Journal of Arid Environments (2001) **49**: 65–89
doi:10.1006/jare.2001.0836, available online at http://www.idealibrary.com on IDEAL®

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

Jaqueline García-Hernández*, Kirke A. King†, Anthony L. Velasco†, Evgueni Shumilin‡, Miguel A. Mora§ & Edward P. Glenn*

**Environmental Research Laboratory, University of Arizona, 2601 E. Airport Drive Tucson Arizona, 85706-6985, U.S.A.*
†U.S. Fish and Wildlife Service, Arizona Ecological Services Field Office, 2321 W. Royal Palm Road, Suite 103 Phoenix, Arizona 85021, U.S.A.
‡Centro Interdisciplinario de Ciencias Marinas, Av. IPN, s/n, Col. Playa Palo de Sta. Rita, A.P. 592, La Paz, B.C.S. 23096, Mexico
§U.S. Geological Survey, Department of Wildlife and Fisheries Sciences, Texas A&M University, 2258 TAMU, College Station, Texas 77843-2258, U.S.A.

Concentrations of selenium (Se) in bottom material ranged from 0·6 to 5·0 μg g^{-1}, and from 0·5 to 18·3 μg g^{-1} in biota; 23% of samples 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.

Keywords: 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 $year^{-1}$ (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 $1{\cdot}8 \times 10^9$ m^3 $year^{-1}$ 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 $63{\cdot}3 \times 10^6$ m^3 and have created the

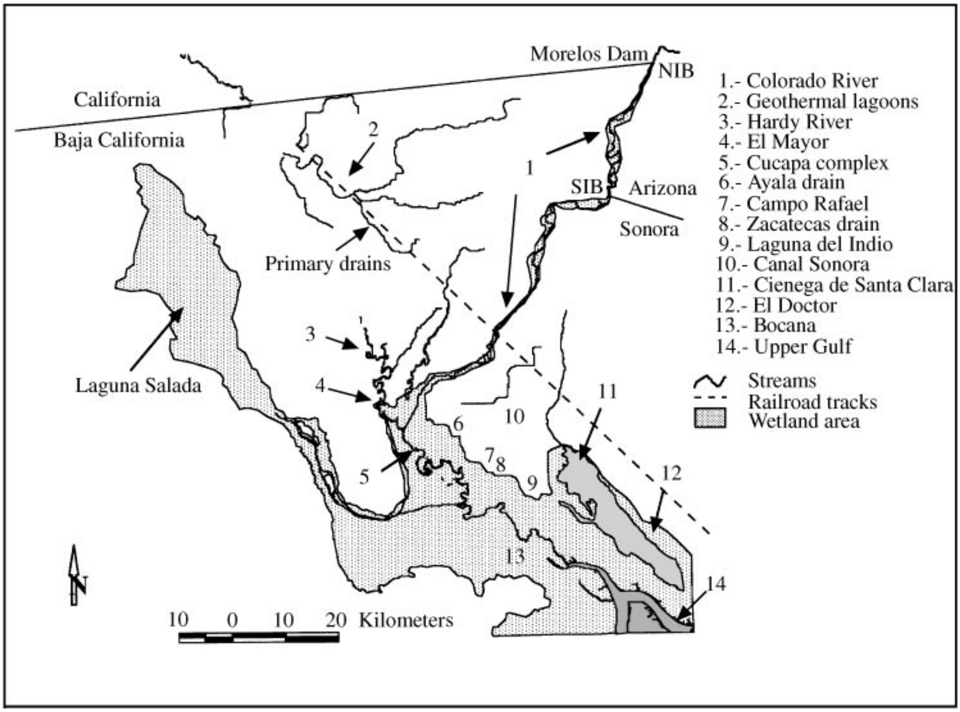

Figure 1. Colorado River delta ecosystems. Sampling locations are indicated with numbers.

