Aspects of ecosystem health in the Colorado River Delta, Mexico

ASPECTS OF ECOSYSTEM HEALTH IN THE COLORADO RIVER DELTA, MEXICO

by

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Finally I'd like to dedicate this dissertation to my husband, Jorge Torre, with all my love and respect.

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ABSTRACT

Two aspects of ecosystem health in the Colorado River delta were investigated as part of the present dissertation. The following is a summary of the most important findings:

Contaminants of natural origin (*e.g.* selenium) and anthropogenic activities (*e.g.* pesticides) represent a potential threat for humans and wildlife in the Colorado River delta. Fourteen locations were sampled for bottom material and biota from March 1998 to April 2000. Concentrations of selenium in bottom material ranged from 0.6-5.0 μg/g. Concentrations of selenium in biota ranged from 0.5 -18.3 μg/g, 23% of these samples exceeded the toxic threshold where reproductive impairment in birds from dietary exposure is reported. Concentrations of DDE exceeded the lower critical dietary level for sensitive species in 30% of biota samples. No clear relationship could be found between the concentration of Se in bottom material and the concentration of Se in fish. Nevertheless, smaller Se concentrations in biota were found at sites that had an outflow and exposure or physical disturbance of the bottom material was uncommon. Greater concentrations of Se in biota were found at sites with strongly reducing conditions, no output, and subsequent periods of drying and flooding or dredging activities, and at sites that received water directly from the Colorado River.

The southwestern willow flycatcher (*Empidonax traillii extimus*) is an endangered neotropical migrant with only 300-500 breeding pairs. The objective of the second study was to determine the presence/absence of this bird in the Colorado River delta. Surveys

were conducted from June to July, 1999 and from May to June, 2000 using an audio tape of this subspecies' songs to elicit responses. We detected a total of 50 willow flycatchers in the Colorado River delta in the months of May to June. None were detected in July, thus, the birds were most likely migrants. Restoration of the intensively used stopover sites of the Colorado River delta appears to be essential for the overall recovery of this subspecies. Additionally, we propose a possible willow flycatcher summer migratory route throughout the series of coastal estuaries found adjacent to the coast of Sonora.

1. INTRODUCTION

1.1. History of the Colorado River delta: native people and the environment

Long before the arrival of the Spaniards, native people of the northwestern Mexico and southwestern United States, depended on the Colorado River to survive. The Cocopa, Mohave, and Yuma people used the summer floods to grow crops in the muddy shores. Seeds were buried and in a period of 60 days, before the sun dried out the mud, the plants were producing. Their crops of corn, squash, and tepary beans were characterized by their rapid growth (Bowden, 1977). Whenever possible, the riverine Pima and desert Papago practiced canal irrigation. The Pima lined tens of miles of stream bank with fields, ditches, and crude dams. The dams, made from mesquite poles and rocks, rarely survived more than a year. Papagos got probably 25 percent of their food from agriculture and Pimas 50 percent or more (Bowden, 1977). A glance on how the cultivated lands looked like at that time was given by Father Eusebio Kino in 1701, he described the area southwest of the confluence of the Colorado-Gila rivers, as "...fertile bottom lands, abundantly cultivated by the Indians..." (Sykes, 1937). In addition to agriculture, native people fished, hunted, and collected wild fruits and plants (Bowden, 1977). According to an early account by Father Consag in 1746, he and his crew saw how the natives harvested a seed from the west shores of the Colorado River delta (Sykes, 1937). He was referring to the Cocopah who harvested the seed of Palmer's saltgrass (*Distichlis palmeri*) as a source of food. This is a salt resistant grass that produces a seed similar to wheat with a high nutrient content (Felger & Moser, 1985).

Well into the twentieth century, the Cocopa Indians were still practicing flood agriculture in the banks of the river, in addition they utilized a large number of native plants, including arrowweed (*Pluchea sericea*) used extensively to build their houses (MacDougal, 1905), this practice still survives in some communities of the delta.

The most detailed descriptions of the prevailing vegetation and geography of the delta at the beginning of the twentieth century was made by D.T. MacDougal and G. Sykes from 1890 to 1935 (MacDougal, 1904a; MacDougal, 1904b; MacDougal, 1905; MacDougal, 1907; Sykes, 1937). MacDougal considered the delta to offer more varied and striking features of natural history than any other watercourse in North America. The delta vegetation was described as:

"...almost pure formations of willow and poplar which cover many square kilometers and furnish food for thousands of beavers that borrow in the banks. Large areas are occupied by the arrowweed and mesquite, and the screwbean mesquite. Two or three species of Atriplex are also to be found. In the upper part of the delta a cane fringes the channel in the lower part of the delta, where the river is affected by the spring tides, the cane is partly replaced by a cattail "tule" which not only lines the shores for many miles but extends back some distance on areas free from trees, forming dense masses that afford shelter for a number of animals, including a peculiar subspecies of a small mountain lion..." (MacDougal, 1904a).

1.2. The great diversions and the delta

The twentieth century brought dramatic changes into the Colorado River and its delta, as hundreds of thousands of newcomers poured into the Southwest. The new settlers were not used to the desert conditions and since their arrival turned their energies to overcome them. The solution was a large-scale development of the Colorado River. Among the earliest advocates of this project was Arthur Powell Davis. What he sought was the gradual comprehensive development of the Colorado River by a series of large reservoirs. The keystone was to build a dam on the lower river "as high as appears practicable from the local conditions" (Hundley, 1986). His ideas were successful among the incipient agricultural district of Imperial Valley and among the city of Los Angeles desperate for new power sources and water to cover their growing demands. Thus, Hoover Dam was built in 1935, this was the beginning of the development of the Colorado River. Arguments on who will own the water of the Colorado River started and resulted with the signature by the upper and lower basin states of a compact. In this compact the states divided 15 million acre feet (maf) (the average discharge of the river estimated by the Bureau of Reclamation at that time) between the upper and lower basins. In 1934, the United States signed a treaty which gave Mexico an additional 1.5 maf, destined for agriculture and domestic purposes. The 7.5 maf received by the lower basin states was divided. California received 4.4 maf (due to the prior appropriation law), 0.3 maf for Nevada, and 2.8 maf for Arizona. The compact delegates easily agreed to give highest priority to water use for "agricultural and domestic purposes". The right of the Indians of the Colorado River was considered "negligible" (Welsh, 1995). There is no record on the acknowledgment of the ecological importance of the River and its delta, and at that time this issue was not considered in any decision made by the signers of the compact.

The construction of upstream dams affected the vegetation and fauna of the delta. According to Sykes (1937) after a one year period of no summer floods in 1931, he described the area as:

"...large tracts of country were bare and dry and the general aspect of the region was one of arid desolation. Extensive beds of tules had died off or been burned and had failed to spring up again. Cottonwoods and other trees had perished by the thousand, adding to the general forlorn appearance of the timbered sections. Even belts of seedling willows which ordinarily cover the upper ends of bars and shoals were noticeably scanty and stunted in growth. Although vegetation suffered severely, the fauna readjustments were even more striking. The various species of river fish that existed in almost incredible quantities in the river channels had practically disappeared from the entire region...".

This extensive damage was caused by the absence of just one summer flood. It is hard to imagine the devastating effects on the delta and the Gulf of California after the complete damming and diversion of the river (Fig. 1). Together with water, the rich sediment that nourished the delta and the Gulf of California, was also cut off from the delta. It is considered that before the Hoover Dam gates were closed, the Colorado River carried an average annual load of 180 million tons of silt past Yuma AZ, and after the closure of the gates and the construction of two other dams on the lower river, this amount was cut to 13 million tons (Welsh, 1995). Nevertheless, Morelos Dam, located at the border retains the last load of sediment, leaving little or no sediment to reach the Upper Gulf of California (Carriquiry & Sánchez, 1999). The loss of Colorado River water and sediment discharge has modified the hydrographic circulation in the area.

Furthermore, the delta construction has come to a halt and the entire deltaic structure is exposed to the destructive hydrodynamic forces promoting resuspension and erosion of sediments in the estuarine basin. The general implications of the lack of sediments are the relocation of the sediment inventory within the system and the export of a large fraction of sediments to the upper Gulf of California (Carriquiry & Sánchez, 1999), all these changes that altered the biological equilibrium of the deltaic sytem might have affected the native species such as the now endangered Totoaba (*Totoaba macdonaldi*) fish and Vaquita (*Phocoena sinus*) porpoise (Cisneros-Mata *et al.*, 1995).

1.3. Agricultural era

In 1904, the "Colorado River Land Co." was formed by a group of Americans with the objective of "acquire agricultural lands, water and water rights, haciendas, mines, minerals; construct and manage roads, maritime and terrestrial communications, bridges, water deposits, aqueducts, industries, warehouses; for the exploitation of mines, agriculture and industry in the Mexicali Valley" (Estrella, 1982). These lands had rich soils with high quality limes and clays, legacy of the former Colorado River seasonal floods. The Mexican government gave this company the permit to exploit all the resources of the delta which was known as the Mexicali Valley. Despite the Mexican revolution from 1910-1917, this situation remained unchanged (Contreras-Mora, 1987) until 1937 when an insurrection movement born in the valley, concluded with the expulsion of the Colorado R. L. Co. and the distribution of lands and water rights among the Ejidos (peasants' cooperatives). By the end of 1937, 44 communities were formed in the Mexicali Valley and 144,000 ha were allocated to the new Ejidos (Contreras-Mora, 1987).

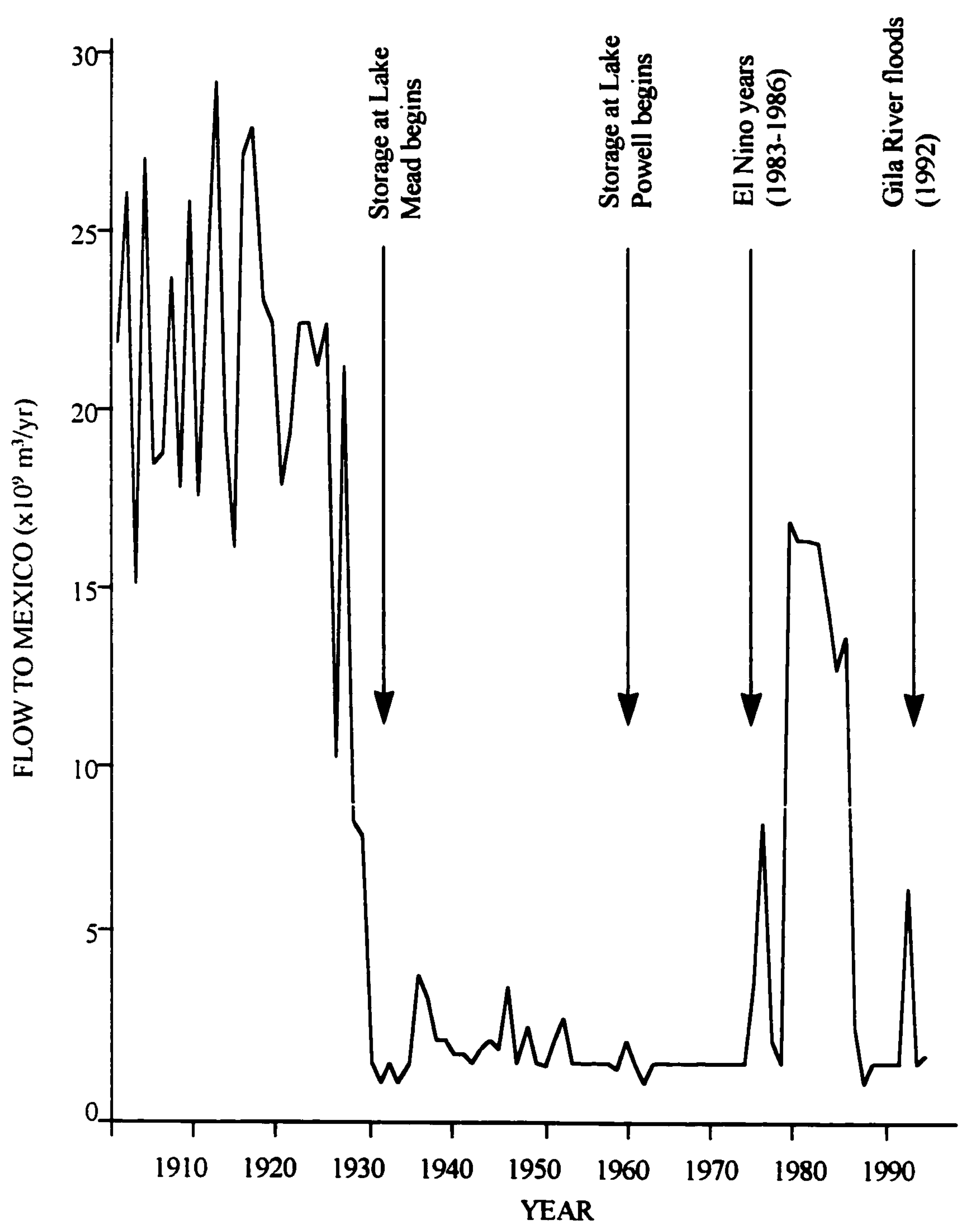

Fig. 1. Estimated flow of the Colorado River across the border (adapted from Glenn *et al.*, 1996).

1.4. Current water uses

There are approximately 23 million people in the lower basin that are at least partially dependent upon water from the Colorado River and it is estimated that by 2020 there could be more than 38 million people living in the region (Table 1) (Morrison *et al.*, 1996). Each subregion has its own specific demands from the Colorado River, although agriculture is the primary user (Morrison *et al.*, 1996). Nevertheless, emerging cities, specially along the border, are demanding more water for their growing needs.

On the Mexican side of the border, maquiladoras (offshore manufacturing plants) have thrived in cities, like Tijuana, Mexicali, and San Luis Rio Colorado. The maquiladora industry has increased employment by 14 percent in Tijuana during 1997, seven times faster than in San Diego, CA (Calbreath, 1998).

Table 1. Population projections in the lower Colorado River divided by subregions (from Morrison *et al.*, 1996).

Area	1990	2020	Percent Increase
Arizona	3,665,000	6,980,000	90
Southern California	16,757,000	26,318,000	57
Southern Nevada	800,000	1,630,000	104
Mexico (using Colorado River water)	1,700,000	3,240,000	91
Lower Colorado River	22,922,000	38,168,000	67

Maquiladoras have priority over the water intended for urban uses. With their high profits, these industries can afford to pay for water. Some industries have bought the liquid from treatment plants in the U.S. while others are trying to buy agricultural water rights from the Mexicali Valley (Coronado, 1999).

1.5. Recent resurgence of native vegetation

At the end of the 1970s the Colorado River delta was described by P. L. Fradkin (1981) as "…to resemble more a vast plumbing system than a river…". However, beginning in 1983, large quantities of snow melt, attributed to the El Niño/Southern Oscillation (ENSO) event, couldn't be contained by the ca. 20 dams along the River, and approximately 16 maf flooded the delta and reached the Gulf of California (Fig. 1) (Glenn *et al.*, 1996). Although this flood was a disaster for the Mexicali Valley crops, it was an extremely beneficial event for the native vegetation that have waited for more than 50 years to get the appropriate water quantities to return. The growth of native vegetation was remarkable, as witnessed by Mexican and U.S. scientists and environmental groups, who turned their attention to the delta in the 1990s.

A description of the principal riparian and wetland ecosystems currently present in the Colorado River delta, is shown in Fig. 2 and described next.

1.- <u>Riparian corridor</u>: This area is a 100 km river stretch from Morelos Dam to the junction of the Colorado River with the Hardy River (Fig. 2). This 14,000 ha stretch contains a mixture of regenerated native trees and scrub vegetation. The most common species found in the area are: salt cedar (*Tamarix ramosissima*) a nonnative salt tolerant invasive species, arrowweed, seepwillow (*Baccharis salicifolia*), willow (*Salix gooddingii*) and cottonwood trees (*Populus fremontii*), and common reed (*Phragmites *australis*) (Zamora-Arroyo *et al.*, 2001). Screwbean mesquite trees are present in less numbers. This corridor of riparian vegetation provides the last stopover habitat for many migratory birds including the endangered southwestern willow flycatcher (*Empidonax traillii extimus*) on their way to breeding grounds in the U.S. (García-Hernández *et al.*, 2001).

2.- The Rio Hardy: This site was described by Sykes as a complex drainage system with cottonwoods and willows (Sykes, 1937). Today it is a reservoir of agricultural runoff from the Mexicali Valley. Dissolved-solids content in the Rio Hardy average 7,000 ppm (García-Hernández unpublished data), this is why vegetation is dominated by salt cedar. The Cucapá village of El Mayor is located south to the Rio Hardy, where native people still fish, hunt, and gather plant material for food, fuel, basket making, and medicinal use (Glenn *et al.*, 1996). Several tourist camps have also established along the Rio Hardy.

