AN INVESTIGATION OF ARSENIC, LEAD AND MERCURY IN SEDIMENT IN THE INTERNATIONAL RIO GRANDE/ RIO BRAVO WATERSHED USING A GEOGRAPHIC INFORMATION SYSTEM

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Dedication

In many ways this thesis represents my expedition to a very large mountain. Regardless of the necessity of my climbing this mountain alone, many people motivated and cajoled me during and facilitated the completion of this expedition. Therefore, while I dedicate this document to myself for actually achieving my goal, I dedicate all that comes as a result of reaching the mountain's top to those who helped me get there.

To my father for always asking how I was doing on the project. To my mother for never asking how I was doing on the project.

To Sean Devin Farrell for providing a constant source of reassurance that the climb was possible and for stepping in with motivation when I thought I could not continue.

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To Dr. Ernst Davis for his unwavering belief that I should just do it.

And especially to my husband, who in the end sacrificed much more than I did to see me reach my goal.

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The Border Environmental Assessment Team worked hand-in-hand with other entities to perform necessary work in the Rio Grande Basin. Several of those cooperative projects directly contributed to the foundation of this thesis. Most notably, the United States Geological Survey (USGS) performed a great deal of work related to understanding the historical water and sediment quality in the basin. In particular, I thank Lloyd Woosley for his constant pursuit of meaningful partnerships between the USGS and other agencies, and Peter Van Metre and Roger Lee for their willingness to share their awesome technical skills and continued work in the Rio Grande.

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This project investigates the transport of sediment and associated contaminants through the lower portion of the Rio Grande/Río Bravo International Watershed. A preliminary review of water quality, bed sediment, and reservoir sediment-coring data in the watershed reveals a complex hydrological system, with varying potential sources of contamination. Within the lower portion of the watershed (defined as from the dams at Elephant Butte Reservoir in New Mexico and Red Bluff Reservoir in Texas to the Gulf of Mexico) arsenic, lead, and mercury appear at levels and/or trends which may be of concern.

Through the use of a geographic information system, this project evaluates the extent of contamination from selected toxic substances, identifies potential sources and/or naturally-occurring conditions for the contribution of these toxic substances, and evaluates the potential for using Geographic Information Systems to model the watershed. The project uses data collected over the thirty year period from 1966 - 1996 by the Texas Natural Resource Conservation Commission, the United States Geological Survey, the International Boundary and Water Commission, and the United States Environmental Protection Agency. The project utilizes water quality, bed sediment, sediment coring, land use, land cover, soils, water-quality permitting, precipitation, flow, and reservoir-release information to attempt to derive a model depicting the movement of sediment through the watershed. Because the United States federal government has not promulgated standards for sediment, the project references standards from both the State of Washington and Canada for screening of sediment quality.

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Introduction

For years scientists and engineers labored to develop models that closely represented natural systems. Over time, these models grew increasingly sophisticated and arguably more accurate. The price for this accuracy is an ever-increasing demand for more comprehensive data collection to feed the models. In the ideal scenario, complex models depict important relationships between the activities of man and their consequences in nature. In less ideal circumstances, models illustrate the lack of sufficient monitoring and data collection to support intelligent, informed decisions. In situations with insufficient data to support existing models, assessors must rely on other techniques for simulating the environment.

Advancing technology presents alternative solutions to collecting extensive field information. Scientists can use technology to provide preliminary screening analyses for large ecosystems, thus allowing researchers to focus collection efforts in identified problem areas. Technology becomes especially critical in watersheds with more complex issues, such as varying ecosystems, extensive human impacts, remote sampling locations, significant seasonal differences, and multiple governmental jurisdictions. With each additional complexity comes the need to gather information to appropriately describe the impact of the complexity upon the watershed. To emphasize the challenges in modeling complex watersheds, this document investigates a particularly intricate system -- the International Rio Grande/Río Bravo (Rio Grande) watershed.

