

## INTRODUCTION

The Tijuana Slough National Wildlife Refuge (NWR) is a coastal plain estuary located in San Diego County, California. This estuary represents one of the few remaining relatively undisturbed tidally influenced wetlands in Southern California, and several rare and endangered species are located at the estuary (Zedler et al., 1992). These species include the California least tern (*Sterna antillarum browni*), the salt marsh bird s beak (*Cordylanthus maritimus* ssp. *maritimus*), and the light-footed Clapper rail (*Rallus longirostris levipes*). The Tijuana Slough NWR has been subject to contamination from a variety of sources in the Tijuana River watershed. These sources include municipal/industrial discharges from Mexico; landfills, agriculture, nonpoint source runoff, and illegal dumping in the United States and Mexico. A review of preliminary data indicated elevated trace metals and polynuclear aromatic hydrocarbon (PAH) concentrations found in sediment and in food items of many bird species.

The Sweetwater Marsh NWR was established as a mitigation bank for several large water resource related projects in San Diego County. It is located close to the Tijuana Slough NWR, and it encompasses the largest remaining wetland area in San Diego. Nearly 200 species of birds are found there (Zedler et al., 1992), including the species listed above for the Tijuana Slough NWR. The Sweetwater Marsh NWR has also been subject to contamination from a variety of sources. These sources include storm water runoff and industrial/municipal sources originating from both the Sweetwater River and the Paradise Creek watersheds. A review of preliminary data indicated that sediment and biota (crabs and small fish) showed elevated concentrations of

several trace metals.

The Tijuana Slough and Sweetwater Marsh National Wildlife Refuge contaminant study took place from 1988 to 1992, and was aimed at monitoring the contaminant levels in various animals, plants, and sediments of the area. We also wanted to monitor the contaminant concentrations accumulating in food items of trust resources (shorebirds, waterfowl, the endangered California least tern and the light-footed Clapper rail) utilizing the refuges. We examined contaminant concentrations relative to threshold values for specific contaminants (organics and inorganics) for each site, and we compared the contaminant concentrations between the two sites. The organics and inorganics sampled for are outlined below.

**Organics:**

**Polynuclear aromatic hydrocarbons (PAH s)** - PAH s make up a group of pollutants that can enter the aquatic environment directly; via petroleum spills, discharges from ships, oil seepage, runoff, and other ways (Beyer et al., 1996). Several organizations, such as World Health Organization and the Environmental Protection Agency, have recommended that 16 PAH s be listed as priority pollutants. These include fluoranthene, benzo(a) pyrene, benzo(k) fluoranthene, fluorene, anthracene, pyrene, chrysene, benzo(b) fluoranthene, indeno(1,2,3-cd)pyrene, and benzo(ghi) perylene (Beyer et al., 1996).

**Polychlorinated biphenyls (PCB s)** - PCB s are a group of synthetic chlorinated aromatic hydrocarbons, and residues have been identified throughout the global ecosystem with widespread contamination. PCB s are used in commercial products such as heat transfer agents, lubricants, insulating and cooling agents, and flame retardants. PCB s, similar to DDT and its

metabolites, have been implicated in reproductive abnormalities in both wild and domestic birds (Beyer et al., 1996).

**Dichlorodiphenyltrichloroethane (DDT)** - DDT is an organochlorine with two principal metabolites-DDD and DDE. DDT was an insecticidal agent used in human health operations during WWII and agriculturally as a pesticide. Numerous problems occurred as the result of DDT being used agriculturally, such as the thinning of eggshells of several bird species. Early field studies with DDT were concerned with the short-term effects after heavy rates of applications. For example, 5.6 kg of DDT per hectare resulted in immediate reductions in the populations of songbirds and invertebrates in an upland hardwood forest. DDT has been shown to cause breeding failure in several species of birds (Beyer et al.1996).

**Dieldrin and Endrin** - Dieldrin and Endrin belong to a class of closely related, highly toxic, organochlorine pesticides (Committee on Water Quality, 1972). They were used commercially, and when they were introduced as seed dressing in the United Kingdom in 1956, there was immediate mortality. Dieldrin is like the DDT compounds in that it can be dispersed through the atmosphere. The greatest hazard of dieldrin is to fish-eating birds, which may accumulate lethal amounts from fish or birds that have not themselves been harmed. These organochlorine compounds are soluble in water and concentrations in fish would indicate high environmental levels. These compounds are more toxic to wildlife than any other chlorinated hydrocarbon pesticides (Committee on Water Quality, 1972).