Hardy River-Cucapa wetlands complex (Fig. 1). Occasional flood releases into the delta (as much as $16 \times 10^9\,m^3\,yr^{-1}$) 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 14,000-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 1300 $\mu g\,l^{-1}$ 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, 1989; Lemly, 1993*a*). 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, 1994, 1997, 2000; Lusk, 1993; Martinez, 1994; Welsh & Maughan, 1994; Mora & Anderson, 1995; King & Baker, 1995; García-Hernández *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 $3000\ \mathrm{mg\,l^{-1}}$, and carries a yearly mean of 70×10^6 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 were 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 was to analyse 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).

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).

Hardy river

This is a reservoir of agricultural runoff from the Mexicali Valley (Fig. 1). Mean dissolved-solids content is $7000\ \mathrm{mg\,l^{-1}}$ (García-Hernández, unpublished data) and vegetation is dominated by salt cedar.

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 water surface of which 4500 ha are thickly vegetated. The marsh is dominated by cattail (*Typha domingensis*) (Glenn *et al.*, 1996).

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 3000 mg l^{-1} which allows for a great diversity of plants (Glenn *et al.*, 1996).

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), nine soil samples, and 34 discrete water samples were collected from 12 locations in the delta in 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 in the field. Bottom 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. All samples were analysed for selenium, 24 of the samples were analysed 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 h, and ground. Prepared samples were analysed 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 h 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 analysed at the Research Triangle Institute, RTI by Graphite Furnace Atomic Absorption (GFAA). Detection limit for selenium in bottom material samples using either method was $0{\cdot}5\ \mu g\ g^{-1}$.

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 analysed by graphite furnace and by cold vapor atomic absorption, respectively. Additional biota samples were analysed at the SWPAL for selenium by graphite furnace atomic absorption. Animal tissue was analysed 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 analysed 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 analysed 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 analysed 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

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

Table 1—*Continued.*

		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

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 $\mu g\, g^{-1}$, and the 90% confidence interval of the mean was between 0·7 and 3·1 $\mu g\, g^{-1}$.

The baseline selenium concentration for western soils is estimated to be < 1·4 $\mu g\, g^{-1}$ 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 $\mu g\, g^{-1}$. Adverse effects are always observed at concentrations greater than 4·0 $\mu g\, g^{-1}$ (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 $\mu g\, g^{-1}$) was lower than the EC10 threshold (one sided p-value < 0·0001 from one-sample t-test, $t = 5{\cdot}8$ 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 $\mu g\, g^{-1}$) was below the EC10 (one sided p-value = 0·001 from one-sample t-test, $t = 4{\cdot}1$ 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, $t = 1{\cdot}6$, df. = 16) nor from El Indio location (one-sided p-value = 0·6 from two-sample t-test, $t = 0{\cdot}3$, df. = 1). The mouth of the river site (Bocana) did have a difference between soil and bottom material samples (one-sided p-value = 0·006 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 $F_{11,29} = 1{\cdot}73$; p-value = 0·11).

Table 2. *Geometric mean and range or individual concentrations of selenium (μg g^{-1} 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 (mV)	pH	Clay (%)	Silt (%)	Sand (%)	OC (%)
		Mean	Range							
*EC10 threshold**		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)							

*EC10 threshold = threshold where sedimentary selenium can cause adverse biological effects in 10% of exposed fish and birds (USDOI, 1998), values in bold exceed this threshold.
[2] ND = no data