3.- The Cienega de Santa Clara: The Cienega de Santa Clara was part of an active arm of the Colorado River along the Sonoran mesa on the eastern edge of the delta when MacDougal visited it (MacDougal, 1904a). This area dried out after the construction of dams, but since 1977 brackish agricultural drain water from Yuma has flowed into the Santa Clara depression via the MODE canal. The flow created a wetland of up to 20,000 ha of water surface of which 4,500 ha are thickly vegetated. The marsh is dominated by cattail (*Typha domingensis*) (Fig. 2) (Glenn *et al.*, 1996). The importance of the Cienega derives from the presence of the largest remaining population of the endangered Yuma clapper rail (*Rallus longirostris yumanensis*) (Hinojosa-Huerta *et al.*, 2001) and desert pupfish (*Cyprinodon macularius macularius*) (Varela-Romero *et al.*, 1998).

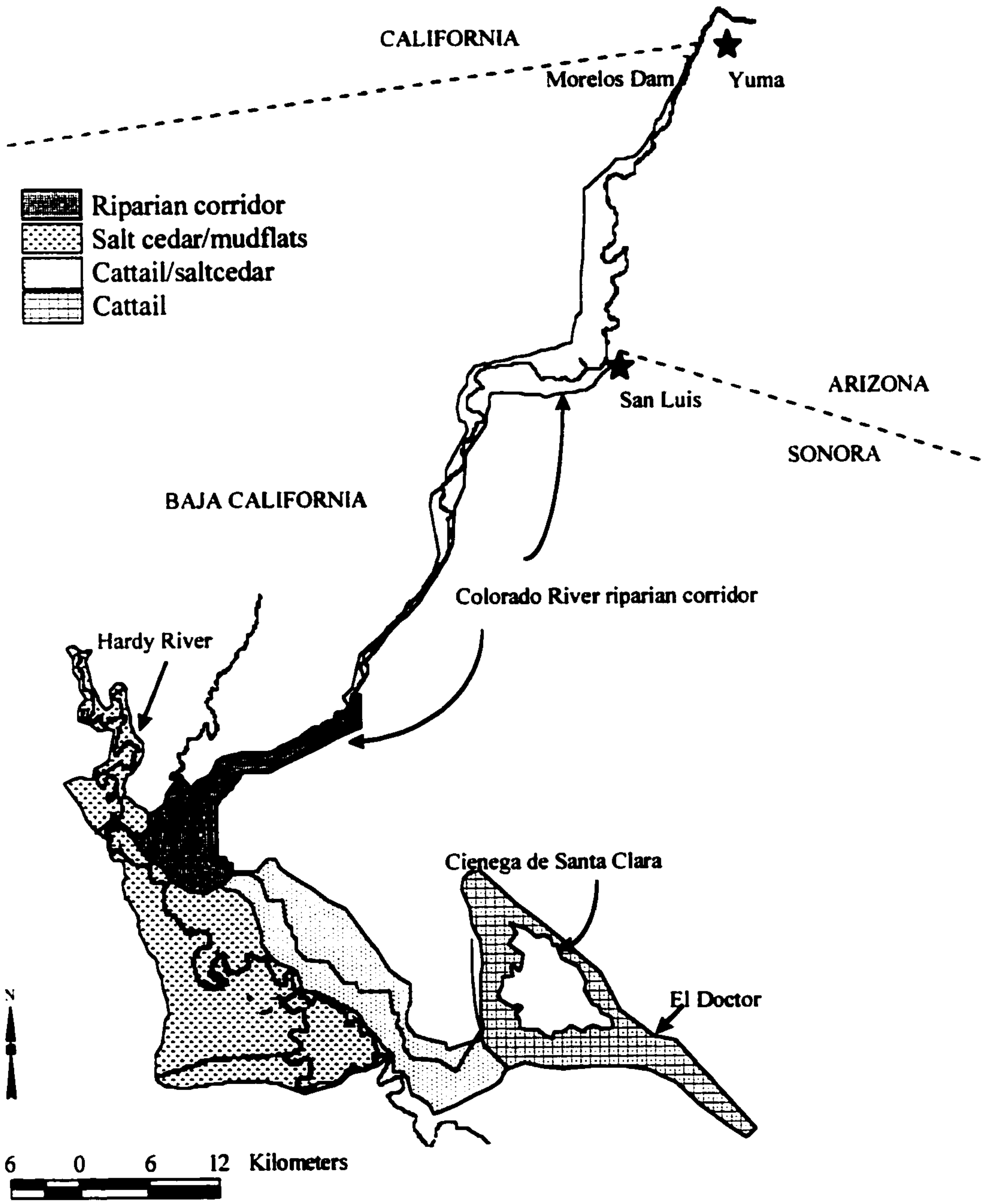

Figure 2. The delta of the Colorado River with its wetland and riparian ecosystems.

4.- The El Doctor wetlands: These wetlands are a separate system with little or no interaction with the Colorado River and with the Cienega de Santa Clara. They are located on the eastern margin of the delta. The wetlands or "pozos" are supported by springs, ranging from 100 to 3,000 ppm dissolved-solids, that support a great diversity of plants including water pennywort (*Hydrocotyle verticillata*) flat sedge (*Cyperus laevigatus*) and spike rush (*Eleocharis geniculata*) (Glenn *et al.*, 1996). The pozos support a population of desert pupfish (Varela-Romero *et al.*, 1998) and they are also important stopover sites for migratory birds including the willow flycatcher (García-Hernández *et al.*, 2001).

5.- Intertidal wetlands: Approximately 33,000 ha of intertidal wetlands are still present in the southern part of the delta. The most common plant is Palmer's salt grass, which carpets the banks of Isla's Gore and Montague, the coastal esteros between San Felipe and El Golfo, and the intertidal portion of the Colorado River channel (Glenn *et al.*, 1996). The mudflats support more than 163,000 wintering shorebirds and Isla Montague provides breeding habitat for herons and seabirds, including the California Least Tern (Massey & Palacios, 1994). The importance of the intertidal wetlands is recognized and they are now considered a designated reserve in the Western Hemisphere Shorebirds Reserve Network (Massey & Palacios, 1994).

1.6. Contaminants

Re-established wetlands of the Colorado River delta usually receive water from different sources including agriculture runoff, Colorado River surplus water, and municipal raw sewage. All of which have different organic and inorganic contaminants that are potentially toxic for wildlife and humans. Pesticides are of special concern because the majority of water is derived from agricultural runoff. Several studies, summarized in Table 2, report the concentrations of DDE in biota from the Colorado River delta from 1975 to 1998. DDE is the most persistent metabolite of DDT, which was banned for agricultural use in Mexico by 1978 (Mora & Anderson, 1995). As reported in Table 2, in 1975, concentrations of DDE in clams from the Mexicali Valley were as large as 11 ppm wet weight. A subsequent study in the mid 1980s, showed that concentrations of DDE in clams collected from the Mexicali Valley were smaller, averaging less than 0.2 ppm wet weight. More recently, in 1998, concentrations of DDE in clams from the Colorado River bed and agricultural drains were also all < 0.2 ppm wet weight. However, concentrations of DDE were much greater in birds of the Mexicali Valley, ranging from 0.04 to 11 ppm wet weight. Compared with other agricultural valleys of the northwest Mexico (Yaqui and Culiacan) the Mexicali Valley is considered as the greatest source of DDE to wildlife (Mora & Anderson, 1991).

One of the inorganic elements of greatest concern in the Colorado River delta wetlands is selenium (Se). This is a naturally occurring element originated in cretaceous formations upstream that concentrates in the river due to the high evaporation rates (Presser *et al.*, 1994). When it reaches the lower section of the Colorado River and the delta, it can concentrate to toxic levels for wildlife. Several recent studies have been conducted to detect if selenium is a potential toxic element for the delta wildlife (Mora & Anderson, 1995; García-Hernández *et al.*, 2000; King *et al.*, 2000). Table 3 shows the different levels of selenium found in fish and birds from the Colorado River delta, the greatest concentration was found in double crested cormorants, the values were near the threshold at which reproductive effects might occur (Mora & Anderson, 1995). Therefore, contaminants in general and organochlorine pesticides and selenium in particular, could constitute a potential threat to the recent established wetlands and its wildlife.

Table 2. Concentrations of DDE in wildlife from the Colorado River delta (ppm, wet wt.)

Species	Year	DDE	Reference
Clams (*Corbicula fluminea*)	1975	11.00	Guardado-Puentes, 1976
Clams (*C. fluminea*)	1985	0.13	Gutierrez-Galindo *et al.*, 1988
Clams (*C. fluminea*)	1998	0.15	King *et al.*, 2000
Pied-billed grebe (*Podylimbus podiceps*)	1986	1.20	Mora & Anderson, 1991
Double-crested cormorant (*Phalacrocorax auritus*)	1986	11.46	Mora & Anderson, 1991
Cattle egret (*Bubulcus ibis*)	1986	1.99	Mora & Anderson, 1991
Great-tailed grackle (*Quiscalus mexicanus*)	1986	3.06	Mora & Anderson, 1991
Red-winged blackbird (*Angelaius phoeniceus*)	1986	1.68	Mora & Anderson, 1991
Mourning dove (*Zenaida macroura*)	1986	0.04	Mora & Anderson, 1991

Table 3. Concentrations of selenium in biota from the Colorado River delta (ppm dry wt.)

Species	N	Se	Reference
Double-crested cormorant	9	16.7	Mora & Anderson, 1995
Cattle egret	15	4.6	Mora & Anderson, 1995
Red-winged blackbird	8	5.1	Mora & Anderson, 1995
Great-tailed grackle	14	5.3	Mora & Anderson, 1995
Mourning dove	15	2.3	Mora & Anderson, 1995
Tilapia (*Tilapia zilli*)	6	6.8	Mora & Anderson, 1995
Largemouth bass (*Micropterus salmoides*)	11	5.1	García-Hernández *et al.*, 2000

1.7. Explanation of dissertation format

The research that will be presented next consists on two aspects of environmental health of the Colorado River delta region. Each paper is in the format of the *Journal of Arid Environments*, where they will be published as part of a special issue on the Colorado River delta edited by Dr. Edward P. Glenn.

The title of the study presented in APPENDIX A is: "Selenium, selected inorganic elements, and organochlorine pesticides in bottom material and biota from the Colorado River delta" by Jaqueline García-Hernández, Kirke A. King, Anthony L. Velasco, Evgueni Shumilin, Miguel A. Mora, and Edward P. Glenn. The role of the dissertation author in this paper was writing research proposals, obtaining collection and export permits for endangered species, planning, coordinating and participating in all the sample collection field trips, analyzing samples at laboratories within the University of Arizona facilities, sending samples to external laboratories, analyzing data and writing the final paper. Co-authors participated in some of the field trips, in the analysis of samples at external laboratories, and with revisions to the manuscript.

APPENDIX B contains the paper titled "Willow flycatcher (*Empidonax traillii*) surveys in the Colorado River delta: Implications for Management" by Jaqueline García-Hernández, Osvel Hinojosa-Huerta, Vanda Gerhart, Yamilett Carrillo-Guerrero and Edward P. Glenn. The role of the dissertation author in this paper was to participate in 60% of the field surveys, analyzing the data, and writing the final paper. Co-authors participated in writing the research proposal, doing field surveys and revising the drafts.

2. PRESENT STUDY

Two aspects of ecosystem health are covered in the studies attached to this dissertation. The first, which is presented in APPENDIX A, investigates the distribution of selenium, selected inorganic elements, and organochlorine pesticides in bottom material and biota from the Colorado River delta. And the second study, presented in APPENDIX B, reports the importance of the Colorado River delta ecosystems for the endangered southwestern willow flycatcher (*Empidonax traillii extimus*).

Next is a summary of the most important findings reported in the first study, included in APPENDIX A:

Ecosystems of the Colorado River delta are supported by agricultural runoff and pulse floods from the Colorado River. Therefore, contaminants of natural origin (*e.g.* selenium) and anthropogenic activities (*e.g.* pesticides), are commonly found and represent a potential threat for humans and wildlife. Fourteen locations in the Colorado River delta were sampled for bottom material, soils, and biota from March 1998 to April 2000. Concentrations of selenium in bottom material ranged from 0.6-5.0 μg/g, 22% exceeded the threshold where sedimentary selenium can cause adverse biological effects in 10% of exposed fish and birds. Concentrations of selenium in biota ranged from 0.5 -18.3 μg/g, 23% of these samples exceeded the toxic threshold where reproductive impairment in birds from dietary exposure is reported. Cadmium concentration in biota from the Colorado River delta ranged from < 0.19 μg/g to 0.8 μg/g dry wt, 17% of the samples exceeded the potential toxic threshold for birds. Mercury concentrations in biota samples ranged from < 0.04 μg/g to 1.29

μg/g, 40% of the samples exceeded the most conservative potential toxic threshold of 0.3 μg/g. Concentrations of DDE exceeded the lower critical dietary concentration for sensitive species in 30% of biota samples. No clear relationship could be found between the concentration of Se in bottom material and the concentration of Se in fish, which signifies that other factors are likely to determine the concentration of selenium in fish and consequently in fish-eating birds, such as the physico-chemical characteristics of each wetland and their effects on the speciation, solubility, and bioavailability of selenium through the food chain. We found that greater concentrations of selenium in biota were found at sites with strongly reducing conditions, no output, and subsequent periods of drying and flooding or dredging activities, and at sites that received water directly from the Colorado River. And the smallest Se concentrations in biota were found at sites that had an outflow and exposure or physical disturbance of the sediments was uncommon.

We recommend from this study, to closely monitor El Mayor wetland to determine if birds are being affected by the large selenium concentrations in bottom material and food items at that site; to monitor reproductive success of Yuma clapper rails from the Cienega de Santa Clara to determine if selenium is a threat to the bird population, and to take the following measures in order to maintain selenium concentrations below toxic thresholds at sites that are being restored or conserved: a) the maintenance of an outflow; b) the preferential use of agricultural runoff or a mix of Colorado River and agricultural runoff, and c) the restraint of physical perturbation such as dredging.

The methods, results, and conclusions of the second study of this dissertation are presented in APPENDIX B. The following is a summary of the most important findings:

The southwestern willow flycatcher (*Empidonax traillii extimus*) is a neotropical migrant that breeds in North America and winters from south Mexico to Panama. The loss of wintering habitat, invasion of exotic plants and nest predation have contributed to population declines. With only 300 to 500 breeding pairs, this subspecies was listed as endangered in 1995 by the U.S. Fish and Wildlife Service. The objective of this study was to determine the presence/absence of southwestern willow flycatcher in the Colorado River delta wetlands. Surveys were conducted from June to July, 1999 and from May to June, 2000 using a tape of southwestern willow flycatcher songs and calls to elicit responses. We detected a total of 50 willow flycatchers (most likely southwestern willow flycatchers due to the closeness to their breeding grounds) in the Colorado River delta, in the months of May to June and none in, or after the month of July, therefore we determined that the birds detected, were migrants. During their migration through the delta, they preferred native broadleaf dominated areas near standing water such as the backwaters from the Colorado River riparian corridor and the desert *pozos* of El Doctor which were used intensively. Therefore, conservation and restoration of these ecosystems is essential for the overall recovery of the species. Additionally, we believe that a possible willow flycatcher summer migratory route, could be traced throughout the series of coastal estuaries found adjacent to the coast of Sonora.

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4. APPENDIX A

Selenium, selected inorganic elements, and organochlorine pesticides in bottom material and biota from the Colorado River delta

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Abstract

Concentrations of selenium (Se) in bottom material ranged from 0.6-5.0 μg/g, and from 0.5-18.3 μg/g in biota, 23% of these exceeded the toxic threshold. Concentrations of DDE in biota exceeded the toxic threshold in 30% of the samples. Greater concentrations of selenium in biota were found at sites with strongly reducing conditions, no output, alternating periods of drying and flooding or dredging activities, and at sites that received water directly from the Colorado River. The smallest Se concentrations in biota were found at sites where an outflow and exposure or physical disturbance of the bottom material were uncommon.

Key words: Colorado River delta, DDE, DDT, dynamics of selenium, metals, redox potential, selenium, wetland management

Introduction

The Colorado River delta has an arid climate with hot summers and mild winters, its annual rainfall is often less than 10 cm and evaporation exceeds 2 m/year (Palacios-Fest, 1990). Agriculture is the mainstay of the region and is supported mostly by irrigation from the Colorado River. The agricultural zone of the Mexicali and San Luis Valleys, located in the northern portion of the Colorado River delta, covers an area of 250,000 ha and uses 52% of the 1.8 x 10^9 m^3/year of water allotted to Mexico from the Colorado River. (Valdés-Casillas *et al.*, 1998).

