
EPA	U.S. Environmental Protection Agency
ER-L	Effects range – low
ER-M	Effects range - medium
FWS	U.S. Fish and Wildlife Service
ICA	International Copper Association
mg/kg	Milligrams per kilogram
ppm	Parts per million
UCL	Upper confidence limit

1.0 INTRODUCTION

The U.S. Fish and Wildlife Service (FWS) is responsible for planning the Tidal Marsh Restoration at Cullinan Ranch, San Pablo Bay National Wildlife Refuge, Solano and Napa Counties, California. As part of the process, FWS tasked Tetra Tech EM Inc. with evaluating the site for the presence of elevated concentrations of chemicals in surficial soils and sediments at the site.

1.1 PURPOSE OF INVESTIGATION

The purpose of this investigation is to identify chemicals with elevated concentrations in soil and sediment at Cullinan Ranch prior to the commencement of tidal marsh restoration activities. The planned restoration entails breaching levees at the site and will result in the flooding of all sampled areas.

1.2 PROJECT OBJECTIVES

Previous investigations conducted in 1990 identified elevated levels of barium, copper, nickel, and zinc at Cullinan Ranch and identified arsenic, mercury, and selenium as data gaps. The 1990 survey also detected elevated concentrations of dichlorodiphenyltrichloroethane (DDT) and dichlorodiphenyldichloroethane (DDD) in the Farmyard Area at Cullinan Ranch (FWS 1990). Prior to the commencement of restoration efforts at the site, additional data are needed to identify contaminants at concentrations potentially posing unacceptable risk to ecological receptors. Therefore, soil and exposed sediment samples were collected and analyzed for metals and pesticides. The detected concentrations were compared to literature values to identify contaminants potentially posing unacceptable risk to ecological receptors. Table 1 provides a complete overview of the data quality objectives for the sampling event.

1.3 SITE DESCRIPTION

Cullinan Ranch consists of a former tidal wetland located west of the Napa River along the northern shore of San Pablo Bay (Figure 1). In the late 1800's and early 1900's, the property was diked and drained for use as farmland; however, the highly acidic, saline soil at Cullinan Ranch limited agricultural activities to the dry farming for oats and oat hay. The property was purchased by the FWS and added to the San Pablo Bay Wildlife Refuge (San Francisco 1993; Coastal America 1996). The following four sample areas were identified at the site: Pole Barn, Farmyard (including the Pump Canal), East Pond, and West Pond (Figure 2).

Physical Setting

Historically, Cullinan Ranch was part of an expansive tidal marsh network interlaced with meandering sloughs in the Napa River Delta (Federal Register 2002). Since being diked and drained for agriculture, the 1,493 acre parcel of land has subsided several feet in elevation

(FWS 1990; Federal Register 2002). Initially, the FWS planned to use dredge materials to increase the elevation of the marsh plain prior to reintroducing tidal flows (FWS 1990). Recently, however, the FWS has decided to breach the perimeter levee and allow the tidal marsh plain and channels to develop through natural geomorphic processes resulting from reintroduction of tidal flows (Federal Register 2002).

Ecological Setting

Currently, Cullinan Ranch is a former tidal wetland predominately consisting of uplands with two ponded areas. There is gravel present in areas around the Farmyard and Pole Barn. The remains of structures including a large concrete foundation (Table 2) are also present. All sites except for the pump canal were dry during the sampling event. The ponded areas provide minimal wetland value for wildlife compared to the large areas of higher quality wetlands in the vicinity. However, the restoration of the salt marsh is expected to provide critical habitat for the endangered California clapper rail (*Rallus longirostris obsoletus*) and salt marsh harvest mouse (*Reithrodontomys raviventris*) (FWS 1990).

1.4 SUMMARY OF PREVIOUS INVESTIGATIONS

Prior to purchasing the Cullinan Ranch, the FWS conducted three surveys of the property in 1988, 1989, and 1990. In 1988, the FWS identified the following areas of concern: (1) trash in the ponded area near the Farmyard; (2) mosquito abatement practices on or adjacent to the property; (3) unknown past pesticide use practices; (4) the proximity of Mare Island Naval Shipyard hazardous waste sites; and (5) the general water quality of the Napa River and San Pablo Bay.

During the survey conducted in 1989, FWS identified the following additional areas of concern: (1) another ponded area used as a dump; (2) two buildings containing cans of pesticides; (3) areas of discolored soil; and (4) “opaque milky green water” in the drainage ditch near the pump house. The 1989 survey also mentioned the possibility of dioxins occurring in areas where herbicide drums or herbicide treated vegetation may have been burned. An interview with the tenant farmer also revealed problems with people dumping trash in the ditch along Highway 37 to the south and the former practice of spraying oil on gravel near the Pole Barn to cut down on dust.