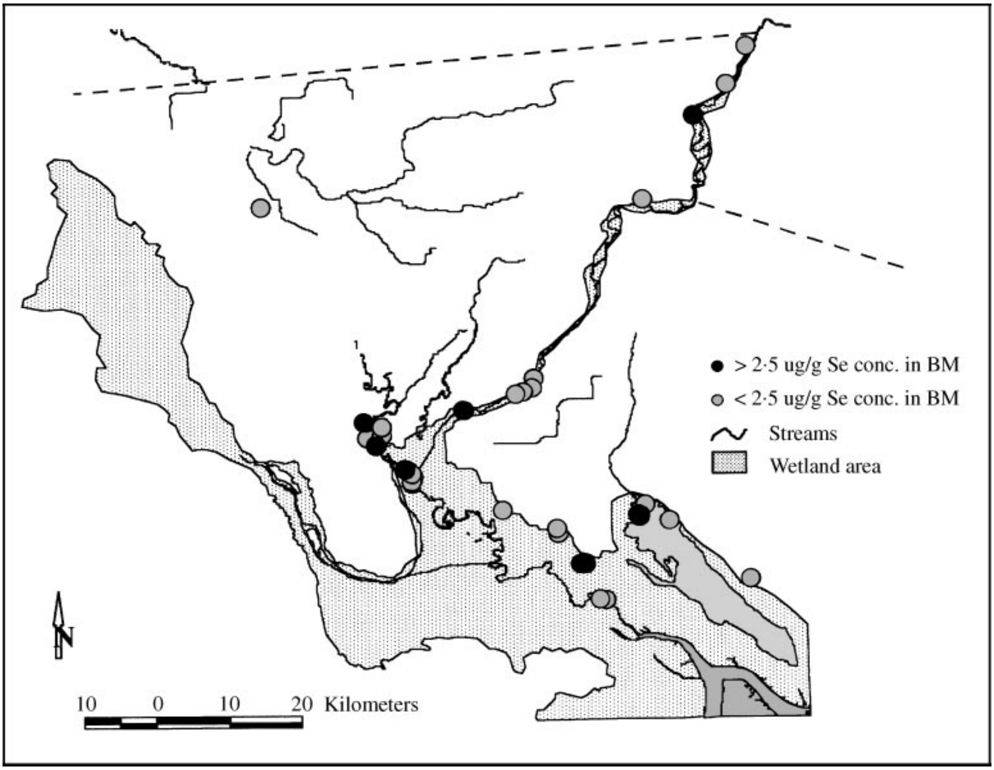

Figure 2. Distribution of Se concentrations in bottom material (BM) cores (< 63 μm) from 41 sampling sites in the Colorado River delta.

For comparisons, we grouped the sites according to their principal source of water, which was: (1) Agricultural runoff: Cienega de Santa Clara, El Indio, Zacatecas drain, Campo Rafael, Ayala drain, El Mayor, Hardy River and Cucapa north; (2) Colorado River water: Colorado River, Bocana and Cucapa south; and (3) 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 $< 0{\cdot}001$ from one-sample z-test, $z = 4{\cdot}8$, df. = 20) or agricultural drains (one-sided p-value $< 0{\cdot}001$ from one-sample z-test, $z = 5{\cdot}6$, df. = 23). Concentration of selenium in bottom material was greater at sites influenced by agricultural drainage ($n = 20$, geom. mean = 1·8 μg g^{-1}) than at sites influenced by river water ($n = 19$, geom. mean = 1·3 μg g^{-1}) (Fig. 3) (one-sided p-value = 0·03 from two-sample t-test, $t = 2{\cdot}1$, 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 $< 0{\cdot}0001$ from two-sample t-test, $t = 5{\cdot}2$, 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 ($R^2 = 0{\cdot}53$, $F_{1,34} = 39{\cdot}5$; p-value $< 0{\cdot}0001$ from a simple linear regression).