Most of the former Colorado River channels are currently irrigation canals or agricultural drains. There are 17 agricultural drains in the Mexicali Valley which flow into the Hardy River with an annual volume of 63.3 x 10^6 m^3 and have created the Hardy River-Cucapa wetlands complex (Fig. 1). Occasional flood releases into the delta (as much as 16 x 10^9 m^3/yr) have re-established an active floodplain from Morelos Dam on the border to the intertidal zone in the Gulf of California, and have restored a 1,800 ha riparian corridor on the north (Zamora-Arroyo *et al.*, 2001). Drainage water from the Wellton-Mohawk Irrigation District in Yuma, Arizona, that began entering the eastern portion of the delta in 1977 created the Cienega de Santa Clara which is a cattail (*Typha domingensis*) dominated marsh (Glenn *et al.*, 1996) (Fig. 1).

These ecosystems cover an area of approximately 60,000 ha and support a great number (up to 213 species) of birds (Glenn *et al.*, 1996; Valdés-Casillas *et al.*, 1998). The Cienega de Santa Clara contains the largest populations of the endangered Yuma clapper rail (*Rallus longirostris yumanensis*) (Hinojosa-Huerta *et al.*, 2001) and desert pupfish

(*Cyprinodon macularius macularius*) (Varela-Romero *et al.*, 1998). The riparian corridor is an important stopover area for neotropical migrants such as the endangered willow flycatcher (*Empidonax traillii extimus*) (García-Hernández *et al.*, 2001), and the intertidal mudflats, on the southern portion of the delta, are important for migratory and wintering waterfowl (Mellink *et al.*, 1997). Two endangered marine species, the totoaba fish (*Totoaba macdonaldi*) (Cisneros-Mata *et al.*, 1995) and vaquita porpoise (*Phocoena sinus*) (Jaramillo-Legorreta *et al.*, 1999) inhabit the upper Gulf of California.

Contaminants derived from natural origin (*e.g.* selenium) and anthropogenic activities (*e.g.* pesticides, metals), are commonly found in the lower Colorado River and delta region and represent a potential threat to the health of wetlands and their wildlife. Cretaceous marine sedimentary rocks or volcanic rocks are direct or indirect sources of selenium in the western United States (Presser *et al.*, 1994). Selenium concentrations of 1,300 µg/L in water have been detected in shallow wells in the upstream reaches of the Colorado and Uncompahgre River Valleys in the States of Utah and Colorado (Presser *et al.*, 1994). Concentrations of selenium in the Colorado River are enhanced due to low rainfall and high evaporation, and topographically restricted basins. It is calculated that an average of 70 kg per day of selenium enters and leaves Lake Powell, formed by Glen Canyon Dam, the northernmost dam on the mainstem of the Colorado River (Engberg, 1992).

Elevated concentrations of selenium in diet or in water have been associated with acute toxicity, impaired reproduction (including developmental abnormalities, embryo mortality, and reduced growth or survival of young), pathological changes in tissues, and chronic poisoning of wildlife (Lemly, 1986; Ohlendorf *et al.*, 1986; Ohlendorf *et al.*, 1989;

Lemly, 1993a). According to various studies in the Lower Colorado River selenium levels in bird tissues and prey species are within the toxic range where adverse effects on reproduction could be expected (Rusk, 1991; King *et al.*, 1993; Lusk, 1993; King *et al.*, 1994; Martinez, 1994; Welsh & Maughan, 1994; Mora & Anderson, 1995; King & Baker, 1995; King *et al.*, 1997; García-Hernández *et al.*, 2000; King *et al.*, 2000).

According to the regional ecological authority in Mexico (Dirección General de Ecología), the agricultural drainage system originating in the Mexicali Valley has a mean salinity of 3,000 mg/L, and carries a yearly mean of 70 x 10^6 kg of fertilizers and 400,000 liters of insecticides (Valdes-Casillas *et al.*, 1998). The use of DDT was banned in Mexico for agricultural use in 1978 due to its persistence in the environment and to the rejection by other countries of DDT contaminated products (Canseco-Gonzalez *et al.*, 1997). Nevertheless, 230,000 kg of DDT were used in 1971 in the Mexicali Valley, which left residual concentrations of DDE in wildlife. However, breeding success of some species studied (Cattle egret, *Bubulcus ibis*), was not seriously affected by this or other organochlorines (Mora, 1991; Mora *et al.*, 2001).

The main objectives of the present study are to determine the distribution of selenium in bottom material and biota among different ecosystems in the delta, relate these results to the physico-chemical characteristics of each site, to find patterns that can be applied in the proper management of these areas, in order to restore or create wetlands that have less possibilities to accumulate selenium at concentrations above toxic thresholds for wildlife. The final objective is to analyze biota for other potential contaminants such as metals and organochlorine pesticides.

Materials and Methods

Study area

Following is a description of the most important ecosystems found in the Colorado River delta (Fig. 1).

1.- *Riparian corridor*: This area is a 100 km river stretch from Morelos Dam to the junction of the Colorado River with the Hardy River This 14,000 ha stretch contains a mixture of regenerated native trees and scrub vegetation. The most common species found in the area are: arrowweed, seepwillow (*Baccharis salicifolia*), willow (*Salix gooddingii*) and cottonwood trees (*Populus fremontii*), common reed (*Phragmites australis*) and salt cedar (*Tamarix ramosissima*) (Zamora-Arroyo *et al.*, 2001).

2.- *Hardy River*: This is a reservoir of agricultural runoff from the Mexicali Valley (Fig. 1). Mean dissolved-solids content is 7,000 mg/L (García-Hernández unpublished data) and vegetation is dominated by salt cedar.

3.- *The Cienega de Santa Clara*: This marsh on the eastern edge of the delta was created in 1977 by brackish agricultural drain water from Yuma via the Main Outlet Drain Extension (MODE). The flow created a wetland of 20,000 ha of water surface of which 4,500 ha are thickly vegetated. The marsh is dominated by cattail (*Typha domingensis*) (Glenn *et al.*, 1996).

4.- *El Doctor*: These desert springs or *pozos*, located on the eastern portion of the delta are a separate system with little or no interaction with the Colorado River or with the Cienega de Santa Clara. Dissolved solids in the springs range from 100 to 3,000 mg/L which allows for a great diversity of plants (Glenn *et al.*, 1996).

5.- *Intertidal wetlands*: Primarily marine area that consists of approximately 33,000 ha of extensive tidal mudflats along the coast of the upper Gulf of California (Glenn *et al.*, 1996).

Sample collection

A total of 41 bottom material cores (Table 1), 9 soil samples, and 34 discrete water samples were collected from 12 locations in the delta on April, 2000. Position was recorded at each site using a GPS unit (Garmin® 12XL). Water depth, temperature, dissolved oxygen (YSI® Model 55 oxygen meter), specific conductance (CON 5® portable conductivity meter), water pH (Digi-sense® digital pH/temp/mV/ORP meter with a general purpose electrode), water and bottom material redox potential (Digi-sense® digital pH/temp/mV/ORP meter with a platinum redox electrode), were measured at the field. Bottom material samples were collected using an AMS® stainless steel sludge sampler with a core tip adapted with a butterfly valve to minimize loses of fines. A cleaned (previously rinsed with 5% nitric acid) butyrate plastic liner was inserted into the sampler and replaced with a clean liner after each sampling to prevent cross-contamination. The core obtained by this method measured 7.6 cm diameter and 20 cm long. Liners were capped and transported chilled to the laboratory, afterwards samples were kept at 4°C until their analysis.

Twelve Colorado River delta locations were visited on ten occasions from March 1998 to May 2000 for biota sampling (Table 1). We collected 98 samples of biota. The total of samples were analyzed for selenium, 24 of the samples were analyzed for metals, and 30 samples for organochlorine pesticides. Fish were collected using gillnets (0.5 cm mesh size), dip nets, or minnow traps baited with cat food. Invertebrates and aquatic insects, were collected using minnow traps. A sample consisted of a composite of more than ten organisms of the same species and similar size. Weight and length of each organism was recorded in the field. Composite samples for organochlorine analysis were stored in precleaned glass containers and composite samples for inorganic analysis were wrapped with aluminum foil inside plastic bags. All samples were transported chilled to the laboratory and stored frozen until chemical analysis.

Chemical Analysis

Each sample of bottom material was homogenized and an aliquot was oven dried at 60 °C for 12 hours, and ground. Prepared samples were analyzed for free iron oxide, percent clay, silt and sand, percent organic carbon, and for water content at the Soil, Water and Plant Analysis Laboratory (SWPAL) of the University of Arizona. Water samples were analyzed for their acid-neutralizing capacity (ANC) and dissolved solids, also at SWPAL.

Another aliquot of the homogenized bottom material sample was used for selenium analysis. This aliquot was sieved through a 63 μm sieve over a 500 ml plastic bottle. The sample was wet-sieved using native water until the bottom material was approximately 1 cm deep in the receiving bottle. The sample was allowed to settle for 3 days, afterwards the supernatant was decanted and the obtained bottom material was used for analysis. The samples were dried at 60°C for 12 hours and they were ground using mortar and pestle. Soil samples were also sieved through a 63 μm sieve (Shelton & Capel, 1994).

Prepared bottom material samples were analyzed for selenium at V.I. Vernadsky Institute of Geochemistry and Analytical Chemistry using Instrumental Neutron Activation Analysis (INAA). In this procedure, 100 mg of each sample and reference material were irradiated in a research reactor using a slow neutron flux. Induced radioactivity of the samples was then measured with a Nokia® gamma ray spectrometer with 4096 channels and with a Ge(Li) high resolution detector. Six check samples were analyzed at the Research Triangle Institute, RTI by Graphite Furnace Atomic Absorption (GFAA). Detection limit for selenium in bottom material samples using either method was 0.5 µg/g.

Each composite sample of biota (whole body) was homogenized using an industrial blender. Prepared samples were sent to RTI laboratory for the analysis of the following elements: Al, As, B, Ba, Be, Cd, Cr, Cu, Fe, Hg, Mg, Mn, Mo. Ni, Pb, Se, Sr, V, Zn. Analysis were done using Inducted Coupled Plasma (ICP) spectrometer except for selenium and mercury which were analyzed by graphite furnace and by cold vapor atomic absorption, respectively. Additional biota samples were analyzed at the SWPAL for selenium by graphite furnace atomic absorption. Animal tissue was analyzed for organochlorine pesticides at Patuxent Analytical Control Facility, PACF. Pesticides were quantified with a gas-liquid chromatograph (GLC), equipped with a 63Ni electron-capture detector.

Quality control/quality assurance procedures

Procedural blanks analyses were performed at each laboratory with no anomalies detected. Relative percent differences (RPD) for bottom material by INAA method averaged 9.5 (n = 2). In most of the trace elements analyzed on fish and invertebrates samples, RPD resulted in < 15 (n = 6), with the exception of boron, lead, and mercury which had an arithmetic mean of 48, 28 and 28 RPD, respectively. For organochlorine pesticides, RPD was 0 (n = 6) on fish and invertebrate samples.

Percent recoveries of reference material (marine sediment IAEA-356, International Atomic Energy Agency-356) had a mean of 70%. The RPD range between samples analyzed by INAA at V.I. Vernadsky laboratory compared to samples analyzed by GFAA at RTI laboratory varied from 0.7 to 11 (n = 6).

NRCC TORT-2 (lobster hepatopancreas) was used as reference tissue for metal scan of biota samples. All samples analyzed at RTI differed by less than 20% from the reference (n = 3 for each element). Spike recoveries obtained for metals were all greater than 90% (n = 3 for each element). Spike recoveries for organochlorines pesticides were 113%, 84% and 88% for DDD, DDE, and DDT respectively.

Statistical analysis

Statistical analyses were performed using JMP® software of the SAS Institute Inc. (Sall & Lehman, 1996). Only concentrations of selenium in bottom material were transformed to their natural logarithm to normalize the distribution, the rest of the data had a normal distribution and no transformation was applied. One sample *t* or *z*-tests were used to compare mean selenium concentrations to a specific threshold. One-way ANOVA was used to compare mean selenium concentrations among the different wetlands of the delta. In order to detect differences between the means of two groups of samples (either geometric means or arithmetic means), we used two sample *t*-tests. These statistics were used to compare the concentrations of selenium in bottom material to the concentrations in soil; to compare redox potential, pH, content of clay, silt and sand, organic carbon and dissolved solids among sites influenced by agricultural runoff to sites influenced by river waters; and to compare concentrations of selenium in fish from sites influenced by the Colorado River to sites influenced by agricultural runoff. Simple linear regression statistic analysis was used to identify relations between concentration of selenium in bottom material and the physical and chemical determinations measured at the field and laboratory.

Results

Selenium in bottom material

Distribution of Se concentrations in bottom material (< 63 μm in size) cores from the Colorado River delta is shown in Table 2 and Fig. 2. Individual concentrations of selenium in bottom material ranged from 0.6 to 5.0 μg/g, and the 90% confidence interval of the mean was between 0.7 and 3.1 μg/g.

The baseline selenium concentration for western soils is estimated to be < 1.4 μg/g dry wt. (Shacklette & Boerngen, 1984; Radtke *et al.*, 1988). Half of the bottom material samples (21 samples) from the Colorado River delta exceeded the baseline for western soils. The sites that had 100% of their samples above the baseline were Bocana, Laguna del Indio, Zacatecas drain, Campo Rafael, and El Mayor. Sites with selenium concentration in all samples below the baseline, were El Doctor, Ayala drain, and Hardy River.

The threshold where sedimentary selenium can cause adverse biological effects in 10% of exposed fish and birds (EC10) is 2.5 μg/g. Adverse effects are always observed at concentrations greater than 4.0 μg/g (EC100) (Skorupa *et al.*, 1996; USDI, 1998). The mean Se concentration in bottom material from all sites in the delta (N = 41, geom. mean = 1.5 μg/g) was lower than the EC10 threshold (one sided *P*-value < 0.0001 from one-sample *t*-test, t = 5.8 df = 40). Nevertheless, 22% (nine samples) exceeded the EC10 toxicity threshold. A hundred percent of the samples from Laguna del Indio exceeded this threshold, 67% from El Mayor, 30% from the Cienega de Santa Clara, 17% from Colorado River and 13% from the Cucapa complex also exceeded the threshold. Only 5% (two samples) exceeded the EC100 threshold in the delta and these were from El Mayor wetland. In soils, the mean selenium concentration (N = 10, geom. mean = 1.03 μg/g) was below the EC10 (one sided *P*-value = 0.001 from one-sample *t*-test, t = 4.1 df = 9), although a sample from Laguna del Indio exceeded the EC10 threshold.

No difference was found between soil and bottom material samples from the Colorado River sites (one-sided *P*-value = 0.12 from two-sample *t*-test, t = 1.6, df = 16) nor from El Indio location (one-sided *P*-value = 0.6 from two-sample *t*-test, t = 0.3, df = 1). The mouth of the river site (Bocana) did have a difference between soil and bottom material samples (one-sided *P*-value = .006 from two-sample *t*-test, t = 12, df = 2), Se concentration in soil was lower than concentration in bottom material.

No differences were found in the concentrations of selenium in bottom material samples among the different locations in the Colorado River delta listed in Table 2 (one-way ANOVA $F_{11,29}$ = 1.73 *P*-value = 0.11).

For comparisons, we grouped the sites according to their principal source of water, which was: a) Agricultural runoff: Cienega de Santa Clara, El Indio, Zacatecas drain, Campo Rafael, Ayala drain, El Mayor, Hardy River and Cucapa north; b) Colorado River water: Colorado River, Bocana and Cucapa south; and c) Other: El Doctor and geothermal lagoons.

El Doctor and geothermal lagoons group had smaller concentrations of selenium in bottom material compared to sites influenced by river waters (one-sided *P*-value < 0.001 from one-sample *z*-test, $z = 4.8$, df = 20) or agricultural drains (one-sided *P*-value < 0.001 from one-sample *z*-test, $z = 5.6$, df = 23). Concentration of selenium in bottom material was greater at sites influenced by agricultural drainage (N = 20, geom. mean = 1.8 μg/g) than at sites influenced by river water (N = 19, geom. mean = 1.3 μg/g) (Fig. 3) (one-sided *P*-value = 0.03 from two-sample *t*-test, $t = 2.1$, df = 37).

