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Heavy Metal Distribution in Open Canals and Drains in the Upper Rio Grande Basin

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The inclusion of reclaimed effluents for irrigated agriculture may allow communities along the U.S.-Mexico border to use water

resources more efficiently and reduce urban costs of wastewater treatment. However, metal inflow from industry and urbanization may threaten food safety. This study examines metal concentrations in sediments from open canal systems charged with flow from the Rio Grande and from effluents discharged from border communities. At the surface of canal beds. sediments were collected from six canal segments that began at the fringe of the El Paso/Juarez metroplex to rural areas downstream, and ranged from 9 to 24 km in length. Sediments were analyzed for Cd, Co, Cr, Cu, Ni, Pb, and Zn. These metals rarely exceeded 20 mg kg⁻¹. Drainage and effluent conveyance increased the variability of metal concentrations in sediments. Geostatistical models did not significantly account for spatial variability of metals, except in Mexico. This may implicate multiple rather than single inflow sources of metals. Peaks in metal concentrations often coincided with growing rural communities. However, most metal concentrations were within conventional global ranges and were not at levels high enough to threaten food safety. Future sampling strategies will require reduced sampling intervals from 1 to <0.13 km.

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IMITED water supplies in arid regions are being reallocated to support urban growth. Sustaining irrigated agriculture will progressively depend on the usage of urban effluents. The inclusion of reclaimed effluents for agriculture may allow municipalities the better use of water resources to maintain environmental quality and reduce urban costs of wastewater treatment (Haruvy, 1997). However, potential hazards need to be identified and calculated to ensure food safety. Heavy metals are of particular importance because they are not biodegradable.

Metals released into either natural or engineered alluvial systems tend to accumulate in sediments through various adsorption and precipitation processes (Alden, 1992 and Coetzee, 1993). Metal remobilization and transport depends on sediment substrates and chemistry, and channel hydrology. Metals typically move through a water system as suspended particles or bed load. Consequently, metals found in sediments, particularly in top layers, reflect the current quality and general character of a water system. Metals in sediments can potentially be attributed to either geogenic or anthropogenic inputs that would include atmospheric fallout.

In the upper reach of the Rio Grande, surface water is managed and released through reservoirs, dams, and an intricate network of canals to convey a reliable supply of water from the Rocky Mountains in Colorado to Fort Quitman in West Texas and to the northern frontier in Mexico. River water supports communities, agriculture, and wildlife in three U.S. states (Colorado, New Mexico, and Texas) and in northern Chihuahua, Mexico. However, water quality is degraded with increasing distance from the source. The poorest quality water is along the western portion of the Texas/Mexico border, particularly after the El Paso/Juarez metroplex. The two sister cities comprise the largest metroplex in the Rio Grande watershed. Return flow from irrigation, urban effluents, and high evaporation rates may contribute to water degradation. Arsenic, Ag, Cd, Cu, Pb, Ni, and Zn in river water are at levels that may threaten the riparian ecosystem (IBWC, 1994; 1997). River inflows from open canal systems have not been extensively monitored and may also be of concern.

We hypothesized that metal deposition at the surface of canal beds would be similar to a localized plume pattern emanating from the El Paso/Juarez metroplex, if urbanization was the primary source of contamination. This study also examined metal concentrations in canal water in relation to surface sediments. Geostatistics was used as a tool to verify this conceptual contamination model related to anthropogenic inputs.

MATERIALS AND METHODS

Study Site

Water flow in the upper reach of the Rio Grande originates from the San Juan and Sangre de Cristo Mountains in southern Colorado and northern New Mexico, and

is stored in a reservoir above Elephant Butte Dam, NM (a 3.25-billion m³ capacity) (Lovejoy, 1980; Miyamoto *et al.*, 1995). An annual flow of 547 million m³ enters west Texas approximately 12.9 km northwest from the International Diversion Dam that conveys water to Mexico. East of this location, the Rio Grande becomes the natural boundary between the U.S. and Mexico; a major source of water for irrigated agriculture (310 million m³ in El Paso County for 16,194 ha); a supplemental source for municipalities (62 to 74 million m³ in El Paso); and the lifeline for the natural ecosystem. In a normal year, 74 million m³ of water are diverted annually to Mexico at the International Diversion Dam to irrigate 14,400 ha.