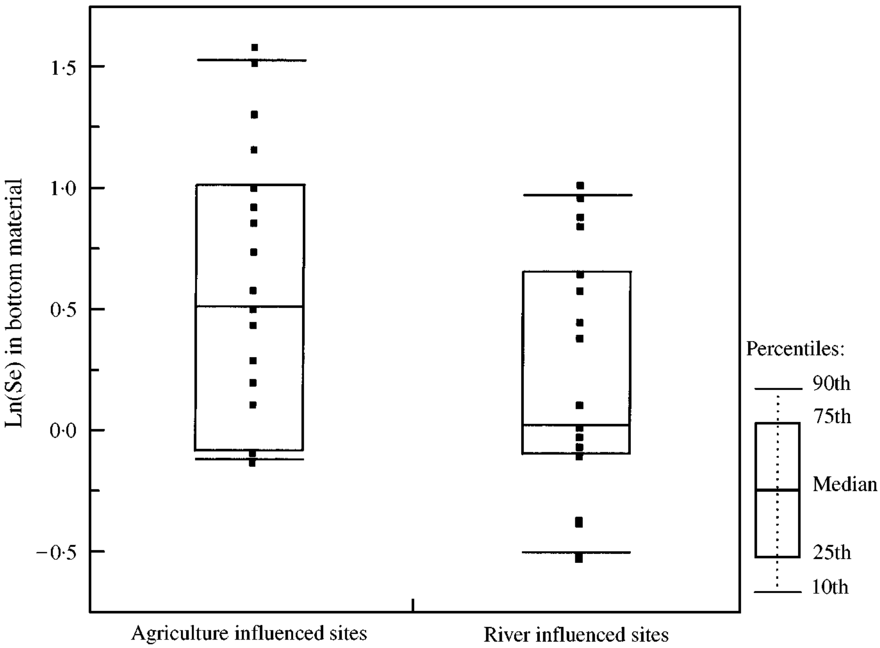

Figure 3. Comparison between the concentration of selenium in bottom material from sites influenced by agricultural runoff to sites influenced by Colorado River water.

Water pH was higher (more basic) at sites influenced by agricultural drains ($n = 20$, mean $= 8{\cdot}4$) than at sites influenced by river waters ($n = 19$, mean $= 8{\cdot}1$) (one-sided p-value $< 0{\cdot}002$ from two-sample t-test, $t = 3{\cdot}3$, 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 ($F_{1,36} = 8{\cdot}3$; p-value $= 0{\cdot}006$ 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 ($F_{1,38} = 5{\cdot}6$; p-value $= 0{\cdot}02$ from a simple linear regression) and silt content of the sample ($F_{1,38} = 4{\cdot}4$; p-value $= 0{\cdot}04$ from a simple linear regression). Selenium decreased with the sand content of the sample ($F_{1,38} = 6{\cdot}1$; p-value $= 0{\cdot}02$ 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 $= 0{\cdot}001$ from two-sample t-test, $t = 3{\cdot}6$, 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 $< 0{\cdot}0001$ from two-sample t-test, $t = 5{\cdot}0$, 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 $< 0{\cdot}0001$ from two-sample t-test, $t = 5{\cdot}0$, 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 ($F_{1,38} = 6{\cdot}5$; p-value $= 0{\cdot}01$ from a simple linear regression). More organic carbon was detected in bottom material from agriculture runoff sites ($n = 20$, mean $= 1{\cdot}3\%$) than from bottom material from river sites ($n = 19$, mean $= 0{\cdot}5\%$) (one-sided p-value $= 0{\cdot}0002$ from two-sample t-test, $t = 4{\cdot}2$, df. $= 37$).