Dynamics of selenium in the Colorado River delta wetlands

Redox potential (Eh in mV) was higher (positive) in bottom material from river water sources (n = 19, mean = 45 mV) than from bottom material derived from agricultural runoff (n = 20, mean = -118 mV) (one-sided *P*-value < 0.0001 from two-sample *t*-test, $t = 5.2$, df = 37). Concentration of Se in bottom material increased with lower (negative) values of redox potential, and decreased with higher (positive) redox potentials (Fig. 4) four outliers (not shown in Fig. 4) from the Colorado River are discussed below ($R^2 = .53$, $F_{1,34} = 39.5$ *P*-value < 0.0001 from a simple linear regression).

Water pH was higher (more basic) at sites influenced by agricultural drains (n = 20, mean = 8.4) than at sites influenced by river waters (n = 19, mean = 8.1) (one-sided *P*-value <

0.002 from two-sample *t*-test, $t = 3.3$, df = 37). Concentration of selenium in bottom material increased with water pH, excluding two outliers from the Colorado River with high pH and low selenium concentration ($F_{1,36} = 8.3$ *P*-value = 0.006 from a simple linear regression).

Other explanatory variables were the clay, silt and sand content of the bottom material. Selenium concentration increased with the clay ($F_{1,38} = 5.6$ *P*-value = 0.02 from a simple linear regression) and silt content of the sample ($F_{1,38} = 4.4$ *P*-value = 0.04 from a simple linear regression). Selenium decreased with the sand content of the sample ($F_{1,38} = 6.1$ *P*-value = 0.02 from a simple linear regression). The amount of clay was greater in bottom material collected from sites influenced by agricultural drains (n = 20, mean = 26%) compared with sites influenced by river water (n = 19, mean = 10%) (one-sided *P*-value = 0.001 from two-sample *t*-test, t=3.6, df = 37). This was also true for silt, which was greater in agricultural runoff sites (n = 20, mean = 40%) compared to sites influenced by river waters (n = 19, mean = 13%) (one-sided *P*-value < 0.0001 from two-sample *t*-test, $t = 5.0$, df = 37). The opposite occurred with sand. Sites influenced with river water had more sand percentage (n = 19, mean = 77%) than sites influenced by agricultural drains (n = 20, mean = 34%) (one-sided *P*-value < 0.0001 from two-sample *t*-test, $t = 5.0$, df = 37).

Percent organic carbon in bottom material was also related with selenium concentration. Higher selenium concentrations were detected in samples with a high organic carbon content ($F_{1,38} = 6.5$ *P*-value = 0.01 from a simple linear regression). More organic carbon was detected in bottom material from agriculture runoff sites (n = 20, mean =

1.3%) than from bottom material from river sites (n = 19, mean = 0.5%) (one-sided *P*-value = 0.0002 from two-sample *t*-test, *t* = 4.2, df = 37).

Dissolved solids concentrations in water correlated positively with selenium concentration in bottom material ($F_{1,32}$ = 4.6 *P*-value = 0.04 from a simple linear regression) excluding the Bocana sites which had very high solid content in water. More dissolved solids were present in sites with agriculture influence (n = 17, mean = 4.4 g/L) than with river water influence (n = 16 mean = 1.8) (one-sided *P*-value < 0.0001 from two-sample *t*-test, *t* = 5.2, df = 31).

The best linear fit model derived from these relationships resulted from the redox potential and the concentration of selenium in bottom material, the rest of the models explained < 20% of the variability in the concentrations of selenium in bottom material samples.

No relationships could be established between selenium concentration in bottom material and the following vaiables: water depth (*P*-value = 0.54), water temperature (*P*-value = 0.71), dissolved oxygen (*P*-value = 0.23), redox potential in water (*P*-value = 0.50), bottom material water content (*P*-value = 0.14), free iron oxide content (*P*-value = 0.97), water ANC (*P*-value = 0.53), or specific electrical conductance (*P*-value = 0.06).

<u>Selenium in biota</u>

Concentrations of selenium in composite samples of biota are shown in Table 3. The threshold for reproductive impairment in birds from dietary exposure is reported to be 3 µg/g dry wt. Se concentration (Lemly, 1993b; USDI, 1998). Considering our specimens samples from the delta as diet for fish and wildlife, we found that 23% exceeded these threshold. Nevertheless, the mean of all biota samples from the delta (N = 98, geom. mean = 1.9 µg/g) was lower than this guideline (one-sided *P*-value < 0.0001 from one-sample *t*-test, $t = 5.7$, df = 97).

The toxicity threshold for nonbreeding birds exposed to winter-stress has been observed to be > 10 μg/g dry wt. of selenium concentration in their diet (USDI, 1998). We found that a sailfin molly sample from the MODE, a freshwater shrimp sample from the Bocana and a mosquitofish sample from El Mayor exceeded this threshold value (Table 3).

None of the edible fish (*e.g.* largemouth bass, common carp, channel catfish, striped mullet, sunfish, tilapia) collected from the Colorado River delta wetlands exceeded the threshold level of 6.5 μg/g dry wt. that warrants advisories by the U.S. health department, recommending limited fish consumption by humans (Skorupa *et al.*, 1996).

The estimated threshold range for reproductive impairment in sensitive fish species (*i.e.* perch, bluegill, salmon) is estimated to be between 4 and 6 μg/g dry wt. whole body concentration (USDI, 1998). Although, specimens from the Colorado River delta are not generally known as sensitive species, 14 samples of sailfin molly, mosquitofish and striped mullet exceeded this threshold (Table 3). It is important to note that none of the samples of the endangered desert pupfish had concentrations near or above the reproductive impairment threshold.

To compare the concentrations of selenium in biota among sites we selected mosquitofish and sailfin molly because they were collected from most of the sites in the delta. Selenium concentration in mosquitofish/sailfin molly samples ranged from 0.7 to 34.1 μg/g and the 90% confidence interval was 0.8 to 12.7 μg/g. The largest concentration of selenium in sailfin molly/mosquitofish samples was from El Mayor (n = 2, geom. mean = 9.4 μg/g), followed by the Colorado River site (n = 2, geom. mean = 6.02 μg/g), the Hardy River (n = 1, conc. = 5.2 μg/g), the Cienega de Santa Clara (n = 13, geom. mean = 3.2 μg/g), Cucapa complex (n = 1, conc. =1.5 μg/g), El Doctor (n = 9, geom. mean = 1.2 μg/g), and Bocana (n = 1, conc. = 0.9 μg/g).

Bioaccumulation (the ability of organisms to accumulate an element to concentrations one or more order of magnitude greater than water or food sources) in biota is measured by the bioaccumulation factor (BF) (Lemly & Smith, 1990). This factor was obtained by dividing the concentration of selenium in mosquitofish/sailfin molly samples of a particular site by the geometric mean selenium concentration in bottom material for that location. Although this is factor can be considered as partial, because bottom material does not constitute the complete food source for these fish, it is a good indicator of the rate of selenium cycling in a particular ecosystem. For instance the highest BF in mosquitofish/sailfin molly samples was from the Colorado River site (n = 2, BF = 6.5), followed by El Mayor (n = 2, BF = 5.3), Hardy River (n = 1, BF = 4.9), Cienega de Santa Clara (n = 13, BF = 3.2), Cucapa complex (n = 1, BF = 1.1) and El Doctor (n = 9, BF = 1.0).

No clear relationship could be found between the concentration of selenium in bottom material (geom. mean Se concentration for each site) and the concentration of selenium in mosquitofish/sailfin molly samples ($F_{1,27} = 2.2$, P-value = 0.15 from a simple linear regression).

Other trace elements in biota

In addition to selenium, other trace elements such as cadmium, mercury and lead are likely to cause toxic effects in fish and birds at large concentrations (Walsh *et al.*, 1977; Eisler, 1985; Eisler, 1987; Franson, 1996; Furness, 1996; USDI, 1998), concentrations of these elements are shown in Table 4. Cadmium concentration in fish and invertebrates collected from the Colorado River delta ranged from < 0.19 μg/g (detection limit) to 0.8 μg/g dry wt. According to Eisler (1985) the potential toxic threshold for birds is about 0.4 μg/g. One sample of marine clams from the Upper Gulf had two times this level, and three other samples had a Cd concentration equal to 0.4 μg/g (Table 4). Nevertheless, according to laboratory tests, a bird dietary intake of less than 1 μg/g would be unlikely to cause any toxic effect (Furness, 1996). None of the collected samples exceeded this last threshold.

Mercury concentrations in samples ranged from < 0.04 μg/g to 1.29 μg/g. To protect sensitive species of birds that regularly consume fish and other aquatic organisms, total mercury concentrations in these food items should not exceed 0.1 μg/g wet weight, equivalent to approximately 0.3 μg/g dry weight (Eisler, 1987). This value was exceeded by 40% (nine samples) of the samples collected from various sites in the delta, the highest values were from a crayfish sample from the Cienega de Santa Clara (1.29 μg/g) and from a mosquitofish sample from El Doctor (1.23μg/g) (Table 4). Nevertheless, other studies have determined that the potential toxic threshold for the protection of fish and predatory organisms is 1.6 μg/g (Walsh *et al.*, 1977). None of the samples exceeded this threshold. In addition, none of the samples exceeded the toxic threshold for lead, established by Franson (1996).

Organochlorine pesticides in biota

From the organochlorine pesticides analyzed, only the DDT-family insecticides were detected in the samples (Table 5). Concentrations of p,p'-DDE were detected in 26 of the 30 samples (86%) collected from the delta. Values ranged from < 0.01 μg/g to 0.34 μg/g wet weight. The lowest dietary concentration of DDE that resulted in critical eggshell thinning and decreased production in the peregrine falcon (*Falco peregrinus*) was estimated by Blus (1996) at 1.0 μg/g wet weight (Blus, 1996). None of the samples from the delta exceeded this value. However, for more sensitive species like the brown pelican (*Pelecanus occidentalis*), the lower critical dietary level of DDE was estimated at about 0.15 μg/g wet weight (Blus, 1996). Nine samples (30%) from various sites in the delta exceeded this value, the highest concentrations (two times higher than the threshold) were detected in mosquitofish from El Mayor and El Doctor (Table 5). p,p'-DDT was recovered in eight samples (26%) from the delta, values ranged from < 0.01 μg/g to 0.13 μg/g wet weight. Also, p,p'DDD was detected in 13% of the samples (Table 5).

Discussion

Extensive experimental and field studies have concluded that redox potential and pH are the most important parameters determining chemical speciation and solubility of Se compounds in wetland environments (Elrashidi *et al.*, 1987; Weres *et al.*, 1989; Lemly & Smith, 1990; Masscheleyn *et al.*, 1990; Masscheleyn *et al.*, 1991; Porcella *et al.*, 1991; Velinsky & Cutter, 1991; Masscheleyn & Patrick, 1993; Naftz & See, 1993; Pardue & Patrick, 1995). The different possible species of selenium at various redox and pH conditions in natural environments is shown in the stability diagram of Fig. 5. At pH and redox conditions occurring in most aqueous and aerobic sedimentary environment, Se exists as oxyanion in the selenate, selenite or biselenite ($HSeO^{3-}$) form. As can be seen from the diagram, at high redox values, selenate is predominant in a wide pH range. In the moderately redox range, biselenite and selenite are the major species at low and high pH, respectively. And in strongly reducing environments, Se (-II) is theorized to exist as hydrogen selenide H_2Se and as insoluble metal selenides (Faust & Aly, 1981; Masscheleyn & Patrick, 1993).

The redox and pH conditions from the sampling sites collected in the Colorado River delta, were superimposed on the stability diagram and represented as an area of points inside the graph (Fig. 5). This theoretical exercise was made in order to have a better idea on which species of selenium could be the most probable to be present in a particular ecosystem. However, we are aware that more research is needed in this field to determine the actual species of selenium present in bottom material and in the water column. From Fig. 5, we observed that most of the samples laid in the area where selenium is likely to be present as inorganic selenium (Se 0,-II) and a few of them reached the area where the most stable form would be selenite. According to this diagram none of the selenium present in bottom material is likely to be in the selenate form due to the moderately and strongly reduced conditions prevailing in the delta wetlands.

The El Mayor site had the most reducing conditions and the largest concentrations of selenium (exceeding the EC10) in bottom material from all the sites surveyed (Fig. 5 and Table 2). This wetland is a backwater from the Hardy River with no apparent output and almost no flow. It has been documented that strongly reducing conditions, high clay, silt and organic carbon content favor the removal of selenium from solution into the bottom material through chemical and microbial reduction of the selenate form to elemental selenium, followed by adsorption onto clay and the organic carbon phase of particulates (Lemly & Smith, 1990). Immobilization processes like these, effectively removed 92% of the total Se inventory in an experimental pond at Kesterson Reservoir (Weres *et al.*, 1989). Therefore, most of the selenium in the El Mayor wetland could be sequestered in the bottom material. Nevertheless, bottom material is a dynamic system and it has been documented that there is a constant movement from selenium in the bottom material into the food chain by plants, bottom dwelling invertebrates and detrital feeding fish and wildlife. In addition, there are the physical activities of burrowing of invertebrates, feeding activities of fish and wildlife that oxidize the reduced selenium making it available for the food chain (Lemly & Smith, 1990). Other physical processes such as subsequent drying and flooding periods result in oxidation of bottom material as well (Weres *et al.*, 1989). The sample of fish that contained the greatest Se concentration (6X above the toxic threshold) was collected at the southern portion of the El Mayor wetland, an area subjected to alternating periods of evaporation and flooding. During dry conditions, reduced selenium trapped in bottom material could be oxidized and transformed to a more soluble selenium species which could become dissolved into the water column when the area is flooded, and then readily taken up by the food chain. This shallow area attracts many birds such as cattle egrets (*Bubulcus ibis*), little blue herons (*Egretta caerulea*), cormorants (*Phalacrocorax auritus*), and raptors (J. García-Hernández, personal observation).

The Hardy River, which is a reservoir of agricultural drainage from the Mexicali Valley had generally, small selenium concentrations in bottom material and biota (Table 2 and 3). This is probably because, unlike the El Mayor, there is a continuous water outflow which results in medium to fast flows, smaller organic carbon load (Table 2) and consequent less reduced condition (Fig. 5 and Table 2).

The Cucapa complex receives its water from the Hardy River on the north and then it mixes with the southern most portion of the Colorado River. Greater concentrations of selenium were found in samples collected in the northern portion of the Cucapa complex compared to the southern portion. The north has reduced conditions, low flow and greater clay content which are more likely to sequester dissolved Se, compared to the southern part, influenced by the Colorado River (Fig. 1), that presented more oxidized conditions, less organic matter, and sandy bottom material. These conditions will favor Se solubility. Selenium concentrations in biota were not particularly great, however, a striped mullet sample collected near the confluence with the Colorado River had concentrations of Se exceeding the potential toxic threshold (Table 3), probably because this is a detritivorous fish (Yáñez-Arancibia, 1976).

The Colorado River sites are characterized by mildly reducing conditions, sandy bottom material, and small organic carbon concentrations (Table 2) which theoretically will favor the dominance of selenium in the selenite and selenate form (Fig. 5). Therefore, small selenium concentrations in bottom material does not necessarily indicate that this element is absent from the system. What it does indicate is that physico-chemical conditions favor the mobilization of selenium from the bottom material. Once dissolved, Se can be taken up readily by algae and plankton, incorporating it into the food chain (Besser *et al.*, 1993). This is probably the reason that a mosquitofish sample from the Colorado River, similarly to the striped mullet sample from the Cucapa complex south, accumulated concentrations of Se exceeding the potential toxic threshold (Table 3). Selenium concentrations were greater than background concentrations for western soils at three points in the river (Fig. 2), these sites were the outliers previously mentioned that presented oxidized conditions but elevated selenium concentrations compared to the rest of the samples on the Colorado River. It is possible that as water flows downstream, evaporation accounts for increased concentrations of organic matter and clays, that might in turn, sequester larger amounts of selenium. Although, more data is needed to investigate this pattern.

The Cienega de Santa Clara has the physico-chemical conditions (Table 2 and Fig. 5) that favor the sequestering of selenium in bottom material. This is specially true for bottom material from the central lagoons, where two of the four samples collected exceeded the EC10 threshold. These lagoons are covered by thickets of cattail (*Typha domingensis*) and the submerged aquatic plant spiny naiad (*Najas marina*) resulting in the greatest content of organic carbon of all the delta sites. Anthropogenic activities such as dredging of wetlands is the most effective way to oxidize the bottom material and dissolve available selenium (Masscheleyn & Patrick, 1993). It is possible that recent dredging at the terminus of the MODE is related to the large concentrations of selenium found in two sailfin molly samples from this site (Table 3). It is also important to note that the densest group of breeding Yuma clapper rails reported for the Cienega de Santa Clara congregate precisely at the terminus of the MODE (Hinojosa-Huerta *et al.*, 2001).