Most open canals, laterals, and drains on both sides of the river were developed over 70 years ago. Drainage and major irrigation canals run parallel to the Rio Grande. Canal hydrology on both sides of the border is based on gravitational flow and a series of headings and checks to divert, restrict, or build water flow in different units of the network. Canals are typically charged with river water from February to October. During winter months, treated effluent is discharged into drains on the U.S. side and various effluents are discharged and blended with well water on the Mexican side.

The Acequia Madre is the singular irrigation canal that conveys river water through the heart of Ciudad Juarez (population >1 million). River water irrigates agriculture within the Valle de Juarez Districto de Riego 009. Effluents, return flow, and river water are blended for irrigation southeast of the city. Ciudad Juarez pumps potable water supplies from the Hueco Bolson and shallow brackish (1000 to 3000 mg L⁻¹ in TDS) groundwater (135 to 148 million m³ yr⁻¹). Lateral drains collect the untreated effluent discharge (~100 million m³ yr⁻¹) that converge with the Interceptor Drain (prior to the development of two wastewater treatment plants in 1998). The flow from the Interceptor Drain is mixed with river water approximately 17.5 km east of Ciudad Juarez and conveyed in the Acequia Madre. Additional shallow groundwater is pumped into the Canal (~36 million m³ yr⁻¹) for a total of 210 million m³ yr⁻¹.

On the U.S. side, river water is diverted into five major irrigation canals that run parallel to the Rio Grande (El Paso County Water Improvement District #1), thus reducing the flow of the Rio Grande to 155 million m³ yr⁻¹. Franklin and Riverside are two of these five irrigation canals (Table 1). The city of El Paso (population > 0.5 million), like Ciudad Juarez, behaves as an artificial tributary that discharges effluents into canals that eventually drain into the river. About 30 million m³ yr⁻¹ of tertiary treated effluents and return flow from irrigation increases river flow to 169 million m³ yr⁻¹ (Miyamoto *et al.*, 1995). All surface water disappears at Fort Quitman on the Texas side and at Vado Cedillos on the Mexican side.

Sample Collection and Laboratory Analysis

A systematic sampling plan was used to collect sediments at regular intervals of 0.8 to 1.6 km within test segments of three pairs of irrigation canals and drains

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TABLE 1 A Description of Selected Irrigation Canals and Drains Evaluated for Metals in Sediments along the U.S.-Mexico Border

		Waterway				San	apling
Type	Name	Inflow Source	Length	Capacity	Lining	Length	Increment
			km	$m^3 sec^{-1}$		km	km
Canal	Acequia Madre	Juarez Valley, Mexico Mexican Diversion Dam	56.5†	6-9	Cement	17	1.0
Drain	Interceptor	Untreated effluents from Ciudad Juarez and industry	51.5	14 [‡]	Cement	6	1.0
Canal	Franklin (FC)	El Paso Valley, USA American Canal	43.2	6.3 – 8.4	Earth	22.4	1.6
Drain	Mesa	Irrigation Drainage from FC and urban run-off	43.2		Earth	24.0	1.6
Canal	Riverside (RC)	Rio Grande Water and limited treated effluents	16.1	8.4	Earth	19.2	0.8
Drain	Riverside	Irrigation Drainage from RC	16.1		Earth	19.2	0.8
The le The dr the rain	angth of the Acequain usually conductive season.	iia Madre before it branches into several laterals downst cts 3.5 to 9 m ³ s ⁻¹ of sewage water alone or mixed with 1	tream at th river wate	ie town of (r. The max	Juadalupe. imum capae	city is 14 m	1 ³ S ⁻¹ during

(Figure 1, Table 1). Linear sampling ran parallel to the hypothesized plume of metal contamination. The starting points were not randomly located, but rather located immediately downstream from the El Paso/Juarez metroplex. Canal bed sediments (the upper 0.15 m) from the U.S. Franklin Canal/Mesa Drain and the Riverside Canal/Riverside Drain were collected during November and December of 1991 at little to no flow. In Mexico, sediment and water collection from the Acequia Madre/Interceptor Drain occurred during October and November of 1993.

Two control areas were selected to reference metal concentrations found in surface sediment samples from designated canal and drain segments. Control areas were unlined and composed of both transported and sedentary parent materials. The first control area was upstream from designated canals and from the El Paso/Juarez metroplex, and located at the Rio Grande, 11 km west of the International and American Diversion Dams (Assadian and Fenn, 2000). Subsurface sediments (1 m) within the Mesa and Riverside Drains test area were designated as the second reference or control area. The site was located approximately 46 km downstream, after being conveyed 36.5 km through the El Paso/Juarez metroplex.