This document focuses on the relationship between water, metals, and sediment in the Rio Grande/Río Bravo watershed. The analysis investigates an alternative solution to the complex sediment and metals modeling approaches typically used in watershed protection. The analysis also demonstrates the use of spatial technology in environmental assessment. Based on the review of previous studies, the thesis focuses on three metals prevalent in the Rio Grande/Río Bravo watershed: arsenic, lead, and mercury.

The Setting

The Rio Grande watershed introduces a wide array of challenges to planners, managers, modelers, and regulators. Scientists examining the Rio Grande face problems typically associated with analyzing a large river; however, they also face the reality of gathering information from two different countries. Both the United States and Mexico monitor water and sediment quality in the watershed; however, the protocols, frequencies, measurements, and standards that guide the monitoring efforts differ greatly. Therefore, data collected at the very same site could significantly vary.

The Rio Grande earns its title of "big river" by spanning over 1,900 kilometers and draining an area twice the size of the State of California. The basin contains divergent ecoregions -- from mountains to deserts to subtropical regions. The human impacts within the basin run the gamut from heavy industrial, urban and agriculture, to protected parks, to pristine areas. Even the flow is diverse, ranging from raging to nonexistent. Modeling such complexity can be daunting. However, the Rio Grande's diversity makes it an excellent test case for any modeling of sediment transport. If the model works under these rigorous conditions, it should work in other complex scenarios.

The Importance of Sediment

Most watershed models focus on the relationship between pollution and water quality. Why does this study analyze sedimentation instead? Models of the fate and transport of sediment in an ecosystem are younger than water-quality models, and therefore less refined. The process of sedimentation is extremely complex and more difficult to simulate than other water-quality processes. Sedimentation naturally occurs as part of the hydrologic process. Water erodes soils and rocks and transports these materials into streams and rivers. During storms, water erodes the landscape more quickly. As the runoff flows rapidly over the landscape, particles suspend in the water and move downstream. When the water eventually slows, the larger suspended materials begin settling onto riverbeds, at the bottom of reservoirs, and in deltas at the mouth of a river (VanMetre, 1997).

Regulatory agencies historically underplay the importance of sedimentation in their overall water-quality analysis, preferring instead to rely on sedimentation as a "cleaning" mechanism for water quality. Canada led the way toward recognizing the important contributions of sediment to the natural ecosystem, and acknowledging the significant impacts of sediment contamination upon the reliant species (benthic communities, fish, plants, and eventually the humans at the end of the food chain). Because of the new awareness of sediment's importance, the need for accurate sediment fate and transport models grew in the last twenty years.

Metals and Sediment

Sediment is a vital part of the ecosystem, providing important nutrients and a habitat for aquatic organisms. Unfortunately, the sediment layer of riverbeds, reservoirs, and deltas provides a convenient resting-place for metals which adsorb to sediments. Through the erosion process, trace metals from rocks suspend in water and move through the system in concert with sediment. Metals also enter the water through atmospheric deposition (e.g. through volcanic activity, metals enter the air and then are deposited back into the water during storm events). As with other contaminants, trace metals tend to bind or "sorb" to suspended sediments and eventually settle out of the water with them. In fact, metals generally exist in very small quantities in the water column because they settle with the sediment.

Human activity contributed to the increasing presence of metals in sediment. Activities like mining, solid-waste incineration, and power plant emission provide substantial pathways for metals to enter the hydrologic system (VanMetre, 1997). The sediment layer itself then provides an excellent mechanism for metals to enter the food chain by providing nutrition for benthic organisms. Bottom-dwelling fish, plants, and other organisms feed on the sediment layer and uptake the metals. This uptake allows the metals to be consumed by other fish, crustaceans, and eventually humans. As the metals move up the food chain, they are continuously magnified and accumulated (EPA, 1997). Poor sediment quality causes a lack of diversity in a benthic community, as several species are sensitive to pollutants. This impairment of diversity can also affect the food chain by significantly altering the available food sources and changing the existing natural competition (Power, 1992).