The fact that no clear relationship could be found between the concentration of Se in bottom material and the concentration of Se in fish implies that other factors are important in determining the concentration of selenium in fish, and in fish-eating birds. The physico-chemical characteristics of each wetland and their effects on the speciation, solubility, and bioavailability of selenium through the food chain, need to be considered.

In general terms, we found that sites that received water directly from the Colorado River and that had mildly reducing or oxidizing conditions, small organic carbon and high sand content, were likely to have large Se concentrations in fish (*i.e.* Colorado River sites). Sites that received water from agricultural runoff, that had strongly reducing conditions, but that had some type of outflow or flushing system (*i.e.* tides), and that were mostly undisturbed by anthropogenic activities, had the smallest concentration of Se in fish (*i.e.* southern portion from the Cienega de Santa Clara, Hardy River). Small Se concentrations in biota from the southern portion of the Cienega de Santa Clara were previously reported in a study of bioaccumulation of Se in the Cienega de Santa Clara (García-Hernández *et al.*, 2000). The largest concentration of Se in fish resulted from sites that received agricultural runoff but that had little or no outflow, large organic carbon content and regular physical disturbance of the bottom material such as dredging or subsequent periods of drying and flooding (*e.g.* MODE canal, south of the El Mayor wetland, Laguna del Indio).

The most stable and extensive wetlands in the Colorado River receive their water mainly from agricultural runoff, which has resulted in smaller overall concentrations of selenium in fish compared to wetlands that receive water directly from the Colorado River. This was observed when we compared mosquitofish/sailfin molly samples collected from Havasu National Wildlife Refuge (NWR), Cibola NWR, Imperial NWR and Mittry Lake, Arizona during 1999 (King *et al.*, 2000), with samples of the same species collected from the

Colorado River delta wetlands during 1998 and 1999 (this study). As can be seen in Fig. 6, concentrations of selenium in fish from the lower Colorado River wetlands, north from Morelos Dam were greater (N= 8, geom. mean = 9.48) than concentrations of Se from the Colorado River delta, south Morelos Dam (N = 26, geom. mean = 2.6) (one-sided P-value = 0.002 from two-sample t-test, $t = 3.3$, df = 35).

Pesticides such as DDE, DDT and DDD were detected in fish and invertebrate samples from the delta wetlands. The DDE:DDT ratio was lower than 50, which is thought to indicate recent exposure to the parent compound (Mora, 1997). Nevertheless, under unknown exposure conditions, these ratios may not be indicative of recent DDT use but of long persistence and heavy use of DDT in the past (Mora, 1997). A pesticide study on cattle egrets from the Mexicali Valley, concluded that hatching success was not significantly affected by DDE or other organochlorines (Mora, 1991). However, more studies are required to determine if organochlorine, organophosphates or carbamates pesticides as well as herbicides, are affecting the density of insects in the delta wetlands, which could potentially impact the habitat quality for insectivorous migratory birds.

Conclusions

The quantity of Colorado River discharge into the delta is unpredictable and varies widely between months. Therefore, the scope of this study applies only to the types of samples collected and at the time collected. More studies are needed to detect differences between dry and flooded conditions and between seasons and their possible relationships with selenium concentrations in wildlife.

From the concentrations of selenium found in bottom material and biota from the Colorado River delta, the following are the main conclusions and recommendations:

1. To closely monitor the wildlife from El Mayor wetland, and if possible open an outflow that will help reduce the organic carbon concentration, and eventually reduce the concentration of selenium in bottom material.
2. Monitor the reproductive success of Yuma clapper rails, or an appropriate surrogate species, from the Cienega de Santa Clara, especially from the MODE site, in order to determine if selenium is having an effect on the bird population. Dredging activities, if absolutely necessary, should be done outside the breeding season of the Yuma clapper rails, which is usually from March to July (Eddleman, 1989), to minimize the potential reproductive impacts due to high selenium concentrations accumulated in the reproductive tissues of the parent (Ohlendorf *et al.*, 1986).
3. In order to maintain selenium concentrations below toxic thresholds in created or restored Colorado River delta wetlands, it is recommended that preferentially agricultural runoff or a mix of Colorado River water and agricultural runoff be used, an outflow should always be included, and physical disturbances such as dredging should be avoided. Nevertheless, a continuous monitoring of selenium concentrations in wildlife at these sites will also be necessary.

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Table 1. Location name, number of bottom material (BM) samples, type of organisms and number of composite samples collected in the Colorado River delta.

Location Name	No. of BM samples	Organisms collected		N
		Common name	Scientific name	
1. Colorado River	12	Freshwater clams	*Corbicula* sp.	2
		Sunfish	*Lepomis macrochirus*	1
		Mosquitofish	*Gambusia affinis*	2
2. Geothermal Lagoons	1	Desert pupfish	*Cyprinodon macularius*	1
3. Hardy River	2	Sunfish		4
		Threadfin shad	*Dorosoma petenense*	7
		Mosquitofish		1
		Channel catfish	*Ictalurus punctatus*	7
4. El Mayor	3	Crayfish	*Procambarus clarki*	1
		Freshwater shrimp	*Palaemonetes paludosus*	1
		Mosquitofish		2
5. Cucapa complex	8	Tilapia	*Tilapia zilli*	1
		Common carp	*Cyprinus carpio*	2
		Largemouth bass	*Micropterus salmoides*	2
		Channel catfish		1
		Sunfish		1

		Striped mullet	*Mugil cephalus*	1
		Bullfrog	*Rana catesbeiana*	1
		Sailfin molly	*Poecilia latipinna*	1
6. Ayala drain	1	no biota sampled		
7. Campo Rafael	1	no biota sampled		
8. Zacatecas drain	1	no biota sampled		
9. Laguna del Indio	2	no biota sampled		
10. Canal Sonora	0	Freshwater clams		2
11. Cienega de Sta Clara	7	Common carp		6
		Striped mullet		1
		Largemouth bass		3
		Sailfin molly		8
		Mosquitofish		5
		Sunfish		1
		Threadfin shad		1
		Desert pupfish		1
		Brine shrimp	*Artemia* sp.	1
		Freshwater shrimp		1
		Crayfish		10
12. El Doctor	1	Mosquitofish		8
		Sailfin molly		1

		Sunfish		2
		Desert pupfish		2
		Beetle	Coleoptera	1
13. Bocana	2	Mosquitofish		1
		Freshwater shrimp		1
		Fiddle crab	*Uca* sp.	1
14. Upper Gulf	0	Clams	*Chione* sp.	2
TOTAL =	41			98

Table 2. Geometric mean and range or individual concentrations of selenium (μg/g dry wt.), water content, redox potential, pH, clay, silt, sand, and organic carbon content in bottom material and/or soil from the Colorado River delta.

Site	N	Se		% water	Redox	pH	Clay	Silt	Sand	OC
		Mean	Range		(mV)		(%)	(%)	(%)	(%)
EC10 threshold[1]		*2.5*								
Bottom sediment samples:										
El Mayor	3	**3.46**	(1.8 - 5.0)	69	-255	8.9	24	43	33	1.68
Laguna del Indio	2	**2.99**	(2.8 - 3.2)	67	-96	8.5	41	45	14	1.17
Bocana	2	2.15	(2.0 - 2.4)	63	2.0	8.1	22	38	40	1.20
Zacatecas drain	1	1.68		65	-36	8.2	43	31	27	1.04
Cienega de Santa Clara	7	1.60	(1.0 - 3.8)	68	-90	8.4	12	37	51	1.54
Geothermal lagoons	1	1.60		72	-10	7.6	ND[2]	ND	ND	ND
Campo Rafael	1	1.57		58	-110	8.2	27	59	15	1.78
Cucapa complex	8	1.43	(1.0 - 2.5)	66	-106	8.2	28	38	34	0.99
El Doctor	1	1.33		76	-270	8.7	46	39	15	1.80

Colorado River	12	1.14	(0.6 - 2.8)	77	110	8.1	1	0	99	0.21
Hardy River	2	1.08	(1.0 - 1.3)	64	-111	8.5	35	24	42	1.02
Ayala drain	1	0.90		73	-80	8.3	35	52	13	1.04
Soil samples:										
Laguna del Indio	1	**3.06**								
Colorado River	7	0.81	(0.3 - 2.3)							
Bocana	2	0.55	(0.5 - 0.6)							

[1]EC10 threshold = threshold where sedimentary selenium can cause adverse biological effects in ten percent of exposed fish and birds (USDOI, 1998), values in bold exceed this threshold.

[2]ND = no data

Table 3. Arithmetic mean or individual concentration of selenium in biota composite samples from the Colorado River delta (µg/g dry wt.).

Site name	Sample type	N	Selenium conc.	SD[1]
Potential toxic threshold[2]	*bird food items*		*3.00*	
El Mayor south	Mosquitofish	2	**18.34**	22.3
Bocana	Freshwater shrimp	1	**17.10**	
MODE	Sailfin molly	2	**11.52**	6.8
Cienega de Santa Clara	Sailfin molly	2	**8.60**	5.8
Colorado River	Mosquitofish	2	**7.29**	5.8
Campo Mosqueda	Mosquitofish	1	**5.20**	
Cienega de Santa Clara	Brine shrimp	1	**5.00**	
Campo Flores	Bullfrog	1	**4.50**	
Campo Flores	Striped mullet	1	**4.13**	
LaFlor del Desierto	Sailfin molly	4	**3.99**	3.9
Campo Flores	Tilapia	1	**3.55**	
Cienega de Santa Clara	Crayfish	5	**3.51**	2.2
Cienega de Santa Clara	Common carp	2	2.46	0.9
Campo Flores	Largemouth bass	2	2.43	0.0
La Flor del Desierto	Crayfish	5	2.43	1.5
Campo Flores	Common carp	2	2.34	0.6

El Mayor	Crayfish	1	2.23	
La Flor del desierto	Mosquitofish	4	2.20	1.9
Upper Gulf	Marine clams	2	2.13	0.0
MODE	Sunfish	1	2.12	
Canal Sonora	Freshwater clams	2	2.09	0.3
Cienega de Santa Clara	Striped mullet	1	2.08	
Campo Flores	Sunfish	1	2.00	
Geothermal lagoon	Desert pupfish	1	1.81	
La Flor del desierto	Common carp	4	1.80	0.6
Cienega de Santa Clara	Largemouth bass	3	1.74	0.7
La Flor del desierto	Freshwater shrimp	1	1.65	
MODE	Mosquitofish	1	1.62	
Campo Flores	Channel catfish	1	1.62	
El Doctor	Predacious beetle	1	1.55	
MODE	Threadfin shad	1	1.54	
El Mayor	Freshwater shrimp	1	1.54	
Campo Cucapa	Sailfin molly	1	1.50	
Colorado River	Sunfish	1	1.47	
El Doctor	Mosquitofish	8	1.44	0.9
El Doctor	Sunfish	2	1.37	0.4
Colorado River	Freshwater clams	2	1.32	0.1

La Flor del desierto	**Desert pupfish**	1	1.28	
El Doctor	**Sailfin molly**	1	1.15	
El Doctor	**Desert pupfish**	2	1.10	0.4
Campo Mosqueda	**Channel catfish**	7	1.03	0.4
Campo Mosqueda	**Sunfish**	4	0.99	0.2
Bocana	**Mosquitofish**	1	0.93	
Campo Mosqueda	**Threadfin shad**	7	0.92	0.3
Bocana	Fiddle crab	1	0.48	

[1]SD = standard deviation.

[2]Potential toxic threshold = the concentration of Se in a food item above which adverse reproductive effects may be expected in fish and wildlife (Lemly, 1993b), values above the threshold are shown in bold.

Table 4. Arithmetic mean or individual concentration of selected inorganic elements in fish and invertebrate composite samples from the Colorado River delta (µg/g, dry weight).

Site name	Sample type	N	Al	As	B	Ba	Cd	Cr	Cu	Fe	Hg	Mg	Mn	Ni	Pb	Sr	V	Zn
Potential toxic threshold[1]	*fish and invertebrates*						*0.4-1.0*				*0.3-1.6*				*100*			
Colorado River	Freshwater clams	1	116	7.9	9.5	6.0	**0.4**	0.4	29.8	228	ND	823	51	0.4	2.0	15	0.5	78
	Mosquitofish	2	245	ND	1.4	17.9	ND	0.9	5.6	267	**0.63**	1833	48	0.3	1.4	174	ND	166
Bocana	Freshwater shrimp	1	114	12.3	47.4	86.3	**0.4**	2.9	69	199	**0.40**	3284	7	ND	ND	545	0.3	51
Cucapa complex	Striped mullet	1	1125	3.2	ND	44.5	ND	78.1	9.4	2439	ND	2603	133	6.5	1.9	177	3.6	45
Hardy River	Mosquitofish	1	529	0.9	8.8	14.2	ND	4	9.9	583	**0.32**	2061	34	2.7	0.9	271	1	108
El Mayor	Crayfish	1	134	2.2	9.1	69.8	ND	6.3	54.7	259	0.05	3910	123	2.2	1.7	1034	ND	85
	Mosquitofish	2	446	ND	4.5	21.6	0.2	1.3	10.4	531	**0.89**	2107	40	1.3	1.9	300	1.2	109
Cienega de SC	Crayfish	3	198	7.5	31.7	83.7	0.2	2.9	44.0	301	**0.69**	4886	1033	1.1	1.8	1550	1.0	105
	Sailfin molly	4	519	7.9	7.6	13	0.1	3.2	14.0	679	0.12	2174	136	1.0	1.3	195	1.8	133
	Common carp	1	ND[2]	ND	ND	4.0	ND	1.3	3.1	103	0.13	1513	10	ND	1.1	327	ND	174
	Mosquitofish	1	467	1.5	7.8	35.5	ND	15.7	7.8	663	0.05	2541	274	3.3	ND	319	1.3	169

El Doctor	Mosquitofish	3	90	2.0	5.8	28.5	0.2	8.9	8.3	268	**0.56**	1787	40	1.3	0.3	249	0.3	205
Canal Sonora	Freshwater clam	1	490	12.2	30.0	12.0	**0.4**	0.9	48.1	765	ND	1191	55	1.3	ND	24	1.1	80
Upper Gulf	Marine clam	1	260	8.3	11.6	5.0	**0.8**	0.6	13.4	348	ND	2828	12	1.3	1.6	14	0.7	44
Range			ND-1125	ND-18.2	ND-59.7	4.0-136	ND-0.8	0.4-78.1	3.1-69.0	103-2439	ND-1.29	1191-6211	7.4-2651	ND-6.5	ND-2.7	14-1826	ND-3.6	44-284

[1]Potential toxic threshold = maximum limit of a contaminant for the protection of birds that consume fish and invertebrates in their diet (Furness, 1996, Franson, 1996, Eisler, 1987, Eisler 1985, Walsh,1977)

[2]ND = below detection limit.

Table 5. Arithmetic mean or individual concentration of DDD, DDE and DDT in fish and invertebrate composite samples from the Colorado River delta (µg/g wet weight).

Collection Site	Sample type	N	%lipid	p,p'-DDD	p,p'-DDE	p,p'-DDT	DDE/ DDT
Colorado River	Freshwater clams	1	2.1	ND[1]	0.050	ND	
	Sailfin molly	1	8.5	ND	0.180	0.080	2
Bocana	Freshwater shrimp	1	3.0	ND	ND	ND	
El Mayor	Mosquitofish	2	9.6	ND	0.245	0.075	3
	Crayfish	1	6.3	0.007	0.020	ND	
Hardy River	Common carp	4	2.1	0.012	0.045	ND	
	Channel catfish	2	24.3	0.005	0.015	ND	
	Threadfin shad	1	29.3	0.014	0.190	0.020	10
Cucapa complex	Crayfish	1	6.7	ND	0.060	ND	
	Common carp	2	6.6	0.008	0.155	ND	
	Channel catfish	1	16.6	0.025	0.120	0.030	4
Cienega de SC	Sailfin molly	3	10.4	0.032	0.105	0.130	1
	Mosquito fish	1	11.2	ND	0.030	0.030	1
	Common carp	2	4.9	0.005	0.050	ND	
	Crayfish	2	1.7	ND	0.010	ND	
	Stripped mullet	1	22.5	0.010	0.030	0.010	3
El Doctor	Mosquito fish	2	8.4	ND	0.170	ND	

Canal Sonora	Freshwater clams	1	2.6	ND	0.150	ND	
Upper Gulf	Marine clams	1	1.0	ND	ND	ND	
Range				ND- 0.032	ND- 0.340	ND- 0.130	1-10

[1]ND = below detection limit

Figure captions

FIGURE 1. Colorado River delta ecosystems. Sampling locations are indicated with numbers.