The survey conducted in 1990 identified elevated levels barium (2,000 milligrams per kilogram [mg/kg]), copper (160 mg/kg), nickel (670 mg/kg), and zinc (1,800 mg/kg). In the composite sample from the Farmyard Area, the detected concentrations of p,p'-DDT (0.25 mg/kg), p,p'-dichlorodiphenyldichloroethene (DDE) (0.1 mg/kg) and total DDT (0.52 mg/kg) were elevated. Overall, the elevated concentrations were limited to a few small areas and clean up was expected to be minimal. The recommended clean up alternatives consisted of removing and disposing the soil in a class I or class II landfill or mixing the contaminated soil and spreading it over a large area on the site before covering with 2 to 3 feet of clean dredged material.

2.0 SAMPLING AND LABORATORY METHODS

The following sections summarize the sampling activities and laboratory methods, and provide a rationale for selecting comparison criteria. The sample areas, site descriptions, and analytical methods are presented in Table 2. The sample areas are shown on Figure 2. Appendix A provides a photograph documentation log of the sampling activities and locations.

2.1 SUMMARY OF SAMPLING ACTIVITIES

Sample point locations were chosen based on the specific spatial and geological dynamics of the sampling area. Site characteristics such as driveways, canals, vegetation, and soil compactness were taken into consideration before selecting specific point locations. Sample point locations were selected randomly, however specific features such as low points where surface runoff might collect were chosen in order to present a “worst case scenario.” As point locations were located, they were systematically marked with flags and the coordinates of each point location were recorded via a global positioning system. Each point location was assigned a unique sample point identification number and photographed (Appendix A). Point identification numbers (e.g. CRWP017) followed the following naming convention:

- two letters to identify the site as Cullinan Ranch (CR)
- two letters to identify the sampling area
 - WP: West Pond Area
 - FY: Farmyard Area (including the Pump Canal)
 - EP: East Pond Area
 - PB: Pole Barn Area
- three numbers to identify the sampling point (001 through 019).

After all sample point location were flagged, the sampling team returned to each location to collect, document, and label samples. At each point location, two shovels were used to extract soil. The shovels were placed adjacent to one another and simultaneously pushed into the soil until the top of the shovel blades were flush with the ground surface or until the point of refusal (see photo 1). At this point, the shovels were simultaneously propped upwards with a slow methodical movement. This effectively exposed a large piece of underlying soil (see photo 2). The mass of soil was measured with a tape measure and samples were collected between 0 and 3 inches from the surface, and again, between 6 and 12 inches from the surface. Discreet samples were collected from the exposed soil mass by either scraping the soil into a 16-ounce jar with the cap for that specific sample, or by placing a small chunk of soil into the jar by hand. The sampling team was very careful to change gloves in between collection of each sample, including samples collected at different depths from the same location. In addition, the sampling team ensured that no sample was collected from an area that was in contact with any portion of the shovels. After samples were collected and capped, the jars were immediately marked with the appropriate point identification and

sample numbers. Sample identification numbers (e.g. FWCRSS010) followed the following naming convention:

- two letters to identify the project as an FWS site (FW)
- two letters to identify the site as Cullinan Ranch (CR)
- two letters to identify the type of sample as surface sediment (SS)
- three unique numbers to identify the sample (001 through 038)

Field notes were recorded in a notebook during all sampling activities and are presented in Appendix D. Sample jars were immediately placed in a cooler with ice. Chains of custody were completed at the end of each sampling day and are presented in Appendix B.



Photo 1: Shovels were used to extract soil samples by slowly and systematically propping large pieces of soil in an upward position.

Photo 2: Once soil masses were exposed, samples were collected between 0 and 3 inches, and again between 6 and 12 inches. Samples were not collected from areas that came in contact with the shovels.



2.2 SUMMARY OF LABORATORY METHODS

Curtis and Tompkins Laboratory, certified by the California Department of Health Services through the Environmental Laboratory Accreditation, and proficient in the use of U.S. Environmental Protection Agency (EPA)-approved methodologies analyzed the samples. The analytical program included the following analyses:

- Pesticides by EPA SW-846 Method 8081
- Metals by EPA SW-846 Method 6010/7470

When reporting results the laboratory assigns the following EPA-defined qualifiers:

- U – indicates the compound was analyzed for but not detected.
- J – indicates an estimated value.

Reasons for estimating data and the cursory data validation process are discussed in Appendix C of this report.

2.3 RATIONALE FOR CRITERIA SELECTION

The analytical results received from the laboratory were compared with the following criteria:

- San Francisco Bay Ambient Sediment Concentrations (California Regional Water Quality Control Board, San Francisco Bay Region [RWQCB] 2000)

- Wetland Surface Material Concentrations for Beneficial Reuse of Dredged Materials (RWQCB 2000)
- Wetland Foundation Material Concentrations for Beneficial Reuse of Dredged Materials (RWQCB 2000)
- Effects Range-Low (ER-L) concentrations (Long and others 1995; Long and Morgan 1990)
- Effects Range-Median (ER-M) concentrations (Long and other 1995; Long and Morgan 1990)
- 95 Upper Confidence Limit (UCL) of the Geometric Mean for Western Soils (Shacklette 1984 as cited in FWS 1990)

The criterion values are presented in Table 3. These criteria are considered acceptable and appropriate for comparing with soils and exposed sediments from Cullinan Ranch because future restoration activities at the site will result in all sampling areas being flooded; therefore, all surficial soils will become submerged sediments. It should be noted that the Wetland Surface and Foundation Material Concentrations are based on San Francisco Bay Ambient Sediment Concentrations and ER-M values, respectively; therefore, concentrations that exceeded one criteria usually exceeded corresponding criteria as well (Table 3). Other regional sediment concentrations such as the mean concentrations from the Regional Monitoring Program's San Pablo Bay sampling location and the U.S. Army Corp of Engineers marsh study (RWQCB 2000) were also evaluated but deemed less appropriate since they are not based on regulatory guidance or toxicological data.