Historically, environmental agencies did not regulate sediment quality because the sediment itself was viewed as a filtration mechanism. In the last several years, agencies recognized that sediments serve as both a reservoir for contaminants and a source of contaminants to the water column and organisms. Various toxic contaminants (including metals) found only in barely detectable amounts in the water column can accumulate in sediments to much higher levels (Power, 1992) and then be consumed by organisms, or be resuspended during storm events.

Purpose of This Project

This project explores several existing sediment transport models and their applicability to a very large river basin. At a simpler level, this project investigates the current status of sediment quality in the Rio Grande watershed, reviews the work of other researchers within the basin, and proposes an approach to assessing sediment quality that may be more appropriate for large watersheds.

To accomplish the assessment of sediment quality, the project builds on research initiated under the Texas Clean Rivers Program (TCRP). The prime directive of the TCRP is to perform water quality assessments for each major river basin in Texas[1]. For the 1996 TCRP assessment in the Rio Grande Basin, the Border Environmental Assessment Team (BEAT) at the Texas Natural Resource Conservation Commission (TNRCC) performed several special studies designed to provide more relevant information about the watershed and to further address the questions of trends and potential sources of contamination.

Four of the BEAT's projects are particularly applicable to this thesis: the Sediment Coring Study, the Sediment Assessment, the Creation of a GIS for the Rio Grande, and the SWAT Model (please see the Literature Review chapter for further details about these four studies). Each of the four studies provided components necessary for completing a GIS-based screening model for sediment transport in the Rio Grande.This thesis completes the cycle begun by the BEAT. Because the BEAT no longer exists, it seemed important to complete the GIS work initiated by the team in another forum. This thesis became such a forum.

The project also evaluates approaches the TNRCC will use in the future to evaluate water quality problems. In 1997 the TNRCC began pursuing a program to develop "Total Maximum Daily Loads" (TMDL) for targeted subwatersheds in the state. Using the theory that the TCRP would perform preliminary assessments in conjunction with federal programs like the Clean Water Act Section 305(b) and identify "priority" watersheds in the state, the agency initiated TMDL projects in a small number of subwatersheds in the state. The projects' goals include the development of a GIS-based model for assessing contaminant loads in the watersheds. The TMDL must be more detailed and analytical in nature than a basin-wide model; however, the process of determining which subwatersheds should be targeted for further analysis or TMDL development could be performed at the basin level. Unfortunately, the TNRCC's approach to TMDL analysis currently relies solely on the agency's internal discussions of water quality and politics and lacks a truly objective scientific methodology. Even the TNRCC's attempt to objectively quantify water quality priorities -- a project called the "Watershed Planner" -- falls short because it relies solely on static, one-time assessments of water quality on the "segment" level without ever adding a trend or geographic component to the analysis. Clearly the TNRCC needs more tools to improve its decision-making and regulation.

In 1997 the United States Environmental Protection Agency (EPA) released a GIS-based modeling tool called BASINS (please see the Literature Review Section for further details about this tool). BASINS goes a long way toward developing standardized tools for states to use in their TMDL development; however, the tool works only at the subwatershed level. Therefore, basin-level models to perform screening-level assessments can complement BASINS.

To answer the question of whether the state and federal agencies can use GIS as a foundation for the TCRP and BASINS in an international watershed, this project reviews the currently-available data and technology using the Rio Grande watershed as a test.

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[1] The TCRP began in 1992 with preliminary assessments in each basin. In 1994, the assessments expanded to include geographic information systems (GIS) as part of the assessment process. The requirements for the program expanded in 1992 to include trends in water-quality over time, seasonally, and versus flow. While the TCRP made strides in 1992 toward comprehensively evaluating environmental conditions, several river basins still lacked basic information, including long-term data collection, any geographic information, or further analysis to identify potential sources of contamination.

Structure of This Document

Four major sections comprise this document: background, literature review, sediment-quality analysis, and GIS-based modeling. For general information about the Rio Grande watershed, monitoring methods, GIS, and baseline assessment, please see the background section. The literature review discusses previous applicable studies in the basin, investigates several existing sediment transport models, and documents health effects associated with the selected metals. The sediment-quality section presents an analysis of the presence and trends of arsenic, lead, and mercury in sediment within the basin and correlates the presence of metals in sediment with other constituents found in water and sediment. The modeling section illustrates how a geographic information system can be used to perform screening-level modeling in the Rio Grande watershed. Conclusions follow the modeling section.