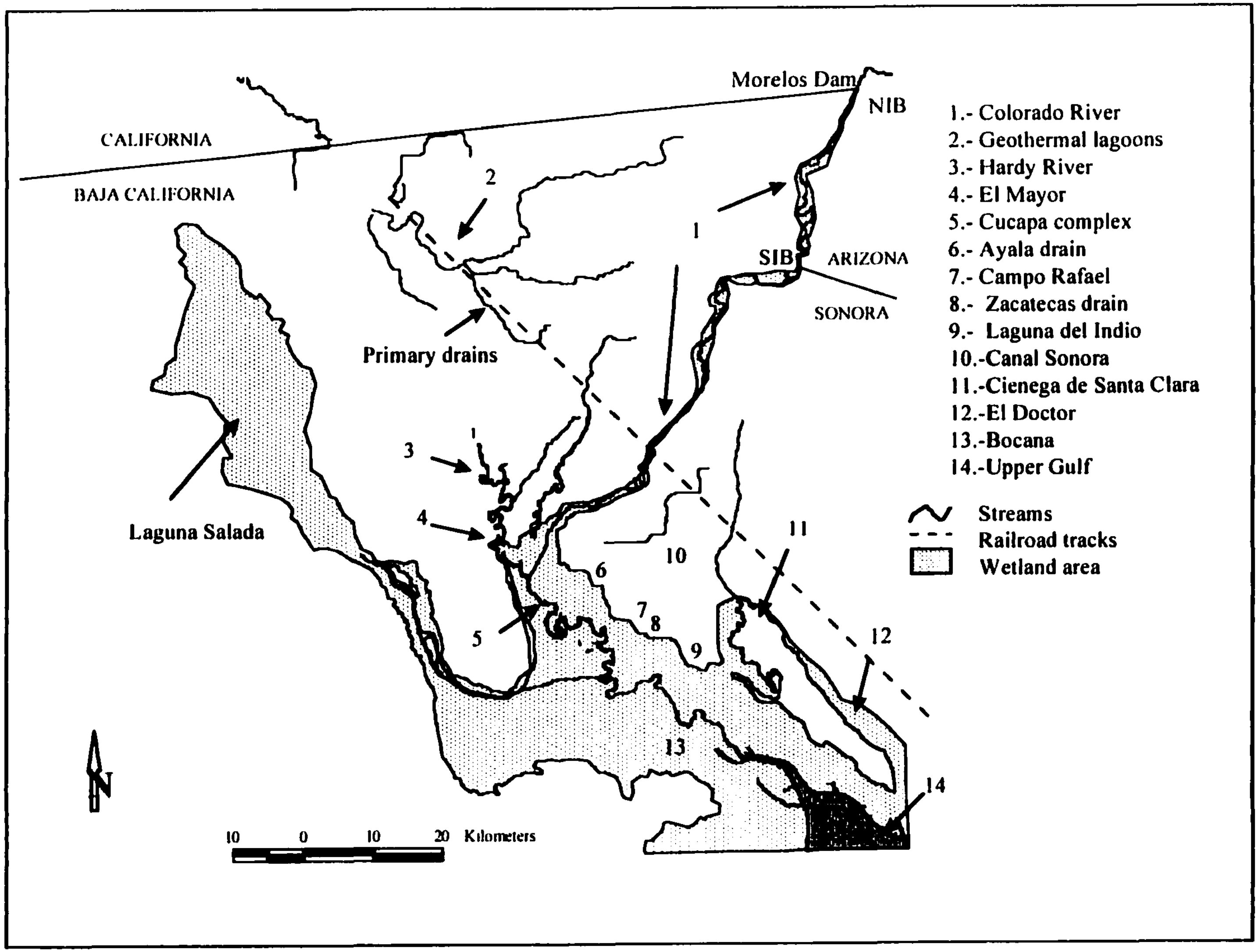
FIGURE 2. Distribution of Se concentrations in bottom material (BM) cores (< 63 μm) from 41 sampling sites in the Colorado River delta.

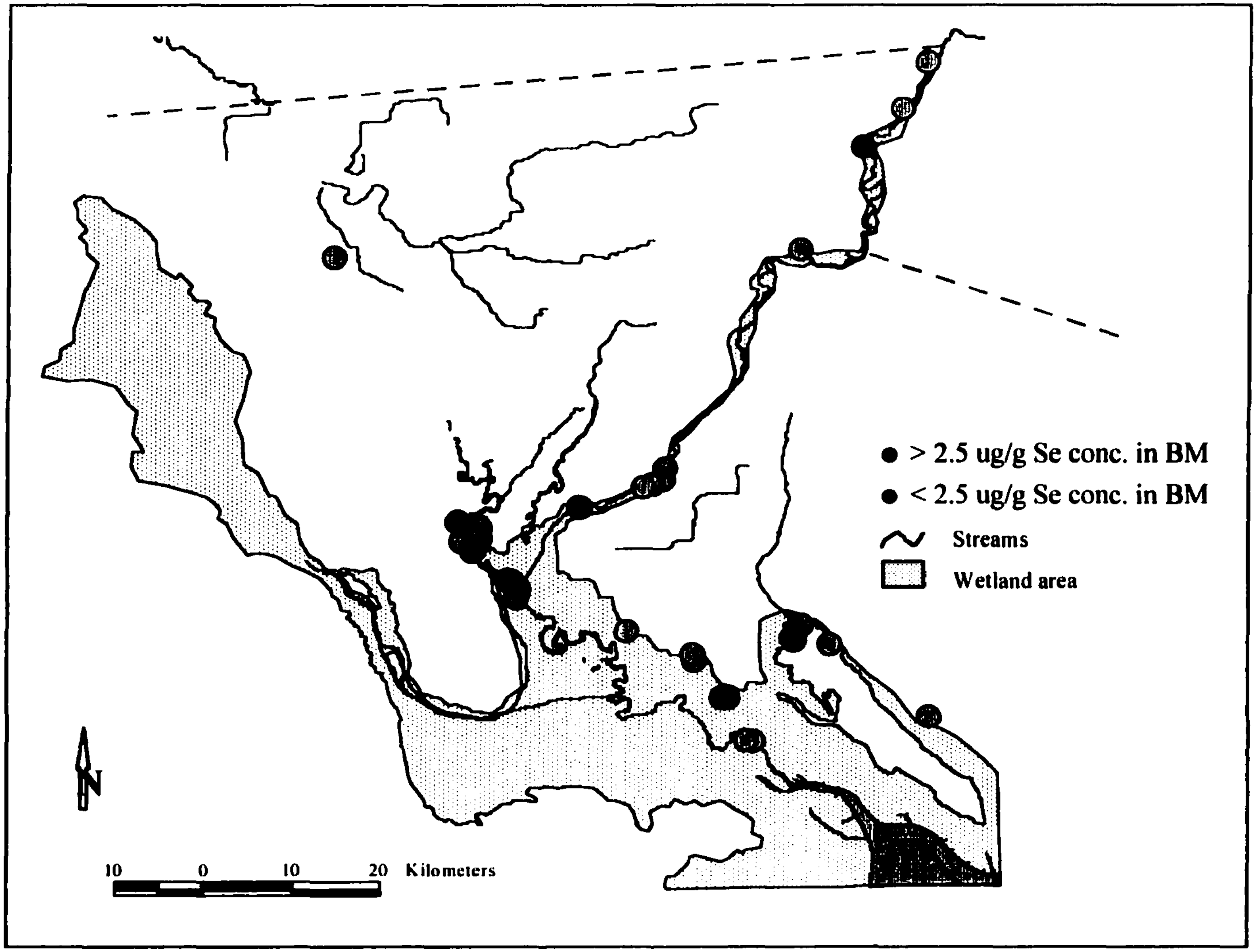
FIGURE 3. Comparison between the concentration of selenium in bottom material from sites influenced by agricultural runoff to sites influenced by Colorado River water.

FIGURE 4. Relationship between redox potential (Eh in mV) and the concentration of selenium in bottom material.

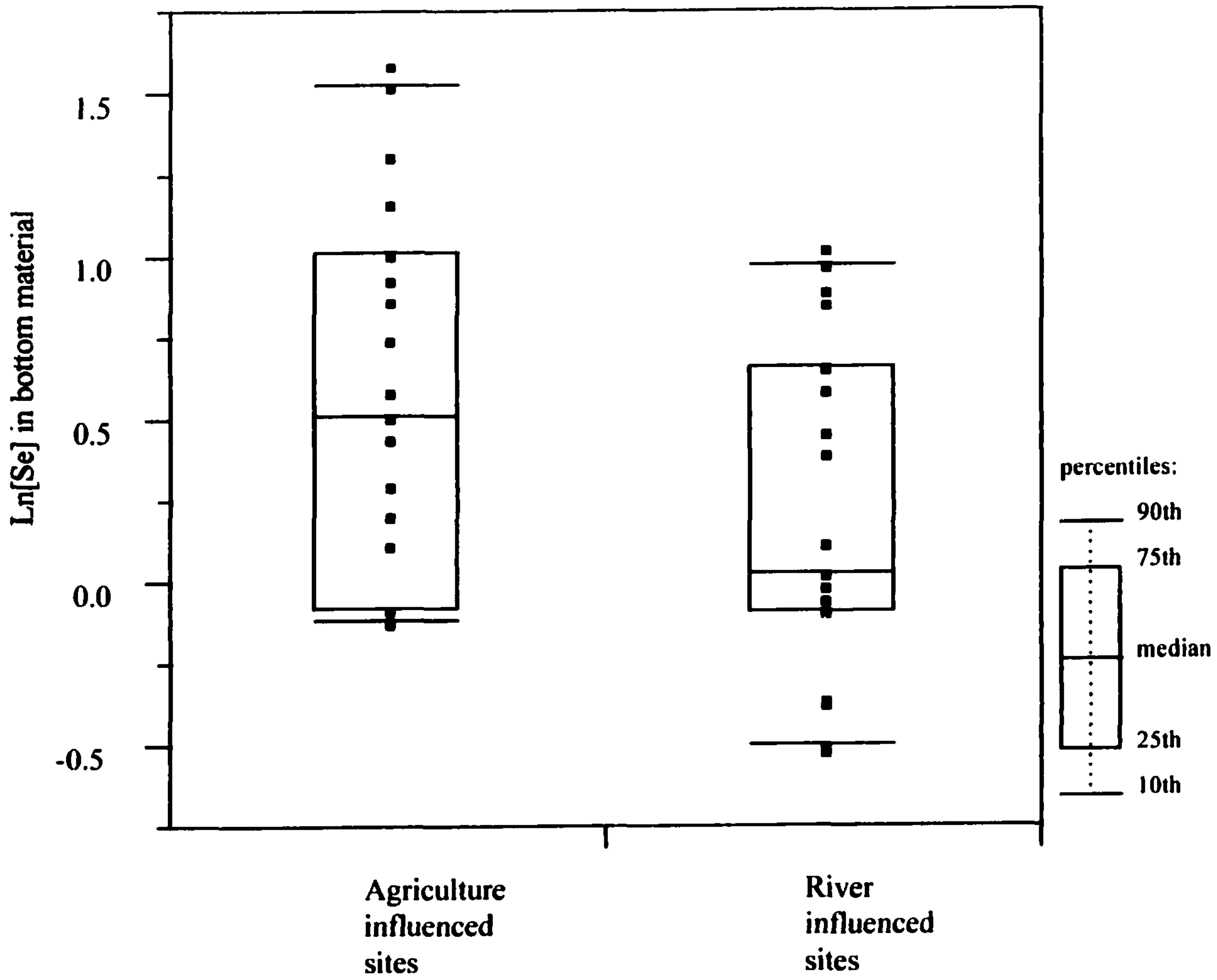
FIGURE 5. Stability diagram for selenium in natural environments. Values of pH and redox potential from each site in the Colorado River are superimposed on the diagram.

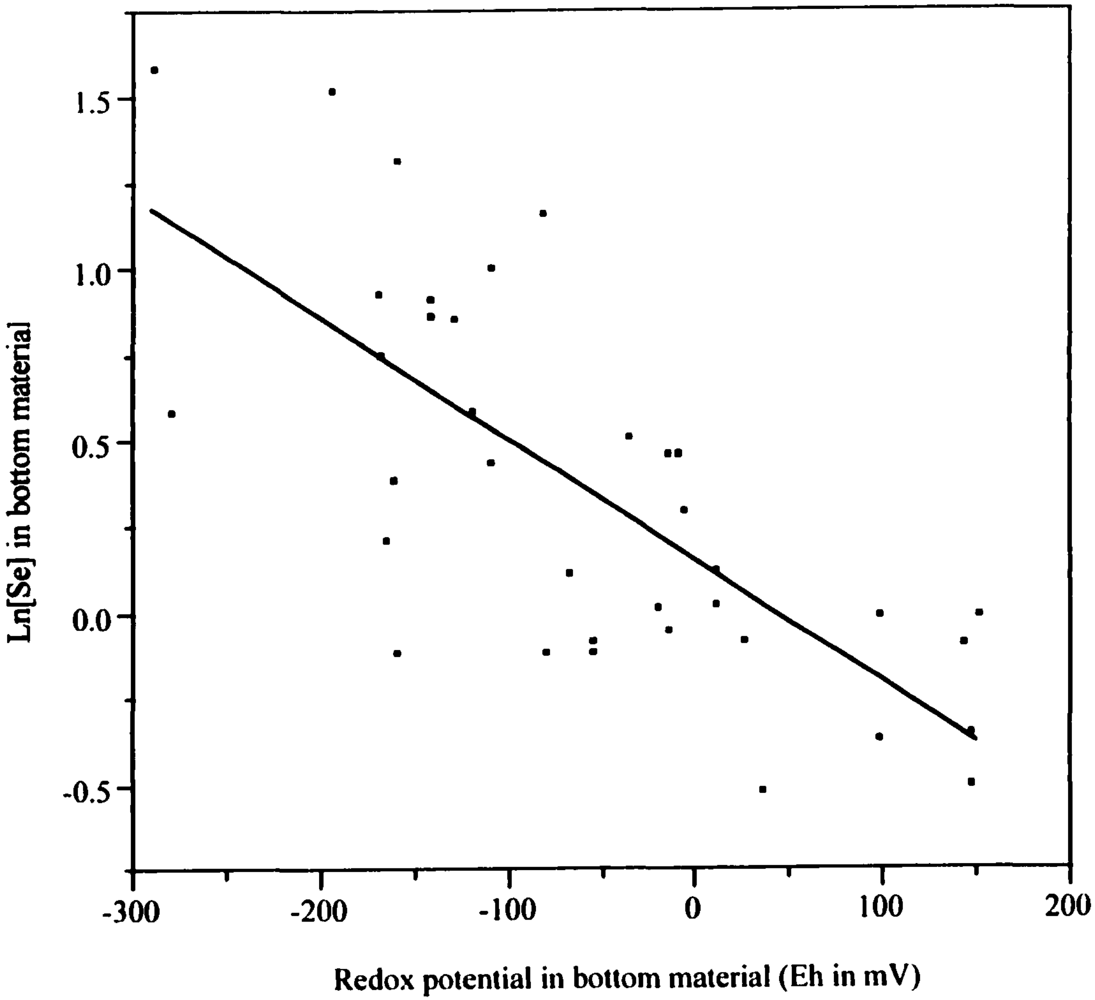
FIGURE 6. Concentrations of selenium in mosquitofish/saifin molly from sites north to Morelos Dam (King *et al.*, 2000) compared to concentrations of Se in the same species from samples collected south to Morelos Dam (this study).