3.0 RESULTS

The following sections present the analytical results from samples collected at Cullinan Ranch and their biological and toxicological significance.

3.1 EXCEEDANCES OF CRITERIA

The analytical results identified several metals and pesticides present in samples collected at Cullinan Ranch. While most of the concentrations did not exceed those of the comparison criteria, some elevated concentrations were detected. The complete analytical results are presented in Tables 4 and 5 and Appendix B. The criteria exceedances are shown on Figures 3 through 6.

Pole Barn Area

In the Pole Barn Area, samples were collected and analyzed for metals from five locations at two depths for a total of ten samples. Only zinc concentrations (with a maximum concentration of 1,500 mg/kg) exceeded all comparison criteria (Figure 6 and Table 4).

Other elevated metal concentrations were above the ER-L criteria, but below the ER-M and San Francisco Bay Ambient concentrations. The level of arsenic (9.1 mg/kg) was greater than the ER-L of 8.2 mg/kg in one sample between 6 and 12 inches. Mercury was identified in one sample (0.16 mg/kg) between 0 and 3 inches at a concentration slightly above the ER-L of 0.15 mg/kg. Nickel and copper were found in all ten samples taken at levels greater than the ER-L criteria.

Concentrations of zinc in six of ten samples were greater than the ER-L, and five samples were greater than the San Francisco Bay Ambient, the San Francisco Wetland Surface Material, and the Western Soils 95 UCL. Two of the five samples from locations CRPB002 and CRPB003 were also greater than the San Francisco Wetland Foundation Material and ER-M criteria (Figure 6).

Farmyard Area

In the Farmyard Area, samples were collected and analyzed for metals and pesticides from six locations, including one located in the Pump Canal, at two depths for a total of twelve samples. The Pump Canal results are discussed separately below since it was the only submerged area during the sampling event.

In the Farmyard Area arsenic was detected in ten of ten samples, with eight samples exceeding the ER-L criteria (Figure 5 and Table 4). The sample taken from CRFY008 between 0 and 3 inches had an arsenic concentration of 16 mg/kg, which slightly exceeds the San Francisco Bay Ambient and the San Francisco Wetland Surface Material criteria; however, the concentration is similar to the San Francisco Bay Ambient of 15.3 mg/kg and is well below the ER-M of 70 mg/kg. The concentrations of cadmium in eight samples also exceeded the San Francisco Bay Ambient and the San Francisco Wetland Surface Material criteria of 0.33 mg/kg; however, even the maximum concentration of 1.7 mg/kg is more similar to the ER-L of 1.2 mg/kg than the ER-M of 9.6 mg/kg.

Six samples had concentrations of copper and mercury that exceeded the ER-L criteria; however, none were greater than the San Francisco Bay Ambient or ER-M. Ten samples exceeded the ER-L criteria for nickel, four of which also exceeded the ER-M criteria; however, only location CRFY019 had concentrations greater than the San Francisco Bay Ambient and ER-M. Lead and zinc were detected in all samples, with maximum concentrations of 110 mg/kg and 210 mg/kg, respectively. Only three detections of each metal exceeded comparison criteria but all concentrations were below the San Francisco Wetland Foundation Material criteria and ER-M criteria.

In the Pump Canal, two samples were collected from one location and analyzed for metals and pesticides. In the surface sample (FWCRSS037) from CRFY019, iron, nickel, and zinc exceeded comparison criteria. In the deeper sample (FWCRSS038) from CRFY019, arsenic, copper, mercury, nickel, and zinc exceeded comparison criteria. Only nickel concentrations exceeded the Wetland Foundation Material and ER-M criteria.

In the Farmyard Area and Pump Canal, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, total DDTs, and total chlordane were the only pesticides with concentrations exceeding comparison criteria (Table 5 and Figure 5).

East Pond Area

In the East Pond Area, samples were collected and analyzed for metals from three locations at two depths for a total of six samples. No samples collected from the East Pond Area had concentrations exceeding the San Francisco Bay Ambient or ER-M criteria (Table 4 and Figure 4). Arsenic was detected in three of the samples with a maximum concentration of 9.8 mg/kg. Two of the detections exceeded the ER-L criteria; however, all of the concentrations were below the San Francisco Bay Ambient. Concentrations of copper exceeded the ER-L comparison criteria in three samples, and concentrations of mercury exceeded the ER-L criteria in two samples. Nickel exceeded the ER-L criteria in all six samples.