Background

This section discusses issues of fundamental concern to the study, including the environmental setting of the Rio Grande basin, the demographics of the basin's residents, sediment assessment methodologies, and geographic information systems.

Location of the Project

Geographically, this project focuses on the lower portion of the International Rio Grande watershed--defined for this study as the drainage area associated with the Rio Grande downstream of the dams at Elephant Butte and Red Bluff Reservoirs (see Figure 1). The study area includes a variety of land uses, ecoregions, rainfall conditions, and human impacts.

From Elephant Butte downstream the Rio Grande flows through several significant urban areas, including the sister cities of El Paso/Ciudad Juárez, Del Rio/Ciudad Acuña, Eagle Pass/Piedras Negras, Laredo/Nuevo Laredo, McAllen/Reynosa, and Brownsville/Matamoros. These border cities represent the majority of the population in the basin. Over the last twenty years, the sister cities experienced tremendous growth as the basin's population gravitated toward the jobs along the border. With this significant growth, water-quality issues increased as the cities struggled to add to their infrastructure. As the population density in the cities increased, the human impacts to the river increased, including discharge of untreated wastewater into the river, heavy industrial inputs to the river from mining and other operations, and increased irrigation.

The character of the river's surroundings changes drastically as it moves downstream. In the El Paso/Ciudad Juárez area, less than eight inches of rain fall in a typical year causing the surrounding areas to be mostly desert and scrub. In the middle of the basin, higher rainfall allows the presence of grassland and cropland while in the lower reaches of the basin the 36 inches per year of rainfall provides a tropical surrounding.

The hydrology of the river changes as it moves through the watershed. From Elephant Butte Reservoir, the river is highly regulated and flows at speeds controlled by the dam. The river meanders through Las Cruces, New Mexico and down to El Paso/Cuidad Juárez where it is actually a paved channel. The river serves as a water supply for the sister cities, and wastewater returns to the river below the urban areas. Downstream of El Paso, the river contains mostly return-flow from water treatment facilities and irrigation until Fort Quitman where the river often dries to a trickle in the summer. A little further downstream, near Presdio/Ojinaga, the Río Conchos replenishes the Rio Grande and it again flows. The river then makes a significant northern turn through Big Bend National Park. Downstream the river slows as it enters