Efforts were made to insure that all equipment and storage containers were metal-free. A metal-free scoop was used to collect shallow sediments at canal centers. The scoop was washed, scrubbed, double-rinsed with deionized and metal-free water, and dried between each collection. Collections were placed and transported in plastic bags. Water samples in Mexico were also collected from the middle of the canal about 0.1 m below the water surface with a submergible bottle apparatus using 1-L polyethylene containers that had been previously acid washed. Water samples were transported in a cooler with ice. Water samples were not acidified prior to short-term storage at 4°C for less than 30 days.

All sediment samples were air-dried, sieved through a 2-mm plastic screen, and ball-milled. Homogenized subsamples were acid-digested following USEPA protocol 200.2 (USEPA, 1991) and analyzed for total Cd, Co, Cr, Cu, Ni, Pb, and Zn, using inductively coupled plasma spectroscopy (ICP) following USEPA protocol 200.7 (USEPA, 1991). Water samples were stored at 4°C. Unfiltered water samples were digested with nitric acid and hydrogen peroxide and concentrated tenfold prior to Cd, Cr, and Pb analyses. For metal analyses, all standards were traceable to the National Institute of Standards and Technology. Quality control included method blanks (MB) and initial calibration verification (ICV), following metal calibration on ICP instrumentation. For continuous quality assurance, MB, continuous calibration verification (CCV), replicate, and split samples were included after every 20 samples. Unprocessed water samples were also analyzed for electrical conductivity, and for soluble Na, K, Ca, and Mg concentrations. Quality assurance measures were similar to those for metal analyses. Additional water samples were recollected in 1999. Both filtered and unfiltered water samples from 1999 were analyzed for hexavalent Cr using Hach® analytical procedures and the Hach DR/2010 Spectrophotometer.



Caballo Reservoir

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MesillaBasin United States Mexico





Data Analysis

Metal concentrations in sediments or water samples were analyzed for means, extremes, standard deviation, and coefficients of variation, and correlated to downstream distance from the El Paso/Juarez metroplex. Analysis of variance was used to delineate differences in metal concentrations among canal segments and control areas (SAS Institute, 1988). Normality of the data was examined by kurtosis and skewness. If skewness coefficients exceeded 1.0 then outlying data greater than four standard deviations from the mean were discarded as outliers. The entire data set for a specific parameter was transformed to natural logarithms to stabilize variance (Gamma Design Software, 1992). Isotropic semivariance of data was calculated to determine if there was spatial dependence of solutes with regard to irrigation delivery using the following equation:

$$\gamma(h) = \frac{1}{[2n(h)]} \sum_{i=1}^{n(h)} [Z(x_i) - Z(x_i + h)]^2$$

where γ is the semivariance for n data pairs separated by a distance of h and Z is the value (in this case metal concentration) at positions x_i and $x_i + h$ (Clark, 1979; Warrick *et al.*, 1986). Lag classes were similar to sampling increments (Table 1). Active maximum lag distance equaled the full distance of each test segment, except for the Acequia Madre irrigation canal, where active lag distance was 83% of the 17-km test segment.

There are four idealized semivariogram models (Clark, 1979; Warrick *et al.*, 1986). The first is simply a random model. There is no spatial interdependence and the semivariogram function $\gamma(h)$ is constant at all values of h. The spherical model has a finite maximum (or sill) C and a random component defined as the nugget C_o . There is a range, "a", which is the separation distance for which the function approaches the sill. Both linear and parabolic models have no sill and hence the variance tends to increase according to the distance over which it is evaluated. For the linear model the value increases linearly from a nugget C_o , which can be zero or positive. For the parabolic model is similar in appearance to cases that are nonstationary. Raw semivariograms from sediment and water data were fitted to either a spherical, linear, or an exponential models (Gamma Design Software, 1992). For simplicity, the fitting was done by a least square analysis rather than by more sophisticated analyses which would be appropriate to remove drift if larger sample numbers were available.

RESULTS

Rio Grande floodplain alluvium is a mixture of materials from mountains and alluvial valleys composed of igneous, volcanic, and sedimentary rocks (USGS,

1996; 1997). Metal concentrations in river sediment and floodplain soil at the first control area located upstream from the El Paso/Juarez metroplex were generally within global soil concentrations (Table 2). Metal concentrations collected from terrace deposits tended to be greater than those from river sediments. Mean Ni concentrations in soil exceeded conventional soil concentrations of 1 mg kg⁻¹, but not in river sediment. Mean metal concentrations from subsurface drain sediments at the second control site (downstream from the El Paso/Juarez metroplex) were significantly greater (p > 0.05) than those concentrations in upstream sediment and soil, except for Cd and Cu.