### **Inorganics:**

**Arsenic** - Arsenic (As) is a relatively common element that occurs in air, water, soil, and all

tissues. Each year, as a result of agricultural and industrial activities, large quantities of arsenicals are released into the environment that may be hazardous to fish and wildlife (Eisler, 1998). Arsenic is present in the water contaminated by mine tailings, smelter wastes, and natural mineralizations.

**Cadmium** - Cadmium (Cd) is a heavy metal that is released into the environment in a variety of ways, such as, from smelting, burning coal and oils, and from wear of vehicle tires. Deposits of cadmium may be found on land, in air, and in the water (from sewage sludge). The effects of cadmium poisoning include bone damage, suppressed egg production, eggshell thinning in birds, and kidney damage (Beyer et al., 1996).

**Chromium** - Chromium (Cr) is imported for the production of stainless steels, chrome plated metals, pigments for inks and paint, and other chemicals (Eisler, 1986). At high environmental concentrations, chromium is a mutagen, teratogen, and a carcinogen. Chromium is introduced into the environment from sewage and solid wastes.

**Copper** - Copper (Cu) is an essential element for many animals and is a component of many metalloenzymes and respiratory pigments. Copper is one of the most common contaminants found in urban runoff. Both deficient and excess amounts of copper can cause adverse effects in all species. Copper is generally more toxic to aquatic organisms than to birds or mammals, and it is a rarity to see toxic effects through excess dietary exposure in birds and mammals under field conditions (U.S. Department of the Interior, 1998).

**Lead** - Lead (Pb) is neither essential nor beneficial to living organisms, and all measured effects are adverse, including those on survival, growth, reproduction, development, behavior, learning, and metabolism. Lead reaches the aquatic environment through industrial and municipal

discharges, atmospheric deposition, weathering processes, and highway runoff (Eisler, 1988). The toxic effects of lead on aquatic organisms are extremely varied. Generally, lead inhibits the formation of heme, adversely affects blood chemistry, and accumulates in hematopoietic organs (Eisler, 1988). Lead poisoning can cause epizootic mortality, such as in the case of Laysan albatross fledglings at Midway Atoll, HI in 1982. Sick albatrosses were unable to retract their wings, causing a droop-wing appearance. There were also neurological effects; such as, degenerative lesions that were present in the myelin of some brachial nerves (Vermeer et al., 1993).

**Mercury** - Mercury (Hg) is a metal that can exist in a range of organic and inorganic forms with varying degrees of toxicity. It is a mutagen, teratogen, and a carcinogen that causes embryocidal, cytochemical, and histopathological effects. In aquatic organisms, mercury adversely affects reproduction, growth, behavior, osmoregulation, and oxygen exchange. Mercury also causes kidney lesions, neurological damage, and reduced food intake leading to weight loss, progressive weakness in wings and legs, and an inability to coordinate muscle movements in marine birds. Mercury can enter the environment through natural causes as well as human activities. These include industrial and domestic coal combustion, waste incineration, gold mining, and the dumping of sewage sludge (Beyer et al., 1996).

**Nickel** - Nickel (Ni) is a heavy metal that enters the environment as a contaminant through mining and smelting operations, combustion of fossil fuels, and other industrial processes. Nickel may also enter natural waterways from wastewater because it is poorly removed by the treatment process. Little is known about the effects of dietary nickel on young animals, but it has been shown that when injected in chicken eggs, the nickel produced embryonic malformations

and death (Cain and Pafford, 1981)

**Selenium** - Selenium (Se) is introduced in to the environment naturally and due to human activities. Selenium has the ability to bioaccumulate in aquatic food chains and thereby contaminate the diet and induce reproductive effects in fish and birds. One source of selenium is the weathering of natural rock. There are two major human related causes of selenium introduction into aquatic systems. The first is processing and combustion of fossil fuels, and the second is irrigation of seleniferous soils or with selenium contaminated water, and the resultant agricultural drainage. Sensitivity to selenium is extremely variable in all classes of organisms, and selenium poisoning can cause significant sublethal physiological, biochemical, and behavioral effects (Lemley et al., 1993).

**Zinc** - Zinc (Zn) is required for the normal growth, development, and function in all animal species studied. Zinc deficiency can lead to death, tumor growth, and some chromosomal aberrations. Excess zinc may suppress or inhibit tumor proliferation, and can be teratogenic to frog and fish embryos, possibly by inhibition of DNA synthesis (Eisler 1993).