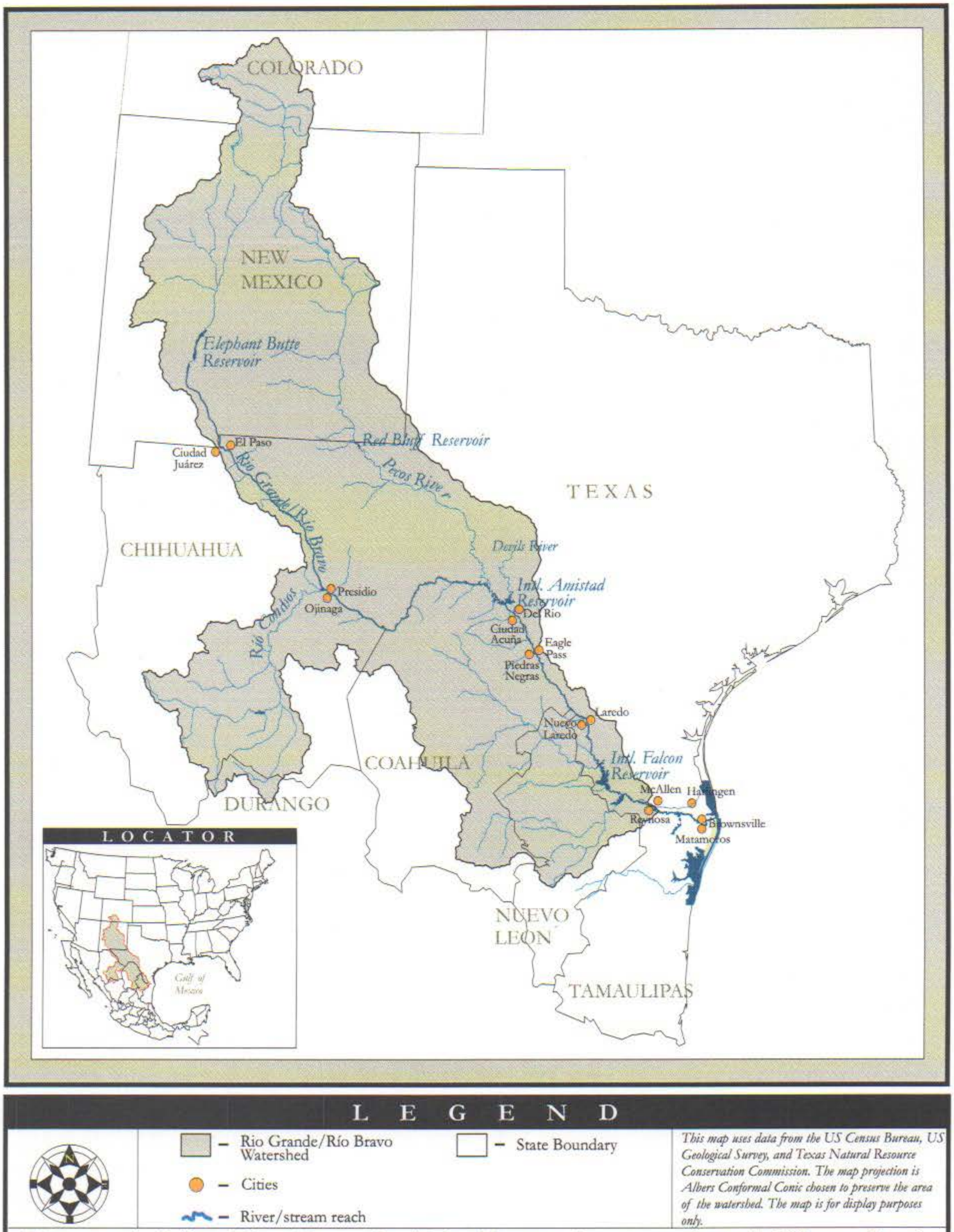

Figure 1: The Rio Grande/Río Bravo International Watershed

International Amistad Reservoir. At this reservoir the highly saline Pecos River, the Devils River, and several springs join the Rio Grande. South Of Amistad Reservoir, the river flows through several communities and irrigation districts on its way to International Falcon Reservoir. Downstream of Falcon Reservoir, the river again becomes a series of channels designed to move irrigation water to crops, return irrigation water to the river, and manage water flow during flood events.

The water quality in the basin changes drastically. Downstream from most of the urban areas, fecal coliform, nutrients, and toxic substances are elevated. In stretches of the river through Big Bend, downstream of Amistad and Falcon Reservoirs, San Felipe Creek, and Devils River, the water quality meets most USEPA standards. However, as irrigation return flows and sediment-laden waters re-enter the river, the water quality again declines (TNRCC, 1996).

Rio Grande Reservoirs

Three major reservoirs exist in the Rio Grande watershed: Elephant Butte Reservoir in New Mexico, International Amistad Reservoir on the Texas/Coahuila border, and International Falcon Reservoir on the Texas/Tamaulipas border.

Elephant Butte Reservoir was constructed in 1916. It currently stores 2,070,000 acre-feet of water and drains a land area of 83,100 square kilometers. The International Boundary and Water Commission (IBWC) constructed Amistad Reservoir in1969. The original storage capacity was 3,380,000 acre-feet and it currently drains land of over 403,000 square kilometers. The IBWC also constructed Falcon Reservoir in 1954. Falcon Reservoir's original storage capacity was 2,670,000 acre-feet and it drains 525,000 square kilometers of land (VanMetre 1997).