Morelos Dam
NIB
CALIFORNIA
BAJA CALIFORNIA
ARIZONA
SONORA
SIB
Primary drains
Laguna Salada
1.- Colorado River
2.- Geothermal lagoons
3.- Hardy River
4.- El Mayor
5.- Cucapa complex
6.- Ayala drain
7.- Campo Rafael
8.- Zacatecas drain
9.- Laguna del Indio
10.-Canal Sonora
11.-Cienega de Santa Clara
12.-El Doctor
13.-Bocana
14.-Upper Gulf
Streams
Railroad tracks
Wetland area
N
10 0 10 20 Kilometers

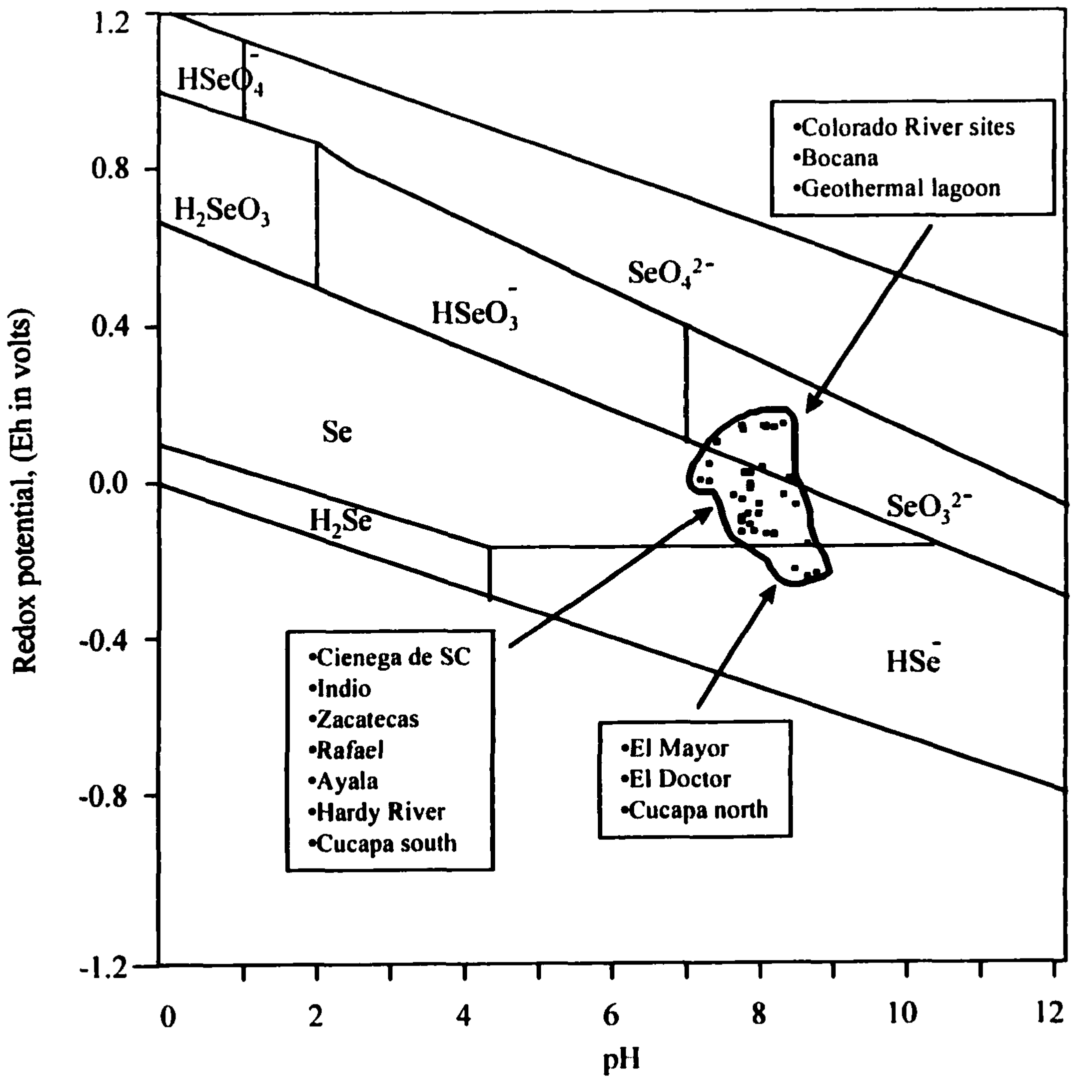


> 2.5 ug/g Se conc. in BM
< 2.5 ug/g Se conc. in BM
Streams
Wetland area
N
10 0 10 20 Kilometers

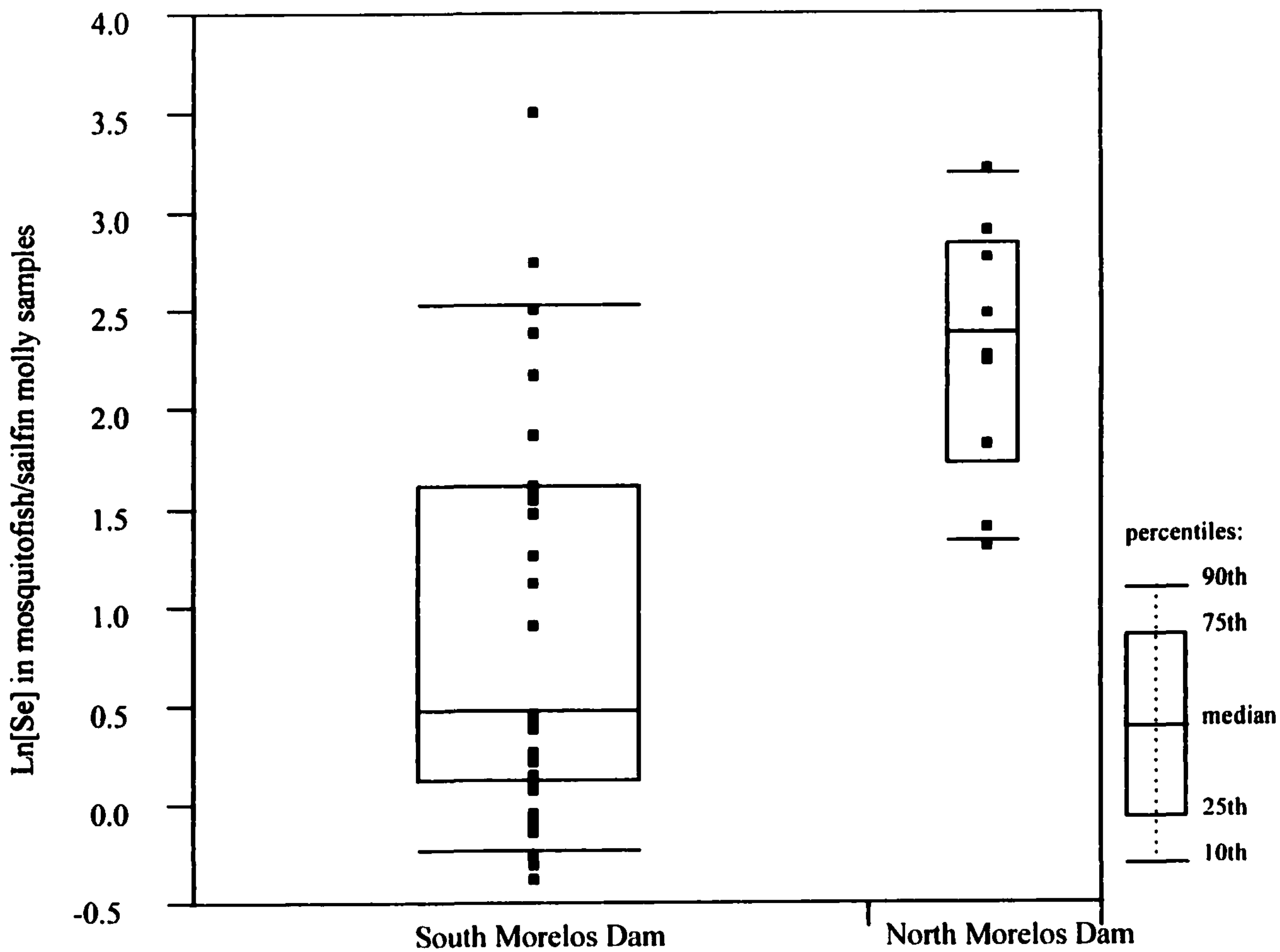

Ln[Se] in bottom material
1.5
1.0
0.5
0.0
-0.5
Agriculture influenced sites
River influenced sites
percentiles:
90th
75th
median
25th
10th



1.5
1.0
0.5
0.0
-0.5
Ln[Se] in bottom material
-300
-200
-100
0
100
200
Redox potential in bottom material (Eh in mV)



Redox potential, (Eh in volts)
pH
1.2
0.8
0.4
0.0
-0.4
-0.8
-1.2
0
2
4
6
8
10
12
$HSeO_4^-$
H_2SeO_3
$HSeO_3^-$
SeO_4^{2-}
Se
SeO_3^{2-}
H_2Se
HSe^-
•Colorado River sites
•Bocana
•Geothermal lagoon
•Cienega de SC
•Indio
•Zacatecas
•Rafael
•Ayala
•Hardy River
•Cucapa south
•El Mayor
•El Doctor
•Cucapa north



Ln[Se] in mosquitofish/sailfin molly samples
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
South Morelos Dam
North Morelos Dam
percentiles:
90th
75th
median
25th
10th

5. APPENDIX B

Willow flycatcher (*Empidonax traillii*) surveys in the Colorado River delta: implications for management

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Abstract

A subspecies of willow flycatcher, the southwestern willow flycatcher, has become endangered in the U.S. The objective of this study was to determine the presence/absence of this subspecies in the Colorado River delta. Surveys were conducted on June-July 1999 and on May-June 2000. We detected a total of 50 birds, most likely southwestern willow flycatchers, from May-June and none in July. It appears that the birds found in the delta were migrants. It is important to restore the intensively used stopover sites for the recovery of the subspecies. Additionally, we postulate a migratory route throughout the estuaries of Sonora.

Key words: Colorado River delta, Cocopah Reservation, desert pozos, migration route, riparian corridor, Sonoran estuaries, southwestern willow flycatcher, willow flycatcher

Introduction

The willow flycatcher (*Empidonax traillii*) was first described by Audubon (1831). Before 1963 willow and alder flycatcher were lumped as traill's flycatchers. However, willow was differentiated from alder flycatcher primarily on the basis of song, interpreted as "fitz-bew", but also differences were supported by other physical, behavioral, and genetic characters (Stein, 1963; Seutin & Simon, 1988; McCabe, 1991). Several taxonomists have recognized five subspecies of *E. traillii*. The southwestern willow flycatcher (*E.t. extimus*) was described by Phillips (1948) with a collection from the San Pedro River and it is differentiated from other subspecies by color (generally paler) and by wing formula (Unitt, 1987).

Neotropical migrants are defined as western hemisphere species all or part of whose populations breed north of the Tropic of Cancer and winter south of that line (DeGraaf & Rappole, 1995). Willow flycatchers of all subspecies are Neotropical migrants that breed in North America and winter from south Mexico to Panama (Peterson, 1990). The breeding range for *E.t. extimus* includes Arizona, southern California, New Mexico, southern Nevada, southern Utah, southwestern Colorado and western Texas. Although, specific wintering sites for the southwestern subspecies are currently unknown (Phillips, 1948; Sogge *et al.*, 1997).

The southwestern willow flycatcher is a riparian obligate bird restricted to dense mesic vegetation and it only breeds near surface water or saturated soil (Sogge *et al.*, 1997). However, loss of wintering habitat, loss and fragmentation of native riparian breeding habitat due to flood control, urban development, agriculture, overgrazing, fire, invasion of exotic plants, and nest predation have contributed to willow flycatcher population declines (Unitt, 1987). With only 300 to 500 breeding pairs in the U.S., *E.t. extimus* was listed as endangered in 1995 by the U.S. Fish and Wildlife Service (U.S. Fish and Wildlife Service, 1995).

Willow flycatcher breeding area formerly included the lower Colorado River and its delta. In 1902, 34 nests of willow flycatchers containing 93 eggs were collected in the Colorado River near Yuma, Arizona (Sferra *et al.*, 1997). South from Yuma, 5 specimens of southwestern willow flycatcher were collected from a breeding area 11 km east from Cerro Prieto in the Hardy River between May and June of 1928 (Unitt, 1987). This breeding area no longer exists in the delta, it has been transformed to solely agricultural lands. However, there are extensive remnant wetlands and riparian corridors that have survived or that were re-established due to agricultural runoff and pulse floods in the Colorado River delta. Approximately 1,800 ha of cottonwood (*Populus fremontii*)-willow (*Salix gooddingii*) gallery forest has regenerated in the delta. (Fig. 1) (Glenn *et al.*, 1992a; Glenn *et al.*, 1992b; Glenn *et al.*, 1996; Glenn *et al.*, 1997; Valdes-Casillas *et al.*, 1998; Glenn *et al.*, 1999). These zones create a structurally complex habitat that has been proven to support greater number of bird species and also provides additional cover from extreme summer temperatures in the lower Colorado River (Rosenberg *et al.*, 1991).

The present work reports the results of two years of casual observations and formal willow flycatcher surveys in the Colorado River delta (1999-2000, respectively) as well as the management implications and challenges that this area represents for the overall recovery of the subspecies.

Materials and Methods

Study area

The Colorado River delta (between the States of Sonora and Baja California) extends 200 km from the Northern International Boundary (NIB) south into the Gulf of California (Fig. 1). The Colorado River south from the NIB supports a riparian corridor of approximately 1,800 ha of cottonwood/willow gallery forest (Fig 1). Vegetation distribution in this river stretch is comprised of an understory of salt cedar (*Tamarix ramosissima*), seepwillow (*Baccharis salicifolia*), arrowweed (*Pluchea sericea*) and Freemont's cottonwood (*Populus fremontii*). A midstory composed by salt cedar, Goodding's willow (*Salix gooddingii*), arrowweed, common reed (*Phragmites australis*), seepwillow and Freemont's cottonwood, and an overstory dominated by Goodding's willows followed by Freemont's cottonwoods (Zamora-Arroyo *et al.*, 2001).

El Doctor *pozos*, on the eastern part of the delta, are originated and supported by desert springs or *pozos* (Ezcurra *et al.*, 1988) with salinity ranging from fresh to brackish. These *pozos* support a variety of hydrophytic plants (29 species) of which the most abundant are flat sedges (*Cyperus laevigatus*), spike rushes (*Eleocharis geniculata*) and cattails (*Typha domingensis*). Salt tolerant species such as halophytes and exotic salt cedar stands are present at the perimeters and between these *pozos* (Glenn *et al.*, 1996). The area covered by the El Doctor has been stable at 500-700 ha over the past 20 years but vegetation is continuously impacted by cattle grazing and watering of cattle (Glenn *et al.*, 1996). These impacts, however, are being controlled by the placement of exclusion fences around some of the major *pozos* by personnel of the Biosphere Reserve of the Upper Gulf of California and Colorado River Delta (J. Campoy, Areas Naturales Protegidas-SEMARNAP and M. Roman, IMADES pers. comm.) of which El Doctor forms part.

Field surveys

Our survey for willow flycatchers in the Colorado River delta started with casual observations during the spring of 1999 and formally during the spring of 2000. Casual observations were done during Yuma clapper rail surveys in the wetlands of the Cienega de Santa Clara and El Doctor on June 7-8, 1999 (Hinojosa-Huerta *et al.*, 2001). And during Rio Grande leopard frog reconnaissance along the Colorado River on June 5-6, 1999 (S. Sferra pers. com.) (Fig. 1). A follow-up extensive survey was conducted on July 6-9, 1999 on which the same sites and 20 others were visited to check for breeding activity. Sites included east and west sides of the Colorado River riparian corridor, southern stretch of the Hardy River, the Cienega de Santa Clara, and El Doctor *pozos* (Fig. 1).

Formal surveys for willow flycatchers were conducted in a stretch of riparian vegetation of approximated 30 km along the lower Colorado River within the Cocopah territory, AZ (Fig. 1). The area was visited on May 23-24, on June 6-7, and on June 26, 2000. Forty sites clustered in three major areas known as Hunter's Hole, Gadsen Pond, and Gadsen Bend (Fig. 1) were surveyed between May and June, 2000. In addition, two sites at El Doctor *pozos* in the Colorado River delta were also surveyed at the same dates. Formal surveys were performed from dawn to late morning, while birds were most active. An audio tape of southwestern willow flycatcher songs and calls was used to elicit responses from the flycatchers. Although, we did not determine subspecies, we suspect individuals detected were *E.t. extimus*, due to geographic proximity of breeding grounds. Nevertheless, individuals might also be *Empidonax traillii adastus* or *Empidonax traillii brewsteri* both of them with breeding grounds in western United States (Sogge *et al.*, 1997).

Results

Nine willow flycatchers were identified at two sites in the Colorado River delta during June 5-8, 1999; six at El Doctor *pozos* and three at the Colorado River mainstream south from the railroad bridge at a site called Colorado II. These results are summarized in Table 1. Willow flycatchers at El Doctor were located vocalizing in a salt cedar stand near the main *pozo*. The three willow flycatchers observed in the Colorado II site were seen near a dense cottonwood/willow forest. No willow flycatchers were detected during the extensive follow-up survey of July 6-9, 1999 (Table 1).