Within U.S. canal and drain test segments, metal concentrations were significantly greater than those from upstream baseline concentrations (p > 0.01), with the exception of sediment Pb and Zn in the Riverside Canal (Tables 2 and 3). Metal concentrations were below global contamination thresholds recommended for soils (Mengel and Kirkby, 1982; Fergusson, 1990), but exceeded mean metal concentrations for U.S. Western soils (Holmgren *et al.*, 1993) and soil metals found in agricultural fields on the Rio Grande floodplain (Assadian *et al.*, 1998; 1999). Relative concentrations of sediment metals among canals were the Franklin Canal > Mesa and Riverside Drains > Riverside Canal (p > 0.05). In general, mean Zn concentrations were >25 mg kg⁻¹. Chromium, Co, Cd, Cu, and Ni concentrations were <20 mg kg⁻¹ in surface sediments. Lead concentrations were ≤ 10 mg kg⁻¹.

In Mexico, the cement-lined canals contained only transported alluvium. The concentrations of metals in surface sediments were also significantly greater than those in upstream river sediment (p > 0.01), but significantly less than those in Franklin Canal sediments in the U.S., with the exception of Pb (Tables 2 and 3). Blending effluents with river water in the Acequia Madre canal probably increased sediment Pb concentrations, but tended to reduce Cd, Co, Cr, and Ni concentrations. Total sediment Cr averaged 15 mg kg⁻¹ in the Interceptor Drain. Lead averaged ≥ 20 mg kg⁻¹ in the Interceptor Drain and in the mixed water segment of the Acequia Madre.

Variability, expressed as coefficients of variation, in metal concentrations generally was greater in drains than in canals (Table 3). Variability ranged from 27 to 70% in canals (Franklin and Riverside Ccanals in the U.S. and the river-water segment of the Acequia Madre in Mexico), from 27 to 102% in drains, and from 67 to 130% in the mixed water segment of Acequia Madre. Sediment Cd, Pb, and Zn showed the greatest variability on the U.S. side (Table 3). Sediment Cd, total Cr, and Pb showed the greatest variability on the Mexican side. Conventional correlation matrices showed no consistent association between metal concentrations in canals and increasing downstream distance from the El Paso/Juarez metroplex (Table 4). Sediment Cd and Co significantly correlated with distance more often than other sediment metals. The positive or negative association with distance depended on metal species and waterway.

Geostatistical models had generally low random components (C_o), but did not significantly describe the spatial variability of most metals in U.S. canal sediments

	The Rio Grand	e and its Floodplain	Subsurface	Drain Sediment	Global
Heavy	Upstream fro	m El Paso/Juarez	Downstream f	rom El Paso/Juarez	Soil
Metal	Surface Soil	Surface sediment	Mesa Drain	Riverside Drain	Conc. ¹
Cd	1.2 A ²	<mdl<sup>§</mdl<sup>	0.6 B	0.6 B	0.3-11
ට	1.7 B	1.4 B	4.9 A	4.6 A	1-40
С С	3.7 B	3.6 B	15.2 A	17.7 A	0-100
Cu	8.4 A	4.6 B	6	4.3 B	5-50
Ni	2.7 B	0.1 B	9.0 A	9.6 A	1
Pb	7.7 AB	2.1 B	10.0 A	10.6 A	2-200
Zn	16.7 B	14.6 A	50.9 A	48.3 A	10-300
† Source:	Fergusson (1990), at	nd Mengel and Kirkby (1982).		