West Pond Area

In the West Pond Area, samples were collected and analyzed for metals from five locations at two depths for a total of ten samples. No samples collected from the West Pond Area exceeded the San Francisco Bay Ambient (Table 4 and Figure 3). Nickel was the only chemical with concentrations exceeding the ER-M criteria; however, these concentrations were below the San Francisco Bay Ambient. Arsenic concentrations exceeded the ER-L criteria in all samples, and mercury exceeded the same criteria in four samples. One sample taken between 6 and 12 inches had a copper concentration of 34 mg/kg, which exceeded the ER-L criteria. The nickel concentrations in all samples exceeded the ER-L criteria, while five samples also exceeded the ER-M criteria, and one sample from location CRWP017 (with a concentration of 68 mg/kg) exceeded the Western Soils 95 UCL criteria (Figure 3).

3.2 BIOLOGICAL SIGNIFICANCE

In order to evaluate the biological significance of the chemical results, sample results were also evaluated together to identify whether any concentrations consistently exceeded toxicological benchmarks such as the ER-Ls and ER-Ms. The frequency of detections, magnitude of exceedances, and spatial distribution were considered qualitatively in the evaluation.

A few chemicals were detected at a frequency of 100 percent in the 38 samples collected: aluminum, barium, calcium, chromium, cobalt, copper, iron, magnesium, manganese, nickel, potassium, sodium, vanadium, and zinc (Table 6). Calcium, iron, magnesium, potassium, and sodium are essential nutrients that are not usually considered to be toxic. Aluminum, barium, cobalt, manganese, and vanadium do not have toxicological criteria; however, concentrations were generally well below the maximum concentrations for ranges of Western Soils presented by Shacklette and Boerngen (1984). Beryllium was detected in 26 out of 38 samples: ten in the West Pond Area, nine in the Pole Barn Area, four in the Farmyard Area,

and three in the East Pond Area. None of the beryllium detections were significant enough to exceed comparison criteria.

Chemicals with no or low frequency of detections may be less likely to No concentrations of antimony, selenium, or silver were detected in any of the 38 samples collected. Cadmium was only detected in the Farmyard Area (nine detections) and the Pole Barn Area (one detection) and no concentration was greater than the ER-L. Thallium was only detected once in the Pole Barn Area at a concentration of 1.3 mg/kg. Molybdenum was found in two samples in the East Pond Area with the maximum detected concentration being 1.7 mg/kg.

Chemicals most frequently exceeding ER-L criteria were arsenic, copper, lead, mercury, nickel, zinc, DDTs, and total chlordane. Only nickel, zinc, DDTs, and total chlordane exceeded the ER-M criteria.

Arsenic was found in all samples collected in the Farmyard and West Pond Areas, in half of the samples collected in the East Pond Area, but only two samples collected from the Pole Barn Area. A total of 27 concentrations were detected out of 38 samples. The maximum detected concentration of 16 mg/kg found in the Farmyard Area in sample FWCRSS015 is twice the ER-L of 8.2 mg/kg. Although some adverse effects to invertebrates from exposure to arsenic may occur, the maximum concentration is more similar to the ER-L than the ER-M of 70 mg.kg.

The maximum detected copper concentration (64 mg/kg) occurred in the Farmyard Area in sample FWCRSS015. The maximum concentration is more similar to the ER-L of 34 mg/kg than the ER-M of 270 mg/kg. Copper concentrations exceeded the throughout the Farmyard, East Pond, and West Pond Areas. Although some adverse effects to invertebrates from exposure to copper may occur, the magnitude of the exceedances is not very significant.

Lead was detected in 35 of the 38 samples with a maximum concentration of 110 mg/kg, which is more than twice the ER-L of 46.7 mg/kg, but only half of the ER-M of 218 mg/kg. The maximum detected lead concentration (110 mg/kg) was found in the Farmyard Area in sample FWCRSS015. Lead concentrations only occasionally (3 samples) exceeded the ER-L in the Farmyard Area and is not likely to cause significant adverse effects to invertebrates based on the magnitude of the exceedance and the limited distribution.

Mercury was detected in 37 of the 38 samples with at least one sample exceeding in the ER-L in each of the sampling areas. Although some adverse effects to invertebrates from exposure to mercury, may occur, the magnitude of the exceedance is not very significant and even the maximum concentration of 0.24 mg/kg was below the ER-M of 0.71 mg/kg. In addition, the San Francisco Bay Ambient concentration of 0.43 mg/kg is greater than the maximum site concentration and invertebrates may have developed a tolerance for mercury at this level.

Nickel exceeded the ER-L in at least one sample in each of the sampling areas. Nickel is very widespread throughout the site at both sampling depths. The maximum nickel concentration of 220 mg/kg detected in sample FWCRSS038 from the Pump Canal is more

than four times greater than the ER-M of 51.6 mg/kg. Some adverse effects to invertebrates from exposure to nickel may occur at the site.