## **METHODS**

### **Study/Sample Sites-**

The following were general sample sites for the Tijuana Slough NWR area; the mouth of the Tijuana River, the Headwaters, the bridge at Dairy Mart Road, Hollister Bridge, Sunset Avenue, South Beach, Grove Road, and Reem Air Field.

The following were general sample sites for the Sweetwater Marsh NWR area; Gunpowder point, the mouth of the Sweetwater River, Paradise Creek, and F&G Marsh.

### **Sample Collection and Analysis -**

\_\_\_\_\_A variety of organisms were collected for each class studied. For the invertebrates, organisms collected for analysis included the razor clam, yellow shorecrab, ghost shrimp, mud crab, fiddler crab, African clawed frog, striped shorecrab, and mussel. The plants included the water hyacinth, brown algae, *Sueadea*, spikerush, *Fundulus*, cattail, pickleweed, and bullrush. Samples for the fish included mosquitofish, California killifish, longjaw mudsucker, sailfin molly, mullet, goby, Pacific staghorn sculpin, and topsmelt. For the birds, samples included coot liver, wigeon liver, black-necked stilt liver, and clapper rail egg.

\_\_\_\_\_Sediments were collected by means of a shovel or post-hole digger. Sediments were transferred from the shovel or post-hole digger to chemically cleaned jars using clean stainless steel scoops. Material in contact with the shovel or post-hole digger was not collected. Sediment samples were placed on ice in the field, then frozen pending submission for chemical analysis.

\_\_\_\_\_The method of field preparation for samples other than sediments involved taking a sample from a beach-seine or forcing the subject out of its burrow, and placing the sample in a chemically cleaned jar by hand. Once the sample was in the jar, the jar was placed in a cooler with ice in the field. Samples were held in a freezer until submitted for chemical analysis. The samples were sent to the Geochemical and Environmental Research Group, Texas A&M (GERG) or the Mississippi State Chemical Laboratory for analyses for contaminant concentrations. See Appendix A for methods from the GERG and Appendix B for methods from the Mississippi State Chemical Laboratory.

## **Chemical Evaluations -**

For the sediments, the comprehensive screening guidelines developed by the National Status and Trends (NST) program of the National Oceanographic and Atmospheric Administration (NOAA) and the Ontario Ministry of Environment and Energy have been used here to evaluate the potential risk of sediment contamination following the procedures used in the South San Diego Bay Level III Pre-acquisition Survey completed in 1995. The guidelines used to gauge sediment contamination were:

1) NST Effects Range-Low (ERL)- The NST sediment concentration below which adverse effects are seldom expected. It is developed by taking the 10<sup>th</sup> percentile of the ranked adverse effect in biota in the NOAA database.

2) NST Effects Range-Median (ERM)- The NST sediment concentration above which adverse effects are likely. It is developed by taking the 50<sup>th</sup> percentile of the ranked adverse effects in biota in the NOAA database.

3) Ontario Low Effect Level (LEL)- The sediment concentration indicating a level of contamination that has the potential to affect some sensitive benthic organisms. The level is derived from the 5th percentile of the Species Screening Level Concentration Distribution database used to protect aquatic sediment quality in Ontario.

4) Ontario Severe Effect Level (SEL)- The sediment concentration indicating a level of contamination that significantly affects benthic organisms. The level is derived from the 95<sup>th</sup> percentile of the Species Screening Level Concentration Distribution database used to protect aquatic sediment quality in Ontario.

For the plants, invertebrates, birds, and the fishes, threshold values or general background



concentrations gained from literature were used to estimate the level of contamination found in those samples. A summary of these thresholds is provided in the Level III Pre-acquisition Survey Report (U.S. Fish and Wildlife Service, 1995).

## **RESULTS**

Analysis was conducted for many organics and inorganics in all the classes studied at both the Tijuana Slough NWR (referred to in the Figures and Tables as TJNWR) and the Sweetwater Marsh NWR (referred to in the Figures and Tables as SWNWR). Maximums for each year sampled are in Table 1 for inorganics and Table 2 for the organics. Means (ppm) for each year sampled are in Figures 4-8 for both inorganics and organics at Tijuana Slough NWR and Sweetwater Marsh NWR. The figures include sediment inorganics and organics at Tijuana Slough NWR (Figures 4a) and Sweetwater Marsh NWR (Figures 4b), invertebrate inorganics and organics at Tijuana Slough NWR (Figures 5a) and Sweetwater Marsh NWR (Figures 5b), plant inorganics and organics at Tijuana Slough NWR (Figures 6a) and Sweetwater Marsh NWR (Figures 6b), fish inorganics and organics at Tijuana Slough NWR (Figures 7a) and Sweetwater Marsh NWR (Figures 7b), and for bird inorganics and organics at Tijuana Slough NWR (Figures 8). No bird samples were collected from Sweetwater Marsh NWR for this study.