† Source: Fergusson (1990), and Mengel and Kirkby (1984). Numbers followed by different upper case letters within rows are significantly different at the 0.05 $^{+}$ Numbers followed by different upper case letters within rows are significantly different at the 0.05 $^{+}$ level of probability. [§]Below method detection limit [¶]Data not collected

TABLE 3	Means and Coefficients of Variation (Percentage given with Parentheses) of Metal	Concentrations (in mg kg ⁻¹) in Surface Sediments from Canals and Drains Downstream	from the EI Paso/Juarez Metroplex on the U.S. and Mexican Sides of the Rio Grande
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	El Pa	so (USA) Coi	rveyance Sys	stem	Juarez (Me	xican) Convey	ance System
	Franklin	Mesa	Riverside	Riverside	Acequi	a Madre	Interceptor
Metal	Canal	Drain	Canal	Drain	River Water	Mixed Water	Drain
Cd	0.9 (48)	0.5 (72)	0.4 (52)	0.6 (45)	0.7 (46)	0.4 (95)	0.6 (80)
Co	6.1 (31)	4.5 (41)	3.4 (37)	4.6 (27)	4.1 (41)	1.6 (67)	2.8 (39)
C	17.9 (30)	13.9 (37)	12.5 (28)	17.2 (32)	9.1 (46)	8.4 (86)	14.8 (80)
Cu	20.8 (67)	+ 	;	6.5 (69)		;	ł
Ni	10.0 (41)	8.1 (44)	5.1 (43)	9.2 (36)	7.4 (43)	4.6 (75)	6.5 (54)
Pb	9.4 (68)	8.2 (82)	3.8 (38)	10.1 (71)	14.8 (42)	19.7 (130)	24.4 (102)
Zn	81.4 (52)	53.5 (75)	29.3 (37)	58.3 (72)	;	f	
†Sample	es not analyzed	l for this para	meter				

_	Correlatior ncreasing Do	r² Values) ו wnstream [TABLE of Sedimen	4 t Metal Concen 1 the El Paso/J	trations with uarez Metropl	ex
	Franklin	Mesa	Riverside	Riverside	Acequia	Interceptor
Metal	Canal	Drain	Canal	Drain	Madre	Drain
Cd	NS	0.46**	0.53**	-0.27*	-0.42**	NS
Co	NS	0.29*	0.44**	0.29*	-0.45**	NS
Cr	NS	NS	NS	-0.26*	NS	NS
Cu	-0.68**	- ! 	1	NS	ł	NS
Ni	NS	0.30*	0.41*	NS	NS	NS
Pb	NS	NS	NS	-0.44**	NS	NS
Zn	NS	NS	NS	NS	I	NS
NS, not s *, ** sign † Sample	ignificant inficant at the is not analyze	0.05 and 0 d for this p	.01 levels of arameter.	probability, re	spectively.	

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 $(r^2 \le 0.24, n = 14, 15, 24, and 24$ for Franklin Canal, Mesa Drain, Riverside Canal, and Riverside Drain, respectively) (Table 5). However, linear models best described the spatial variability of sediment Cd in the Mesa Drain and Riverside Canal ($r^2 \ge 0.45$). Linear and spherical geostatistical models described the spatial variability of sediment Zn in the Riverside Canal and Drain, respectively. The range of spatial influence for Cd and Zn was >19.2 km or the lengths of test

Geostatistical Models Describing the Metal Concentrations in Canal and Drain Sediments Downstream from the								
	El Paso/	Juarez Metrople	ex along the l	J.SMex	ico Bord	er		
Canal/Drain	Metal	Transformation	Model	C	$C_{o} + C$	a	<u>r</u> 2	
		El Pas	so Valley, USA					
Franklin	Cd	None	Spherical	0.01	0.2	4.9	0.17	
Canal	Cr	Ln (z+0)	Exponential	0.1	0.7	>0.1	0.00	
	Pb	None	Spherical	26.2	37.5	>3.2	0.002	
	Zn	None	Spherical	1.0	1949	3.3	0.05	
Mesa	Cd	Ln (z+0)	Linear	0.1	>0.6	>14.4	0.45	
Drain	Cr	None	Spherical	0.01	12.1	1.9	0.02	
	Pb	Ln(z+0)	Spherical	0.0001	0.3	2.7	0.06	
	Zn	None	Spherical	1.0	215	1.9	0.02	
Riverside	Cd	Ln (z+0)	Linear	0.05	>0.5	>19.2	0.53	
Canal	Cr	Ln (z+0)	Spherical	0.06	>0.1	0.8	0.00	
	Pb	Ln (z+0)	Linear	0.1	>0.2	>19.2	0.24	
	Zn	Ln (z+0)	Linear	0.03	>0.2	>19.2	0.38	
Riverside	Cd	Ln (z+0)	Spherical	0.1	0.2	2.3	0.05	
Drain	Cr	None	Linear	20.9	>20.9	>11.5	0.18	
	Pb	Ln (z+0)	Spherical	0.5	>0.6	>11.5	0.02	
	Zn	Ln (z+0)	Spherical	0.4	0.4	0.8	0.42	
		Juarez	Valley, Mexic	:0				
Acequia	Cd	None	Spherical	0.0001	0.183	6.83	0.59	
Madre	Cr	None	Spherical	0.1	47.93	6.37	0.93	
	Pb	Ln (z+0)	Spherical	0.2	1.17	5.8	0.52	
Drain	Cd	None	Spherical	0.0001	0.28	2.12	0.10	
Interceptor	Cr	None	Spherical	0.1	151.6	2.13	0.13	
···· ·	Pb	Ln (z+0)	Spherical	0.0	1.62	2.13	0.11	