Demographics

In the early part of the twentieth century, people began migrating to the sister cities in the Rio Grande watershed. Growth rates in the basin soared due to increased investments in defense facilities in World War II, and in tourism, trade and manufacturing in the later part of the century (TNRCC, 1994).

In the 1960s, United States companies exploited inexpensive Mexican labor by developing subsidiary firms along the Mexican portion of the border. This foreign investment encouraged tremendous population growth from the migration of many people toward newly-available manufacturing jobs. Through the subsidiary firms, often called "maquiladoras," United States companies transported raw materials to Mexico, and then returned finished products to the United States for sale. Maquiladora development resulted in increased employment opportunities in the Mexican border region, but development encouraged over-migration to unprepared sister cities.

In the early 1990s, the United States and Mexico passed the North American Free Trade Agreement (NAFTA). NAFTA promised to deliver thousands of new jobs and prosperity to the United States/Mexico border region as it opened trade between the two countries. In anticipation of the new jobs, an increasing number of people again moved into the border region. While NAFTA and the maquiladora program improved employment conditions in the border region, the average annual income of border families remains far below national and state averages (TCPA, 1994). In fact, the 1990 census shows that the Rio Grande watershed contains nine of the ten poorest counties in Texas, and two of the poorest counties in the nation (TNRCC, 1994).

One unfortunate result of the poorer conditions in the basin is the substandard living conditions for several basin residents. Along the border these conditions are referred to as "colonias." Colonias lack the most basic infrastructure needs, including water and wastewater treatment, sewerage and drainage systems, garbage services, public transportation, and even electricity. Based on promises given by developers, colonia residents purchased property with the expectation that developers would install infrastructure. For colonia communities, these promises remain unfulfilled. Currently almost 300,000 people in the Rio Grande basin live in colonias (TWDB, 1992).

Historically colonia residents lacked the political power to solve the infrastructure problem; however, in the last five years many state agencies began loaning money to communities to construct basic facilities like water and wastewater treatment.

The economic difficulties in the watershed – especially in the Lower Rio Grande Valley – translate into stressed environmental conditions and provide potential human exposure routes to contaminants. Because the sister cities have not kept pace with the population growth, the capacity of the wastewater treatment facilities in the basin, especially in the border region, does not meet the requirements for the surrounding communities. In fact, from El Paso/Ciudad Juárez downstream, several untreated sewage streams enter the river. Until the construction of the new wastewater treatment facility in Nuevo Laredo in 1995, hundreds of thousands of gallons of untreated sewage per day were entering the Rio Grande in Nuevo Laredo alone. Untreated wastewater is not just a Mexican issue—several of the United States cities along the border also inadvertently discharge untreated sewage through infiltration of the sewerage system and from colonias.

In relationship to this thesis, two points are especially troublesome. First, with the continued growth in the region comes increased demand for drinking water. Surface waters supply the vast majority of drinking water needs in the basin; therefore, the basin's population depends both on the capacity of the reservoirs to store water, and on the reservoir's inherent ability to "cleanse" water through sedimentation. According to the USGS, however, the rate of sedimentation in Amistad Reservoir exceeds the national average ten times over (USGS, 1997). Therefore, the life expectancy of Amistad Reservoir may be significantly less than originally projected without dredging. If the IBWC is forced to dredge the reservoir to preserve its life expectancy, the activity will resuspend the contaminants originally deposited at the reservoir's bottom.

Second, many of the basin's residents along the border rely on subsistence fishing to supplement their diets. The majority of fish available, especially in the Lower Rio Grande Valley, are bottom-dwelling species. These fish are particularly susceptible to consumption of contaminants in sediment. Therefore, the economic conditions in the basin potentially support a direct human exposure-route to the metals found in the riverbed sediment.

Monitoring and Assessment of Sediment Quality

The first steps toward understanding the impact of metals contamination in sediment in the Rio Grande include assessing the extent of contamination, determining the impact to the surrounding biota, and isolating potential sources of contamination. A typical monitoring approach for determining sediment contamination would involve a sample of sediment, a collection of benthic organisms near the site, a water-quality sample, and a compilation of permitted and unpermitted activities near the sampling site. Generally the monitoring will also include fundamental measurements like flow, pH, and suspended sediment.