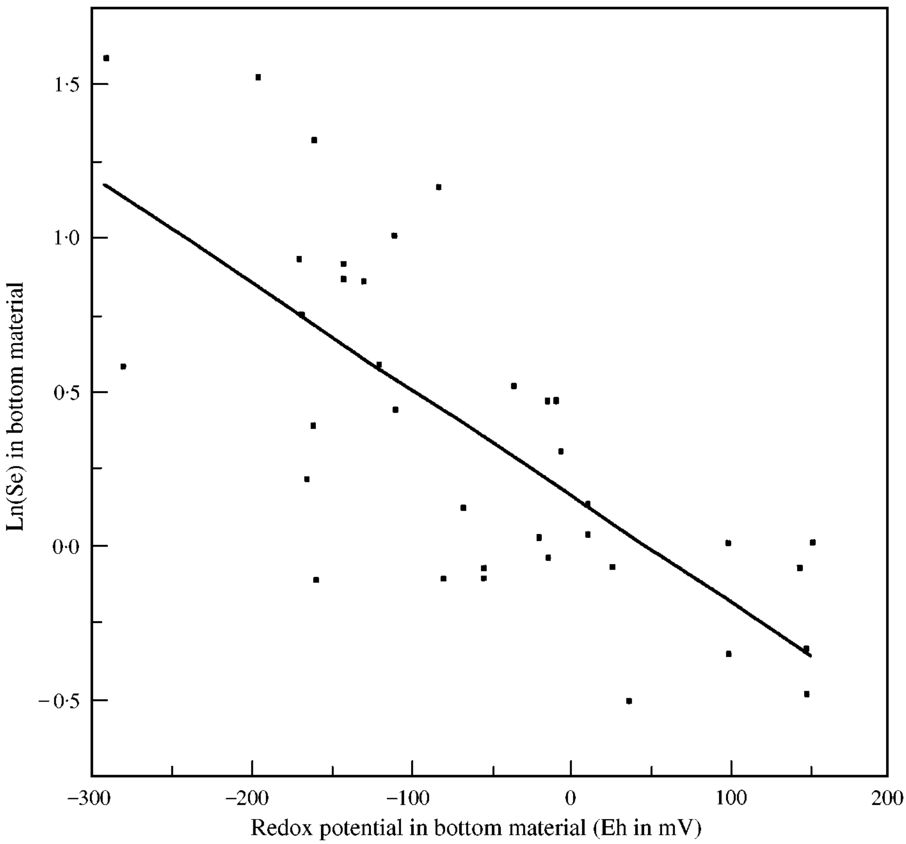

Figure 4. Relationship between redox potential (Eh in mV) and the concentration of selenium in bottom material.

Dissolved solids concentrations in water correlated positively with selenium concentration in bottom material ($F_{1,32} = 4{\cdot}6$; p-value $= 0{\cdot}04$ 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 $= 4{\cdot}4$ g l^{-1}) than with river water influence ($n = 16$ mean $= 1{\cdot}8$) (one-sided p-value $< 0{\cdot}0001$ from two-sample t-test, $t = 5{\cdot}2$, 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 $= 0{\cdot}54$), water temperature (p-value $= 0{\cdot}71$), dissolved oxygen (p-value $= 0{\cdot}23$), redox potential in water (p-value $= 0{\cdot}50$), bottom material water content (p-value $= 0{\cdot}14$), free iron oxide content (p-value $= 0{\cdot}97$), water ANC (p-value $= 0{\cdot}53$), or specific electrical conductance (p-value $= 0{\cdot}06$).

Selenium in biota

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

Table 3. *Arithmetic mean or individual concentration of selenium in biota composite samples from the Colorado River delta (μg g^{-1} dry weight)*

Site name	Sample type	N	Selenium conc.	S.D.[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]S.D. = 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, 1993*b*), values above the threshold are shown in bold.

3 μg g^{-1} dry wt. Se concentration (Lemly, 1993*b*; 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^{-1}) was lower than this guideline (one-sided p-value $< 0{\cdot}0001$ from one-sample t-test, $t = 5{\cdot}7$, df. = 97).

The toxicity threshold for nonbreeding birds exposed to winter-stress has been observed to be > 10 μg g^{-1} 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^{-1} 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^{-1} 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^{-1} and the 90% confidence interval was 0·8–12·7 μg g^{-1}. The largest concentration of selenium in sailfin molly/mosquitofish samples was from El Mayor ($n = 2$, geom. mean = 9·4 μg g^{-1}), followed by the Colorado River site ($n = 2$, geom. mean = 6·02 μg g^{-1}), the Hardy River ($n = 1$, conc. = 5·2 μg g^{-1}), the Cienega de Santa Clara ($n = 13$, geom. mean = 3·2 μg g^{-1}), Cucapa complex ($n = 1$, conc. = 1·5 μg g^{-1}), El Doctor ($n = 9$, geom. mean = 1·2 μg g^{-1}), and Bocana ($n = 1$, conc. = 0·9 μg g^{-1}).