## **DISCUSSION**

\_\_\_\_\_Most organic and inorganic compounds tested were found to be below threshold levels in the various plants, fish, sediments, birds, and invertebrates sampled from the Tijuana Slough NWR and the Sweetwater Marsh NWR. However, there were a few compounds that were above threshold levels, and should be considered when evaluating the overall contamination of the two

sites. Inorganic or organic compounds that were not over the applicable threshold level are not discussed. It is important to note that not all classes studied (sediments, invertebrates, plants, fishes, and birds) were sampled from both sites every year. Some years were skipped and some samples were taken only from one site. Also, due to insufficient information in the literature, there was not enough information on background thresholds to discuss all organic and inorganic levels observed at both the Tijuana Slough NWR and the Sweetwater Marsh NWR. Those compounds lacking thresholds were not discussed. However, that does not mean that they were insignificant or that they were present at acceptable levels.

**EXAMINING THE THRESHOLD LEVELS:** Comparison of the mean concentrations for each year sampled with the thresholds is described below. If a specific threshold is not discussed, it was not exceeded in the data set.

**SEDIMENTS:**

Tijuana Slough National Wildlife Refuge -

Cadmium was found to be above the Ontario LEL of 0.6 ppm in 1991 and 1992. Cadmium was also above NST ERL level of 1.2 ppm in 1992. Chromium was determined to be above the Ontario LEL of 26 ppm only in 1992. Copper was found to be above the NST ERL of 34 ppm in 1989, 1991, and 1992. In 1992, copper levels were quadruple that of the NST ERL of 34 ppm and were more than doubled the ERL level in 1991. Lead was found to be above the NST ERL of 46.7 ppm and the Ontario LEL of 31 ppm in 1988-1992. Lead concentrations were noticeably higher in 1991 and 1992. Mercury was above the Ontario LEL of 0.2 ppm, and the NST ERL of 0.15 ppm in 1991 and 1992. Nickel was observed to be above the Ontario LEL of

16 ppm in 1992. Nickel was also found to be above NST ERL levels of 20.9 ppm in 1992.

Finally, zinc was above the NST ERL of 150 ppm in 1989 and 1991, and above the NST ERM of 410 in 1992 (Figures 4a).

To summarize, the following inorganics were found to be above low effect thresholds in the sediments at Tijuana Slough NWR; cadmium, chromium, copper, mercury, lead, nickel, and zinc. These can cause adverse impact on the biota, which in turn are important food resources for wildlife in the area. However, because only zinc exceeded its NST ERM concentration, these impacts are not likely to be major.

For organic compounds, PP DDE was found to be above NST ERL levels of 0.0022 ppm and was equal to the ERM concentration of 0.027 ppm in 1989 (Figures 4a). This could also add to the overall impact of contaminants on biota, with at most a moderate level of effects anticipated.

#### Sweetwater Marsh National Wildlife Refuge -

Arsenic was found to be above the Ontario LEL of 6 ppm in 1990 and 1992, and above the NST ERL of 8.2 in 1990. There was no NST or Ontario guidelines recommended for boron, therefore, the use of Shacklette and Boerngen s (1984) geometric mean of western soils (23 mg/kg) is used for comparison. Based on that data, the samples collected from Sweetwater Marsh NWR were all above the geometric mean for western soils. This guideline is not treated as a threshold value for biota. Cadmium was detected above the Ontario LEL of 0.6 ppm in 1989-1992. The cadmium levels also exceeded the NST ERL of 1.2 ppm in 1990-1992. Chromium was detected above the Ontario LEL of 26 ppm in 1989, 1990, and 1992. However, in 1991, the chromium level was below the Ontario LEL. Copper was determined to be above

the NST ERL of 34 ppm in all four years tested, 1989-1992. Mercury was also detected to be above the NST ERL of 0.15 ppm in 1989 and 1992. Lead was found to be above the Ontario LEL of 31 ppm in 1989-1992, and above the NST ERL of 46.7 ppm in 1989, 1990, and 1992. Nickel was determined to be above the Ontario LEL level of 16 ppm in all years, 1989-1992. Nickel was also above the NST ERL level of 20.9 ppm in 1990 and 1992. Finally, zinc was found to be above the NST ERL of 150 ppm in all years 1989-1992, and above the NST ERM of 410 ppm in 1992 (Figures 4b).