Texas's Monitoring Approach in the Rio Grande Basin

The TNRCC's approach to sediment-quality monitoring changed significantly between 1966 and 1996. Sediment sampling became part of the state's standard sampling protocol in the early 1970s. Originally, the agency monitored a few sites in the Rio Grande annually. The United States Geological Survey (USGS) limited their sediment sampling to special studies, and the International Boundary and Water Commission (IBWC) performed little or no sediment sampling in the basin. By the 1990s, TNRCC expanded their sampling to include special studies, and signed agreements with IBWC and USGS to monitor sediment quality jointly. Currently TNRCC limits the majority of its sediment sampling to annual samples at sites targeted to demonstrate ecological impacts for permitted facilities or for special studies. The TNRCC plans to expand their monitoring protocol in the middle portion of the Rio Grande basin to support more extensive monitoring at several sites, including biological and fish tissue monitoring in conjunction with sediment sampling. TNRCC gathered sediment information during the first two phases of their Binational Toxic Substances Study (See the "Literature Review" chapter for further discussion of this study).

Analysis of the sampling data indicates that none of the agencies responsible for water quality monitoring in the Rio Grande monitor the water with any guaranteed frequency either currently or in the past except at a very few isolated sites (see the "Data Analysis" chapter for further discussion on the historical data). The agencies collected data at only two sites in the basin consistently throughout the study period–one near El Paso and the other in the Arroyo Colorado subwatershed in the Lower Rio Grande Valley. Both of these sites are located near significant permitted activities and are likely designed to determine the impact of specific activities on the surrounding ecosystem, not to comprehensively assess conditions throughout the basin.

Traditional sediment sampling in the basin did not assess the impact of the metals concentration – just the concentration itself. In the later part of the study period, the agencies began collecting more tissue and biologic information in response to the United States Environmental Protection Agency's (USEPA) guidance to include this monitoring as part of the statewide water-quality assessment.

In the future, other types of monitoring need to be conducted to establish a link between sediment quality and environmental and human health impacts. To date, no monitoring has absolutely confirmed or denied a link between sediment and human health; however, biological monitoring had demonstrated ecological impacts (USEPA, 1997).

Assessment of Metals in Sediment

The second step toward understanding the consequences of metals in sediment is to perform an assessment of the data. A truly comprehensive assessment of sediment quality should include an analysis of trends in sediment quality over time, an investigation of the relationship of concentrations versus influencing factors like flow, pH, and total organic carbon, a determination of the impact of the sediment quality on the biologic communities, and an examination of potential sources of contamination.

Historically the USEPA did not require agencies to perform comprehensive sediment assessments as part of the routine Clean Water Act (CWA) reporting; therefore, many agencies simply reported "snapshots" of sediment conditions. In 1997 for the first time the USEPA performed a preliminary sediment inventory for the entire United States. The USEPA relied on sediment information that agencies report to the nationwide STORET database. The USEPA screened all available sediment quality information against a set of proposed sediment criteria for exceedances and reported general areas of concern based on these exceedances. One discovery made during this assessment was that the STORET data did not represent conditions throughout watersheds, but rather represented sediment conditions in land use conditions the agencies already expected to be contaminated.

The USEPA's sediment inventory demonstrates the need to have additional tools to improve the inventory process. One of the most important tools available to expand the analysis is a geographic information system.

What is a Geographic Information System?

Geographic Information Systems (GIS) connect data to a physical location. With this information, the GIS analyst answers complex questions and performs detailed analysis not available with other computer systems. For example, a statistician can determine relationships between monitoring station numbers (under the assumption that the monitoring entity numbered the stations from upstream to downstream) and observe concentrations in arsenic. A GIS analyst instead can analyze the relationship between the monitoring site's physical location and the observed concentration. The spatial abilities provided by the GIS add significant dimension to the scientist's attempts to understand the environment.