Zinc concentrations exceeded the ER-L in samples from the Farmyard and Pole Barn Areas. The maximum detected zinc concentration of 1,500 mg/kg was detected in sample FWCRSS003 in the Pole Barn Area. The maximum concentration is more than three and a half times the ER-M of 410 mg/kg. Some adverse effects to invertebrates from exposure to zinc may occur at the site.

In the Farmyard Area and Pump Canal, 4,4'-DDD, 4,4'-DDE, 4,4'-DDT, total DDTs, and total chlordane were detected at concentrations exceeding the ER-L and ER-M criteria (Table 5 and Figure 5). Concentrations of pesticides appear to be widespread throughout the Farmyard Area at both sampling depths. The toxicological effects of DDTs and chlordane are presented in Section 3.3.

3.3 TOXICOLOGICAL EFFECTS

The following sections describe the toxicological effects of chemicals detected in sampling results from Cullinan Ranch.

3.3.1 Arsenic

Arsenic is a naturally occurring element that is widely distributed in the environment. The anthropogenic sources of arsenic include (1) metal smelting, (2) coal burning, and (3) pesticides use and manufacturing (Brown and others 1983, as cited in U.S. Department of the Interior [DOI] 1998; Nriagu 1994; Tanner and Clayton 1990).

The arsenic concentration in soil normally ranges from 1 to 50 mg/kg, though it does not generally exceed 10 mg/kg (Brown and others 1983, as cited in DOI 1998). The maximum concentration of arsenic detected at Cullinan Ranch was 16 mg/kg, though the average range throughout the samples was 9.5 mg/kg. Terrestrial flora and fauna, birds, and freshwater biota usually contain less than 1 milligram of arsenic per kilogram wet weight (DOI 1998).

The bioavailability and toxicity of arsenic depend on its chemical and physical forms, the exposure route, and the species of concern. The bioavailability of arsenic in soil depends on several soil factors. Generally, arsenic toxicity varies with soil pH, clay content, ion exchange capacity, temperature, and oxidation-reduction potential. Specifically, soil conditions that affect the bioavailability of arsenic to plants are acidity, concentration of aluminum and iron oxide, concentration of phosphate, and temperature of the soil (Peterson and others 1981; Asher and Reay 1979; Jacobs and others 1970).

Arsenic has been used as a pesticide in the past. Soil arsenic concentrations of 375 mg/kg may reduce growth and metabolism of soil microbiota, while concentrations of 150 to 165 mg/kg were found to reduce numbers of bacteria and protozoans, as well as the number of earthworms in the soil (NRC 1978, as cited in Eisler 1988a). However, some soil

microorganisms can tolerate and metabolize relatively high concentrations of arsenic (Wang and others 1984, as cited in Eisler 1988a).

Some species of birds are more sensitive to arsenic than others (Eisler 1988a; DOI 1998). The acute oral exposure of inorganic arsenic by birds destroys the blood vessel lining in the gut, which can result in lower blood pressure, and causes hepatocyte damage by arsenic inhibition of the sodium pump in cells (Nystrom 1984, as cited in [Eisler 1988a](#)). Toxic effects of arsenite in birds include loss of muscular coordination, debility, slowness, jerkiness, falling hyperactivity, fluffed feathers, drooped eyelids, huddled position, unkempt appearance, loss of righting reflex, immobility, and seizures (Eisler 1988a; Camardese and others 1990, Opresko and others 1994, both as cited in DOI 1998; Stanley and others 1994).

3.3.2 Copper

Copper is a naturally occurring element that is widely distributed in the environment. The mean soil concentration of copper throughout the world is 20 mg/kg ([Kabata-Pendias and Pendias 1992](#)). The mean soil concentration of copper at Cullinan Ranch is 35.5 mg/kg. Copper is the main component of metal alloys, including brass, bronze, and gun metal, and has been used for centuries to make tools, ornaments, and utensils. Copper is also used as an ingredient in many fungicides and insecticides applied on agricultural crops ([Meister 1995](#)). Copper is a common contaminant in urban runoff. It is present in landfill leachate and sewage sludges and leaches from drinking water pipes, particularly where water is acidic (Irwin 1996, as cited in DOI 1998). Copper is both a nutrient and a toxicant; therefore, either a copper deficiency or an excess of copper can cause adverse effects in organisms.

Copper exists in soil in five states: (1) dissolved and exchangeable copper, (2) copper weakly bound to specific sites, (3) organically bound copper, (4) copper precipitated on oxides, and (5) residual copper in clay lattice structures (Baker and Amacher 1982, as cited in [DOI 1998](#)). About 90 percent of the available copper in soils is associated with organic materials. Organo-copper complexes are extremely stable, and copper in such complexes is not available. Adsorption to organic materials increases with increasing pH. Copper in soil is mobile under oxidizing and acidic conditions and immobile in organic-rich and reducing environments.