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 ($F_{1,27} = 2{\cdot}2$, 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, 1987; Franson, 1996; Furness, 1996; USDI, 1998), concentrations of these elements are shown in Table 4. Cadmium concentration in fish and invert

Table 4. *Arithmetic mean or individual concentration of selected inorganic elements in fish and invertebrate composite samples from the Colorado River delta ($\mu g\, g^{-1}$, 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.

ebrates collected from the Colorado River delta ranged from $< 0{\cdot}19\ \mu g\ g^{-1}$ (detection limit) to $0{\cdot}8\ \mu g\ g^{-1}$ dry wt. According to Eisler (1985) the potential toxic threshold for birds is about $0{\cdot}4\ \mu g\ g^{-1}$. One sample of marine clams from the Upper Gulf had two times this level, and three other samples had a Cd concentration equal to $0{\cdot}4\ \mu g\ g^{-1}$ (Table 4). Nevertheless, according to laboratory tests, a bird dietary intake of less than $1\ \mu g\ g^{-1}$ 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 $< 0{\cdot}04$ to $1{\cdot}29\ \mu g\ g^{-1}$. To protect sensitive species of birds that regularly consume fish and other aquatic organisms, total mercury concentrations in these food items should not exceed $0{\cdot}1\ \mu g\ g^{-1}$ wet weight, equivalent to approximately $0{\cdot}3\ \mu g\ g^{-1}$ 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 ($1{\cdot}29\ \mu g\ g^{-1}$) and from a mosquitofish sample from El Doctor ($1{\cdot}23\ \mu g\ g^{-1}$) (Table 4). Nevertheless, other studies have determined that the potential toxic threshold for the protection of fish and predatory organisms is $1{\cdot}6\ \mu g\ g^{-1}$ (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 analysed, 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 $< 0{\cdot}01\ \mu g\ g^{-1}$ to $0{\cdot}34\ \mu g\ g^{-1}$ 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 $1{\cdot}0\ \mu g\ g^{-1}$ 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 $0{\cdot}15\ \mu g\ g^{-1}$ 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 $< 0{\cdot}01\ \mu g\ g^{-1}$ to $0{\cdot}13\ \mu g\ g^{-1}$ 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, 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).

Table 5. *Arithmetic mean or individual concentration of DDD, DDE and DDT in fish and invertebrate composite samples from the Colorado River delta* ($\mu g^{-1} g$ *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	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	Salifin 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