TABLE 5

segments. In Mexico, spherical models best described ($r^2 > 0.5$) spatial dependence of metal concentrations in the Acequia Madre. The range of influence for sediment Cd, Cr, and Pb ranged from 5.8 to 6.8 km. This consistent finding was unique since geostatistical models did not significantly explain ($r^2 < 0.14$) the spatial dependence of metal concentrations in the Interceptor Drain.

A look at heavy metal concentrations in sediments plotted against increasing distance from the El Paso/Juarez metroplex showed considerable variability within test segments (Figure 2). The zero point within each collection segment of a canal or drain represents the area closest to the metroplex. Peaks in metal concentrations occurred beyond the start or zero point, except in surface sediments from the Interceptor Drain. Metal accumulation tended to increase with downstream distance from established urban centers. Concentration trends were similar among metal species in all waterways except for Pb and Zn (p > 0.01, data not shown). Therefore, Cd and Cr graphs in Figure 2 are representative of spatial concentrations of Co, Cu, and Ni.

In Mexico, the quality of river water changed prior to blending with untreated effluent. Sodium concentrations and electrical conductivity (EC) increased to more than 250 mg L⁻¹ and 2 dS m⁻¹, respectively, from and average of 105 mg L⁻¹ and 0.8 dS m⁻¹. After blending with untreated effluent, water Na and EC averaged 150 mg L⁻¹ and 1.5 dS m⁻¹, respectively. Changes in salinity were not associated with changes in metal concentrations. Concentrations of Pb in eventual irrigation water were detected twice above method detection limits (Figure 3). Lead detection occurred 10 km prior to and at the point of effluent blending (Figure 1, E6). Detectable amounts of total Cr of up to 52.2 μ g L⁻¹ and Cd of up to 2 μ g L⁻¹ were also found in irrigation water (Figure 3). Water was recollected and analyzed for hexavalent Cr before and after effluent blending in 1999. Cr VI was not detected $(< 0.01 \text{ mg } \text{L}^{-1})$. Given the limited sampling frequency, it was difficult to account for metal peaks in earlier water sampling. Analysis of variance showed that concentrations of Cd and Cr in river water were not significantly different from those in sediment. Lead concentrations were significantly higher (p > 0.06) in canal sediment.

DISCUSSION

Despite possible contamination sources and modes of transport in an urban setting, effluent discharge has repeatedly been shown to be the dominant source of metals in waterways (Bubb *et al.*, 1991; Seidemann, 1991). Therefore, it was reasonable for us to hypothesize that metal concentrations in both U.S. and Mexican canal sediments would be greater at close proximity to the discharge of effluents from the El Paso/Juarez metroplex. This exploratory work found that metal concentrations in canal and drain sediments downstream from the border metroplex were greater than those upstream, but within conventional concentrations for soils,



FIGURE 2

Concentration distribution of Cd, Cr, Pb, and Zn in surface canal sediments downstream from the El Paso/Juarez metroplex along the U.S.-Mexico border.



FIGURE 3

Concentration distribution of Pb, Cr, and Cd in unfiltered water in comparison with surface bed sediments in an irrigation canal in Mexico, along the U.S.-Mexico border.

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except for Ni. Geostatistical analyses did not support any evidence of a characteristic pollution plume in the downstream canal environment from the El Paso/Juarez metroplex. This suggested effluent discharge from either El Paso or Juarez was not a point source of metal contamination. The presence of Pb, Zn, and other metals in sediment could be attributed to mineralized areas of the Rio Grande Basin (USGS, 1997). However, elevated metals in downstream sediment were indicative of anthropogenic activity. Contrary to Bubb *et al.* (1991) and Seidemann (1991), the data suggested that there were alternative metal sources other than the discharge of effluents from the El Paso/Juarez metroplex and perhaps different modes of transport into border canal systems. There were nonpoint sources of metal inflow in all canals, except the Acequia Madre in Juarez. In this case, discharge from the Interceptor drain was the point source of metal inflow.