Copper availability in contaminated soils is influenced by organic matter content, cation exchange capacity, pH, and the chemical form of the metal ([Hughes and others 1980](#)). One hundred mg/kg total copper in the soil is considered to be the threshold concentration for toxicity to plants (EPA 1987, Bengtsson and Tranvik 1989, both as cited in International Copper Association [[ICA](#)] [1992](#)). For soil invertebrates, 100 mg/kg is the threshold copper concentration for toxicity (EPA 1987, Bengtsson and Tranvik 1989, both as cited in [ICA 1992](#)). Copper can also be toxic to birds, although they appear to be fairly tolerant of chronic copper exposure.

3.3.3 Lead

Lead is found at a worldwide mean concentration of 16 µg/g of soil in the earth's crust. The average concentration is slightly higher at Cullinan Ranch (20 mg/kg). Lead has been characterized as a poison for centuries, and environmental pollution from lead is well documented (Eisler 1988b; Sadiq 1992; Pain 1995). Lead has been used in the production of solder, pipes, paint, ceramics, roofing materials, caulking, ammunition, and as a gasoline additive. From a geochemical perspective, lead is ubiquitous and occurs in rocks, soils, water, plants, animals, and air. Lead is neither essential nor beneficial to living organisms, and all data show that its metabolic effects are adverse.

The biological availability and fate of lead in soil is affected by such factors as soil pH, organic content, ion-exchange characteristics, and the amount of lead in the soil (Sadiq 1992; Pain 1995).

Lead is not considered to be an essential element for plants (Demayo and others 1981). Plants can bioaccumulate lead (Crowder 1991, as cited in Pain 1995; Sadiq 1992; Suedel and others 1994), but there are no reported events of biomagnification to higher trophic levels. Lead affects plant physiological processes only when found in soil at very high concentrations.

Lead produces a variety of toxic effects in birds, including damage to the nervous system, muscular paralysis, inhibition of heme synthesis, damage to kidneys, damage to the liver, and death (Mudge 1983, as cited in Eisler 1988b).

3.3.4 Mercury

Mercury, a heavy metal, is volatile, even at temperatures below its melting point. Mercury occurs as both organic and inorganic forms in soil, with the three most common forms being methylmercuric chloride, phenyl mercuric acetate, and mercuric chloride (Hogg and others 1978; Demayo and others 1981; FWS 1988). Mercury is a known mutagen, teratogen, and carcinogen. Its toxicity varies with its form, dose, route of ingestion, species, sex, age, and general condition of the organism (Heinz 1996a; Thompson 1996; Wolfe and others 1998). Mercury bioaccumulates and biomagnifies (Heinz 1996a; Thompson 1996; Wolfe and others 1998).

Mercury in soil is usually immobile and unavailable to plants because of its high binding capacity for clays and other charged anions (Beauford and others 1977; Hogg and others 1978). In soil, mercury may leach to the subsoil, be adsorbed by plants, volatilize, be absorbed by soil colloids, or precipitate as insoluble mercury (Hogg and others 1978). Its fate depends on the chemical form of the mercury and the organic content, pH, and cation exchange capacity of the soil (Hogg and others 1978). The average mercury concentration at Cullinan Ranch is 0.13 mg/kg.

Sublethal effects of mercury on birds include adverse effects on growth, development, the immune system, reproduction, blood and tissue chemistry, metabolism, and behavior (Peterle 1991; Spalding and others 1991, 1994; Zillioux and others 1993). Various biochemical and enzyme effects have also been reported (Wolfe and Norman 1998).

3.3.5 Nickel

Nickel is strongly adsorbed by soil, although to a lesser degree than lead, copper, and zinc (Rai and Zachara 1984; Alloway 1990). Many species of nickel occur in soil, and many factors affect the extent to which these different forms of nickel are adsorbed, making nickel adsorption highly site-specific. The maximum nickel concentration found at Cullinan Ranch was 200 mg/kg; however, the average concentration is only 51.3 mg/kg.

Nickel, especially as a constituent in sewage sludge or similar complex mixtures, tends to be less available in soils than zinc or cadmium, but is generally more available to plants than copper, owing to the latter's tendency to be more strongly complexed to organic matter (Alloway 1990). Not surprisingly, nickel becomes more soluble with decreasing pH, but the clay content and soil texture will influence the bioavailability of nickel, especially to plants. The effects of nickel toxicity on plants include: reduced growth of roots and shoots, poor branching, deformation of plant parts, decreased dry matter production, leaf spotting, abnormal flower shape, mitotic root tip disturbance, germination inhibition, and chlorosis (McIlveen and Negusanti in press, Rauser 1978, both as cited in Environment Canada 1994; Mishra and Kar 1974).

In birds, specifically poultry, decreased growth was observed at dietary concentrations of 500 ppm or greater (National Academy of Sciences [NAS] 1980). The expression of nickel toxicity is influenced by the age, reproductive status, nutritional content of the diet, and exposure duration in test organisms. This information needs to be considered in the interpretation of the risk posed by nickel to terrestrial wildlife (NAS 1980).