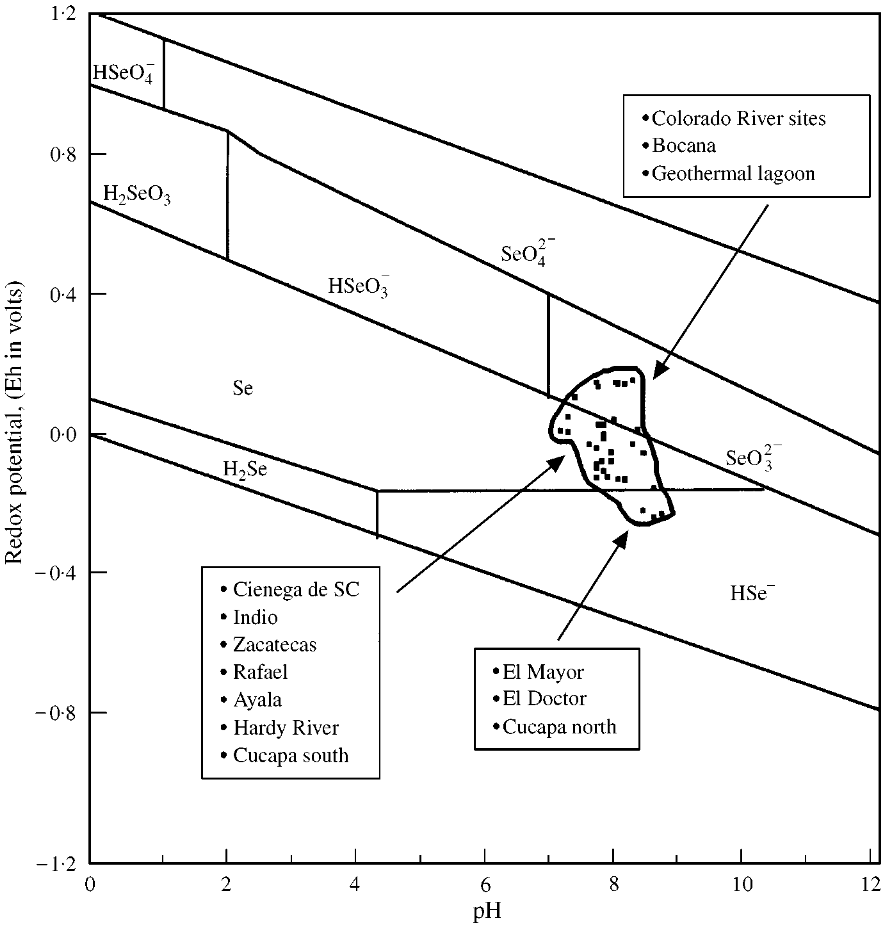

Figure 5. Stability diagram for selenium in natural environments. Values of pH and redox potential from each site in the Colorado River are superimposed on the diagram.

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 ($6 \times$ 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, pers. comm.).

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, $t = 3{\cdot}3$, 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

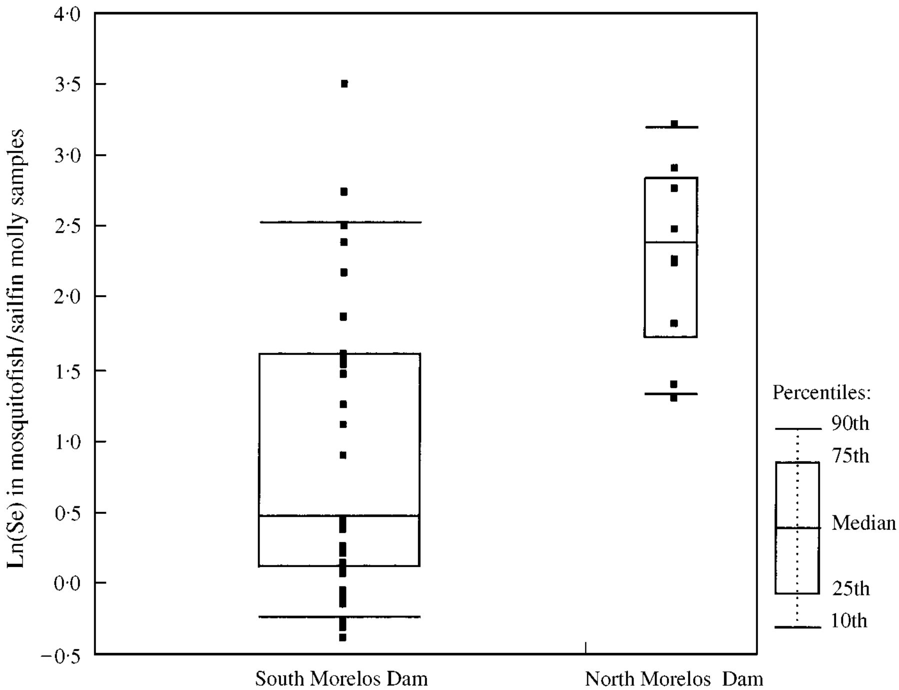

Figure 6. Concentrations of selenium in mosquitofish/saifin molly from sites north to Morelos Dam (King *et al.*, 2000) compared to concentrations of Se in the same species from samples collected south to Morelos Dam (this study).

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.

This research was funded in part by the North American Wetland Conservation Council (NAWCC), the Wallace Foundation for Latin American Students, The University of Arizona Graduate Student Final Project Fund, and by a fellowship from CONACYT (Consejo Nacional de Ciencia y Tecnología). We thank the Instituto Nacional de Ecología, for issuing the collecting permits. Many thanks to our friend and host José Campoy, director of the Upper Gulf of California and Colorado River delta Biosphere Reserve. We are also very grateful to the following volunteers: Jorge Torre-Cosío, Jeff Conn, Osvel Hinojosa, Charles Bergman, Butron family, Mosqueda family and Onesimo and family. Special appreciation is expressed for the support, encouragement, and mentoring of Dr O. Eugene Maughan throughout this project.

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