To summarize, the following inorganics were found to be above LEL or ERL threshold levels at Sweetwater Marsh NWR; arsenic, cadmium, chromium, copper, mercury, lead, nickel, and zinc. Zinc also exceeded the NST ERM in 1992. Boron was found to be above the geometric mean for western soils in the U.S. These can cause adverse impact on biota, which in turn are important food resources for wildlife in the area. Based on the concentrations found, minor to moderate impacts to benthic invertebrates are possible.

For organic compounds, the only exceedance noted was PP DDD (the only DDT compound analyzed for) being detected above the Ontario LEL for total DDT s of 0.007 ppm in 1992 (Figure 4b). This could contribute in a minor way to the overall impacts to benthic invertebrates.

## **INVERTEBRATES:**

### Tijuana Slough National Wildlife Refuge -

There were no sampled organics that appeared to be (Figures 5a). Invertebrates were also examined as important food-chain biota for birds. In that respect, all inorganics and organics were within the known acceptable normal to



there were no detectable organics.

Samples were also analyzed in consideration of being food resources for birds. Samples were also analyzed for lead (Pb) that was below the acceptable dietary threshold for birds (10 ppm) in 1989, but above the high dietary threshold level for birds (25 ppm) in 1990. Lead acts as a nonspecific poison affecting all body systems. Absorption of lead in a wide range of sublethal effects and death (Beyer and Puls, 1988). Lead concentrations were within acceptable thresholds for bird dietary sources (Puls, 1988).

In summary, copper was above a toxicity threshold for birds in 1990. At this level, a wide range of sublethal effects and death may occur (Figures 6b).

### **FISH:**

#### Tijuana Slough National Wildlife Refuge -

Zinc was found to be slightly elevated above the normal level of 88 ppm (Eisler, 1998). This site was sampled for five years and each year showed elevated levels (Figures 7a). Exposure to high levels of zinc can have an impact on the growth and survival of the fish (Eisler, 1993). Fish were also analyzed for organics and inorganics. In this respect, it was found that all organics and inorganics analyzed were within acceptable threshold levels (Eisler, 1995).

In summary, TJNWR fish had elevated zinc concentrations. Based on the threshold levels, there were no minor impacts to fish populations using Tijuana Slough NWR.

Sweetwater Marsh National Wildlife Refuge -

Zinc was found to be above normal in 1989-1992, with a range of 123-148 ppm (U.S. Department of the Interior 1998; Figures 7b). Exposure to high levels of zinc can have an impact on the growth, reproduction, and survival of the fish (Eisler, 1988). In examination of fish as dietary items of birds, it was found that inorganics were within acceptable levels (Puls, 1988).

In summary, SWNWR fish had elevated zinc concentrations. Based on the exceeded by zinc, we anticipate the possibility of moderate impairment at Sweetwater Marsh NWR.

**BIRDS:**

Only birds from the Tijuana Slough NWR were collected and their liver tissues were analyzed for contaminants. Selenium was found to be above the threshold for reproductive impairment. The selenium concentrations were above this threshold if collected (Figure 8).

**COMPARING BETWEEN THE TWO SITES:**

In addition to investigating thresholds within each site, we also compared examining the maximums (Tables 1 mentioned were considered to be about equal concentrations at both sites.





In summary, it appears that in comparison, Sweetwater Marsh National higher levels of environmental contaminants than did Tijuana Slough National variety of organic and inorganic contaminants were present in Sweetwater Marsh NWR in sediments and an array of species. The plants, fish, and birds. However, the concentrations of most organic compounds appeared to be below biologically significant threshold levels. Nevertheless, long-term bioaccumulation of contaminants can result in impacts and is cause of concern.

We recommend additional sampling of trace metals at Sweetwater elevated concentrations of these contaminants that were We also recommend minimal sampling International Wastewater Treatment Plant (IWTP) and the South Bay Ocean IWTP and SBOO take sewage out of the Tijuana theoretically resulting in decreases in contaminant inputs to the of such reductions would facilitate management of the refuge. Lastly, we recommend Service participation in watershed management and pollution prevention efforts to facilitate the reduction of contaminant loads into these two refuges SBOO for Tijuana Slough NWR by reducing non-point sources of contaminants.

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