3.3.6 Zinc

Zinc is an essential trace element for all living organisms; therefore, both elevated zinc concentrations in the water or diet and zinc deficiency can cause adverse effects in plants and animals. Zinc is used as a protective coating for metals and in the production of alloys such as bronze and brass. Other sources of anthropogenic zinc include effluents from pulp and paper mills (zinc dithionite is the whitening agent for paper), use in agriculture as a fungicide, combustion of solid waste and fossil fuels, and road surface runoff (Eisler 1993). The mean, worldwide zinc concentration in surface soils is 17 to 125 mg/kg; the mean zinc concentration in soils worldwide is 64 mg/kg (Kabata-Pendias and Pendias 1992). Background zinc concentrations in uncontaminated soils worldwide seldom exceed 200 mg/kg (Eisler 1993). By comparison, the mean zinc concentration of samples taken from Cullinan Ranch was 153.3 mg/kg. However, the maximum concentration detected at the site was quite high at 1,500 mg/kg.

The background concentration of zinc in plants growing in uncontaminated soil ranges from 8 to 150 mg/kg (Bodek and others 1988). Factors such as organic content, pH, and metal or mineral content of the soil affect the availability of zinc to plants. A direct correlation exists between the amount of organic matter and soluble zinc: the greater the concentration of organic matter, the lower the solubility of the zinc present in the soil (Eisler 1993).

Elevated concentrations of zinc in soil can cause mortality in some terrestrial plants and inhibit photosynthesis in others (Eisler 1993). However, many vegetation studies indicate little uptake of zinc by plants from the soil. Low soil pH promotes zinc uptake by plants, and high soil pH reduces zinc uptake. High clay content, high soil cation exchange capacity, and high phosphate concentration in the soil also inhibit zinc uptake (Bodek and others 1988).

Birds are relatively tolerant to zinc ingested in the diet or drinking water (Eisler 1993). Different species of birds have varying sensitivities to dietary zinc exposure; normal tissue zinc concentrations are less than 210 mg/kg dry weight worldwide (Eisler 1993).

3.3.7 Dichlorodiphenyltrichloroethane

Historically, DDT was used for pest control worldwide. In 1972, DDT was banned in the United States because it caused adverse effects on non-target species. Commercial DDT is a mixture of chlorinated organic compounds, including DDT, DDE, and DDD. All three compounds have similar fate and transport properties. DDT is persistent in the environment, volatile, lipophilic, and is metabolized into toxic metabolites (Peterle 1991). DDT and related organochlorine chemicals are very slowly biodegraded in soil (Alexander 1965, as cited in Forsyth and others 1983). As a result, these chlorinated hydrocarbons are highly persistent in soil, with estimated half-lives exceeding 15 years (Stewart and others 1971, as cited in Agency of Toxic Substances and Disease Registry [ATSDR] 1992b). The half-life of DDT in soils is influenced by the method of application, soil type, soil fertility, chemical formulation, topography, climactic conditions, farming practices, soil pH, and organic carbon content. In sediment, DDT persistence is influenced by pH, organic carbon content, turbidity, and oxygen content (EPA 1975, as cited in DOI 1998).

Terrestrial plants accumulate DDT (Forsyth and others 1983). DDT reduces photosynthesis in plants, retards growth, and reduces the plant's ability to withstand environmental changes (EPA 1980, as cited in DOI 1998).

Over time, many invertebrates (through selection) developed a tolerance for DDT; thereafter, these invertebrates accumulated high concentrations of DDT with minimal adverse effects (Forsyth and others 1983). DDT causes immobilization, reproductive impairment, embryo deformation, reduced growth, and mortality in unacclimated terrestrial and aquatic invertebrates (EPA 1975). DDE is bioavailable to soil invertebrates even though it is highly bound to soil. Mobilization of DDT in soil to more bioavailable forms has been observed in earthworms (Verma and Pillai 1991 as cited in EPA 1999).

Effects of DDT and its metabolites on bird reproduction have been well characterized. DDT and its metabolites can mimic estrogen by binding to specific estrogen receptors inside cells. Because of this mode of action, the toxicity of DDT primarily affects reproduction.

3.3.8 Chlordane

Chlordane is a broad-spectrum, organochlorine pesticide consisting of about 45 components. Chlordane was historically used to control soil invertebrate pests; however, chlordane also adversely affected non-target species. Although federal law currently prohibits use of chlordane in the United States, persistent chlordane residues and metabolites from past use continue to pose an ecological threat (Eisler 1990). Because of chlordane's low water solubility, high lipid solubility, low vapor pressure, and strong tendency to adsorb to soil and sediment particles, it persists in soil and sediments for extended periods (EPA 1988, as cited in Eisler 1990). Volatilization is the most important pathway for chlordane release from surface soils (Beeman and Matsumura 1981, as cited in ATSDR 1992a), and its vapor toxicity can be persistent and extreme.

Residues of chlordane have been detected in vegetable crops grown in soils treated with chlordane (U.S. Department of Agriculture 1965, as cited in U.S. National Library of Medicine [NLM] 1995). Chlordane is taken up by rooted aquatic vascular plants from both water and sediment. Chlordane bioconcentrates in roots and is translocated to shoots (ATSDR 1992a).