During the formal surveys from May to June, 2000, a total of 41 willow flycatchers were identified at the sites visited in the Colorado River delta (Table 1 and Figure 1), 26 were at the riparian corridor between the NIB and the SIB, on the U.S. side of the border. This included 15 birds at Hunter's hole, eight at Gadsen Pond, and three at Gadsen Bend. The latest these birds were detected in the area was mid June and they were not seen breeding.

Fifteen individuals were detected at El Doctor *pozos* including 13 individuals on May 22 in a small stretch of *pozos* named "El Mirador", and on June 6, two birds were detected, in the main *pozo*. Insects were exceptionally abundant in El Doctor compared with other areas in the delta. No birds were detected on June 26 at this location (Table 1).

Large groups of the parasitic brown headed cowbird (*Molothrus ather*) were detected at all sites during the 1999 and 2000 surveys.

During their migration through the riparian corridor of the Colorado River between the NIB and SIB, the majority of willow flycatchers (70 % or 18 birds) preferred native broadleaf dominated areas near standing water. Backwaters from the river were present at the boundaries of the vegetation where mosquitoes and other insects were seen near the water surface in all our three visits. Water temperature from the backwater remained at 26 °C and specific electrical conductance (SpEC) remained constant at 3.5 mS/cm (approx. 2,200 ppm salinity) from May to the end of June, 2000.

The rest of the southwestern willow flycatchers (30% or eight birds) were found in fragmented patches of native (Goodding's willows) and exotic (salt cedar) vegetation found adjacent to the river. No backwaters were present in these areas, although soils were saturated at sites where willow flycatchers were present.

No willow flycatchers were detected in any of the surveys in segmented and narrow linear habitat types dominated by exotics (salt cedar). Nor they were in native broadleaf vegetation along the mainstream of the river where the currents are relatively fast and insects not as abundant as they were at the backwaters.

Discussion

A total of 50 willow flycatchers, most likely southwestern willow flycatchers, were detected in the Colorado River delta.

Arizona Partners in Flight, an interagency program dedicated to conserve native land birds, has reported in their surveys, an annual mean of 37 willow flycatchers from

1993 to 1999 along the 30 km stretch of river between the NIB and the SIB. Of these, a mean of 16 were detected at Hunter's hole, eight at Gadsen Pond and 12 at Gadsen Bend (Muiznieks *et al.*, 1994; Sferra *et al.*, 1995; Spencer *et al.*, 1996; Sferra *et al.*, 1997; Paradzick *et al.*, 1999; Paradzick *et al.*, 2000). A similar number of birds were found at these three locations for the 2000 survey.

Results from our surveys along the Colorado River delta suggests that the willow flycatchers no longer breed in the area. However, the remnant habitats of riparian corridors and desert *pozos* are used intensively during their spring migration between the months of May and June. Willow flycatchers appear to prefer areas where backwaters are present and insects are abundant because one of the major priorities of migrants is to restore their depleted energy storage in order to continue their flight (Petit, 2000).

Willow flycatcher surveys (1998, 1999) by Arizona Partners in Flight, show that the sites with the largest number of migrant birds occurred in the lower Colorado River (86% of the total migratory birds were detected in the lower Colorado River, Yuma County) (Paradzick *et al.*, 1999; Paradzick *et al.*, 2000). It is possible, then, that the Colorado River delta acts as a passage for the majority of migratory birds on their spring migration. This information further justifies the importance of the Colorado River delta riparian areas and its urgent restoration to help in the recovery of the southwestern willow flycatcher.

Wetland and riparian management and restoration efforts in the Colorado River delta, both in Mexico and in the U. S., would be greatly rewarded if a series of permanent backwaters are created along the Colorado River. This habitat type will probably be attractive for the migrants and if sufficient area is restored, they could even return to their historic nesting grounds. However, backwaters will need to be closely monitored for selenium and pesticide concentrations in order to prevent any adverse effect on wildlife (García-Hernández *et al.*, 2000). Selenium is a naturally occurring contaminant, widely distributed along the lower Colorado River (Radtke *et al.*, 1988) and known for its toxic effects on wildlife (Ohlendorf *et al.*, 1986). Nevertheless, the rate of selenium uptake by the food chain in the created backwaters, could be minimized by the use of a mix of Colorado River water and agricultural runoff, a continuos outflow, and restraint of dredging activities in these areas (García-Hernández *et al.*, 2001).

El Doctor *pozos* seem to be a very important stopover site for the willow flycatchers. Six to 15 birds were detected in only 1 km of *pozos*, but it is possible that the complete area of 500-700 km could be used as a stopover site. Physical barriers such as the Gran Desierto on the east and southeast and the ocean on the west make this area particularly important for migratory birds. Isolated stopover areas have been recognized in the population dynamics of shorebirds, waterfowl, and rails (Petit, 2000). A thorough willow flycatcher survey at the El Doctor needs to be conducted to support this idea. Immediate actions such as exclusion fences around some of these *pozos* are already helping these areas and their migratory visitors.

This study confirms that willow flycatchers use El Doctor *pozos* and the Colorado River riparian corridors as a migratory route. However, a complete migratory pattern for the willow flycatcher, and specifically for the southwestern willow flycatcher, is largely unknown (Sferra *et al.*, 1997) despite their influence in the nesting success of the subspecies (Petit, 2000).

It is proposed that a possible willow flycatcher summer migratory route, could be traced throughout the series of coastal estuaries found adjacent to the coast of Sonora (Fig. 2). There are previous records of willow flycatchers found along the coastal estuaries of Bahia Adair, Estero Sargento, Estero Santa Rosa and Estero la Cruz (Russell & Monson, 1998). Thirty three birds from the Isla Tiburon area were captured on May 1970 using a mist net (Russell & Monson, 1998). There are 20 wetlands along the Sonoran coast with an approximate 173,000 ha of halophytes and mangroves (Cervantes, 1994). Although, these areas have different a vegetation composition to their summer and wintering habitats, many long-distance migratory species are capable of using a wide variety of habitat types during their migration (Petit, 2000). The most important factors for the distribution of birds among habitat types during migration are: (1) food abundance or effectiveness in exploiting the food base, (2) competition with other species, (3) predation pressure or relative safety from predators, and (4) productive opportunities (Petit, 2000). The proposed migratory route could provide enough food and protection from predators for migrants.

It is evident that more surveys are needed in the Colorado River delta and along the coast of Sonora. Nevertheless, we encourage continued binational cooperation between institutions from Mexico and the U.S. to protect the breeding areas and migratory routes of the southwestern willow flycatcher.

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Table 1. Site name, location, date surveyed, and number of willow flycatchers detected during the 1999-2000 surveys in the Colorado River delta.

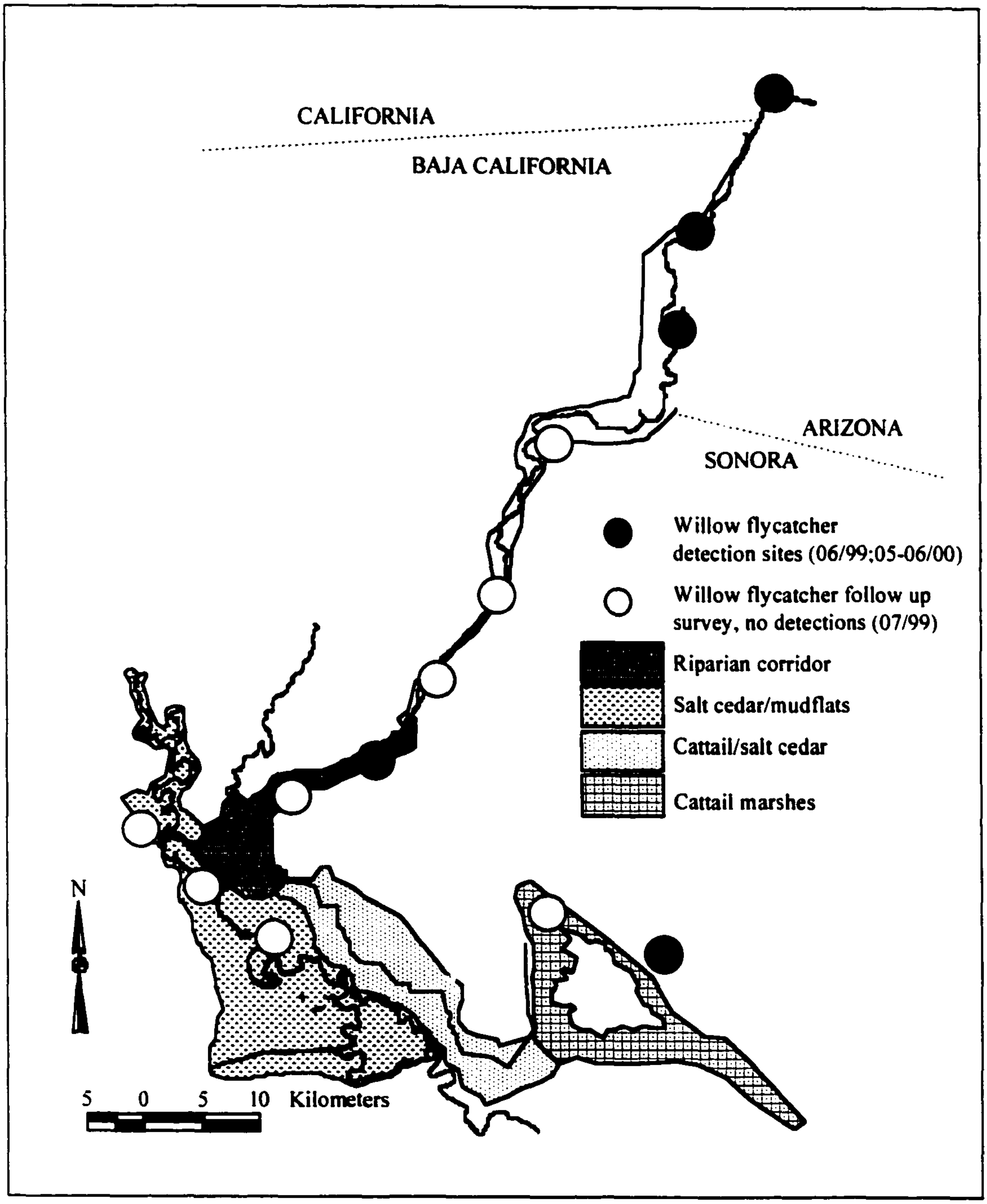
Site name	Latitude	Longitude	Date surveyed	No. of willow flycatchers
Gadsen Bend (12 sites)	32°44'24"	114°41'24"	May 23-24, 2000	1
			June 6-7, 2000	2
			June 26, 2000	0
Gadsen Pond (19 sites)	32°36'36"	114°48'36"	May 23-24, 2000	2
			June 6-7, 2000	6
			June 26, 2000	0
Hunter's Hole (10 sites)	32°34'12"	114°42'00"	May 23-24, 2000	11
			June 6-7, 2000	4
			June 26, 2000	0
North railroad crossing (4 sites)	32°18'00"	113° 00' 25"	July 6-9, 1999	0
Vado Carranza (2 sites)	31°11'55"	115°09'22"	July 6-9, 1999	0
Colorado II (2 sites)	32°10'09"	115°10'47"	June 5-6, 1999	3
			July 6-9, 1999	0
Cucapa Complex (9 sites)	32°06'16"	115°14'22"	July 6-9, 1999	0
Cienega de Santa Clara (2 sites)	32°03'19"	114°54'27"	June 7-8, 1999	0
			July 6-9, 1999	0

			June 6-7, 2000	0
El Doctor (2 sites)	31°56'51"	114°44'51"	June 6-7, 1999	6
			July 6-9, 1999	0
			May 23-24, 2000	13
			June 6-7, 2000	2
			June 26, 2000	0
				TOTAL = 50

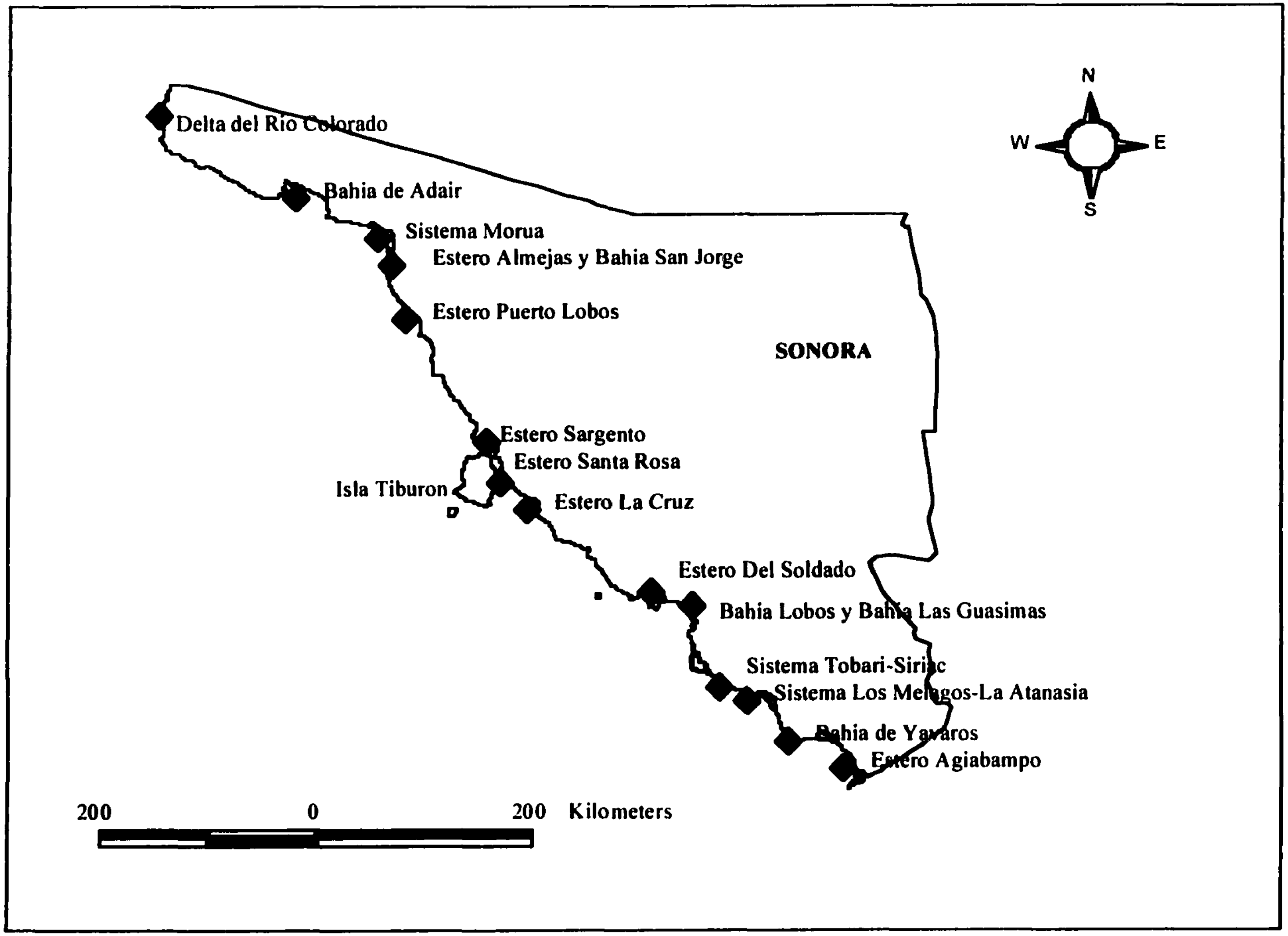
Figure Captions

FIGURE 1. Colorado River delta with its different ecosystems. Locations where willow flycatchers were detected are shown with gray circles, and follow up survey sites with no willow flycatcher detection, are indicated with white circles.

FIGURE 2. Map of the Sonoran coastal estuaries (Cervantes, 1994)



CALIFORNIA
BAJA CALIFORNIA
ARIZONA
SONORA
Willow flycatcher detection sites (06/99;05-06/00)
Willow flycatcher follow up survey, no detections (07/99)
Riparian corridor
Salt cedar/mudflats
Cattail/salt cedar
Cattail marshes
N
5 0 5 10 Kilometers


N
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Delta del Rio Colorado
Bahia de Adair
Sistema Morua
Estero Almejas y Bahia San Jorge
Estero Puerto Lobos
SONORA
Estero Sargento
Estero Santa Rosa
Isla Tiburon
Estero La Cruz
Estero Del Soldado
Bahia Lobos y Bahia Las Guasimas
Sistema Tobari-Siriac
Sistema Los Melagos-La Atanasia
Bahia de Yavaros
Estero Agiabampo
200 0 200 Kilometers