In Texas, increased metal concentration often coincided with the location of growing townships and/or changes in hydrology inflow (listed on the x-axis in Figure 2 with map location in Figure 1). For example, increased metal concentrations in Franklin Canal sediments coincided with Socorro and Fabens townships (Figure 1, C5 and D15). Between these townships, water from the Riverside Canal recharges the flow in the Franklin canal (Figure 1, D6), and likely reduces sediment metals. Runoff from the interstate freeway and peripheral commerce is captured in the Mesa Spur, which feeds into the Mesa Drain (Figure 1, B8). There also appears to be inflow from the township of Clint (Figure 1, C9). Metal increases in both Riverside irrigation and drainage canals were associated with the township of San Elizario (Figure 1, D8). On the Mexican side, multiple inflows into the Acequia Madre canal were minimized and metal concentrations in sediments gradually increased where drainage effluents and river water converged and blended (Figure 1, E6). In Mexico, high, but infrequent metal concentrations in water have also occurred in other regions of Mexico (Mendoza et al., 1996). We suspect that that an illegal surge from plating or other industry may have increased water Pb and Cr concentrations.

Alternative metal sources at the border region include atmospheric fallout from metal smelting for over a hundred years (Landrigan *et al.*, 1975; Woodside and Roberts, 1958). Leaded fuels were also used in Mexico for an extended period and phased-out in 1994. Galvanized fencing protects the Acequia Madre, but could be a contributing source of Zn concentrations from runoff. In Texas, run-off from the interstate freeway and industry entered the Mesa Drain. It is also likely that regular foliar Zn applications in U.S. pecan orchards (close to the metroplex) may have contributed to sediment Zn via return flow. In most cases, however, increased metal concentrations were associated with rural growth, especially in the U.S..

Texas border townships have experienced a 20% increase in population every decade since 1970 (RGCOG, 1993). Socorro is the largest township with a population of 22,995 in 1990 and the closest township to El Paso. In 1998, city officials (personal communication) were hopeful that 30% of all public and domestic

buildings would be connected to a sewer system by 2000. It appears that septic seepage, the lack of public infrastructure, and generally limited disposal options may have contributed to elevated metal concentrations in the canal system. In Mexico, enriched metal concentrations in Acequia Madre canal sediment prior to effluent blending may also be attributed to indiscriminate waste discharge. Runoff passing through galvanized fencing could also contribute to increased sediment Zn concentrations. Urban sprawl into rural areas outside Ciudad Juarez is not as extensive as it is in Texas. Therefore, there was limited metal inflow from rural areas.

A second question was whether metal concentrations found in surface sediments would reflect the current quality and character of a water system. Limited and onetime samples collected in the Acequia Madre, respectively, suggest that surface sediments may overestimate potential metals in canal water with regard to Cd, Cr, and Pb. Overestimation may be attributed to total rather than soluble metal analyses. However, if we assume that total suspended solids (TSS) in canal waters were similar to those in the adjacent Rio Grande, the approximate TSS averaged 192 mg L^{-1} (USGS, 1996). If growers applied $12.2 \times 10^{-6} L$ ha⁻¹ yr⁻¹ (4 acre feet annually), then each irrigated hectare would have received 2342 kg of suspended sediment per year. Given an average sediment concentration of 81 mg kg⁻¹ for Zn and a concentration of 24 mg kg⁻¹ for Pb (Table 3), approximately 0.18 kg and 0.05 kg of Zn and Pb, respectively, would have entered an irrigated hectare via irrigation over a 10-year period. Therefore, it is unlikely that irrigation water conveyance is a primary transport pathway for metals. At the same time, water conveyance and irrigation management should minimize disturbance of sediments that would increase suspended solids.

These data also suggested that future sampling strategies to monitor metals in open conveyance systems in the border region should be modified to reduce the coefficients of variation that often exceeded 80% (Table 3). The estimated number of samples required to achieve a minimum relative difference of 20% within an 85% confidence interval would require about 183 samples using a one-sided, one sample *t*-test (USEPA and CNWRS, 1995). Given that the length of the test segments ranged from 17 to 24 km, sediment samples should be collected at intervals of 0.09 to 0.13 km.

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