Lethal effects of chlordane in birds result primarily from chlordane metabolites, most notably oxychlordane and heptachlor epoxide; oxychlordane is the most toxic and persistent of the two (Stickle and others 1983, as cited in Eisler 1990).

4.0 CONCLUSIONS AND RECOMMENDATIONS

Conclusions and recommendations for the Cullinan Ranch site were developed based on best professional judgment using a preponderance of evidence approach as recommended by in the "Beneficial Reuse of Dredged Materials: Sediment Screening and Testing Guidelines (RWQCB 2000). Although all criteria identified in Section 2.3 were considered in the evaluation of chemical results, San Francisco Bay Ambient concentrations should be considered with more weight because sediment deposition at the site during tidal marsh restoration will likely accumulate additional sediment at ambient concentrations. If remediation action is taken, remediation goals should not be set below these ambient concentrations.

At the Pole Barn Area concentrations of zinc may pose unacceptable ecological risk under current site conditions. The detected concentrations of zinc at two locations (CRPB002 and CRPB003) exceeded the ER-M criterion. The maximum concentration of zinc exceeded the San Francisco Bay Ambient and San Francisco Wetland Surface value by a factor of 10. The two locations area relatively close together (Figure 6) and may represent a small localized

hotspot rather than widespread contamination. In addition, there was metal debris located nearby these locations (Appendix D). No other metal concentrations exceeded the San Francisco Bay ambient, San Francisco wetland surface, ER-M, or Western soil 95 UCL values at the Pole Barn indicating that other metal concentrations do not pose unacceptable risk at the site.

At the Farmyard Area concentrations of nickel, DDTs, and total chlordane may pose unacceptable ecological risk at the site. Although concentrations of nickel are widespread at both depths, only concentrations in two samples from location CRFY019 in the Pump Canal exceeded the San Francisco Bay Ambient. Because concentrations above ambient are not widespread, adverse effects at the site are likely to be similar to those posed by ambient sediments.

4,4'-DDT, 4,4'-DDE, 4,4'-DDD, total DDTs, and total chlordanes exceeded all available comparison values in the majority of samples taken from the Farmyard. Concentrations of these pesticides exceeded the ER-M by factors of 1.3 to 44.5. Therefore, pesticides may pose unacceptable ecological risk at the Farmyard Area; however, concentrations are likely to continue naturally degrading because pesticide application has been discontinued.

At the Farmyard Area, concentrations of lead were about 1.75 and 2.5 times greater than the San Francisco Bay ambient, San Francisco wetland surface, and ER-L values in 2 of 10 samples, but did not exceed the ER-M or San Francisco Wetland Foundation Material value. Concentrations of zinc were about 1.3 times greater than the San Francisco Bay Ambient, San Francisco wetland surface, and ER-L. However, the concentrations of lead and zinc did not exceed the ER-M or the Wetland Foundation Material values. Therefore, lead and zinc do not pose unacceptable risk at the Farmyard. Arsenic was 1.05 times greater than the San Francisco Bay ambient and San Francisco Wetland Surface Material values in 1 of 10 samples taken from the Farmyard Area indicating that arsenic does not pose unacceptable ecological risk at the site. Although cadmium concentrations exceeded the San Francisco Bay Ambient and San Francisco Wetland Surface Material value in eight samples, all the detected concentrations of cadmium were about 0.7 to 0.02 times lower than the ER-L for cadmium indicating that cadmium does not pose unacceptable ecological risk at the Farmyard. All other detected metal concentrations were below the San Francisco Bay Ambient and San Francisco Wetland Surface Material values at the Farmyard Area; therefore, metal concentrations do not pose unacceptable ecological risk.

Although zinc concentrations in the Pump Canal exceeded the San Francisco Bay Ambient, zinc concentrations were 0.75 to 0.53 times less than the ER-M and San Francisco Wetland Foundation Material values. No other metal concentrations exceeded the San Francisco Bay ambient, San Francisco wetland surface value, ER-M, or Western soil 95 UCL values.

No further action is warranted in the East Pond Area because metal concentrations are low in respect to comparison values. Although arsenic, copper, mercury, and nickel were detected at concentrations greater than ER-L values, none of the detected concentrations exceeded any of the other comparison values, including the San Francisco Bay Ambient concentrations.

No other metal concentrations exceeded the San Francisco Bay ambient, ER-M, or Western soil 95 UCL values at the East Pond Area. Therefore, metal concentrations do not pose unacceptable risk to ecological receptors at the site.

No further action is warranted in the West Pond Area because metal concentrations are low in respect to comparison values. Although arsenic, copper, and mercury were detected at concentrations greater than ER-L values, none of the detected concentrations exceeded their respective San Francisco Bay Ambient values. Similarly, nickel concentrations did not exceed the San Francisco Bay Ambient. No other metal concentrations exceeded the San Francisco Bay Ambient, San Francisco Wetland Surface Material value, or ER-M at the West Pond Area. Therefore, metal concentrations do not pose unacceptable risk to ecological receptors at the site.

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