The true power of the GIS comes in its ability to combine different types of information into one system. The GIS uses two different data types: vector and raster. Vector information represents physical space through a series of points, lines, and shapes. For example, a map of a city in the GIS would show lines for streets, polygons for buildings, and points for stop signs. Raster data on the other hand describes physical space by placing a grid over the information and showing data within each box and representing information within the box with a value. For example, raster data could include a photograph of a city with each grid cell containing a pixel or color value.

The GIS can compare several different layers of information to provide a detailed analysis. If a person were trying to choose a location for a new home, they could compare data layers of streets, neighborhoods, school locations, parks, grocery stores, property tax rates, and employment location, to determine the best areas to target the search.

GIS and the Rio Grande Basin

Compiling a GIS for the study of sediment transport in the Rio Grande proved much more challenging than originally anticipated. First, the entire Rio Grande watershed covers over 860,000 square kilometers. Representing such a large area requires extensive storage capacity in the computer system for all of the data layers used and substantial computing power to perform any analysis on the data. Second, the watershed is international; therefore, data between the countries was not necessarily compatible. Third, because the data from the southern portion of the basin is Mexican, international agreements allowing use of the data needed to be in place (accomplished through IBWC, TNRCC, the USGS, the Mexican Institute of Water Technology (IMPTA), the Mexican National Water Commission (CNA), and the Mexican International Boundary and Water Commission (CILA)).

Finally, because the research for this thesis began in conjunction with three other studies within the Rio Grande watershed, it became necessary to wait for the completion of the other studies before beginning the GIS analysis because data from these studies was necessary to complete the analysis. This waiting period proved a substantial delay.

Despite the challenges, however, a basic GIS for the Rio Grande watershed now exists. The fundamental data layers for the sediment transport model include land use, land cover, elevation, flow, climate, monitoring sites, geology, and soils. Attribute information is also linked to the GIS data (e.g. water-quality data associated with the location of the monitoring site) so that more detailed analysis can be performed. From these original layers, several new layers were created, including flow direction, flow accumulation, slope, aspect, Manning's coefficient, and water balance. Combined, these data layers form the foundation of the sediment model.

Before beginning development of the sediment transport model, it was necessary to first determine what models and studies already existed in the basin. The Literature Review chapter discusses the results of the review of previous studies.

Literature Review

The Literature Review section focuses on four important considerations for developing the sediment transport model: other water quality and sediment analyses performed in the study area, the potential health effects of the metals of concern, potential sources of metals in the environment, and available sediment transport models.

Previous Applicable Studies in the Rio Grande Watershed

Environmental conditions in the Rio Grande watershed inspired many researchers to perform studies over the last fifty years. Hundreds of papers touch upon issues related to this thesis—especially because in the last ten years many "politically motivated" studies focused on the Rio Grande. As "environmental justice", "sustainable development", and "holistic ecosystem analysis" became fashionable, many entities saw opportunities to leverage funds for their projects on the Rio Grande "gravy train". Because a sociologist could develop a separate thesis on the dynamic of proliferating so many "socially relevant" studies in the Rio Grande watershed, this thesis limits discussion of applicable studies to those that meet strict criteria. The study must directly relate to sediment quality in the Rio Grande, end within the last two years, and be conducted by a governmental entity.

Rio Grande Assessment of Water Quality

The TNRCC completed three regional assessments of water quality under the TCRP since 1992. Each of these assessments performed basic screening level analyses of water quality, sediment, and fish tissue for the portion of the Rio Grande basin that resides in Texas. The assessments relied on ten years of data, and in general did not evaluate trends in metals. The screening analysis determined whether a constituent was a "concern", "possible concern", or "no concern", or that there was insufficient data for the analysis[2]. Figures 2, 3, and 4 illustrate the results of the CRP assessment.

[2] A "concern" for toxic substances is defined as three or more values exceeding the screening levels for aquatic life and are above the Minimum Analytical Level (MAL), or, the 10-year average concentration exceeds the secondary screening levels for human health and is above the MAL. A "possible concern" is defined as one or two values exceeding the screening levels for aquatic life and are above the MAL (TNRCC, 1994).

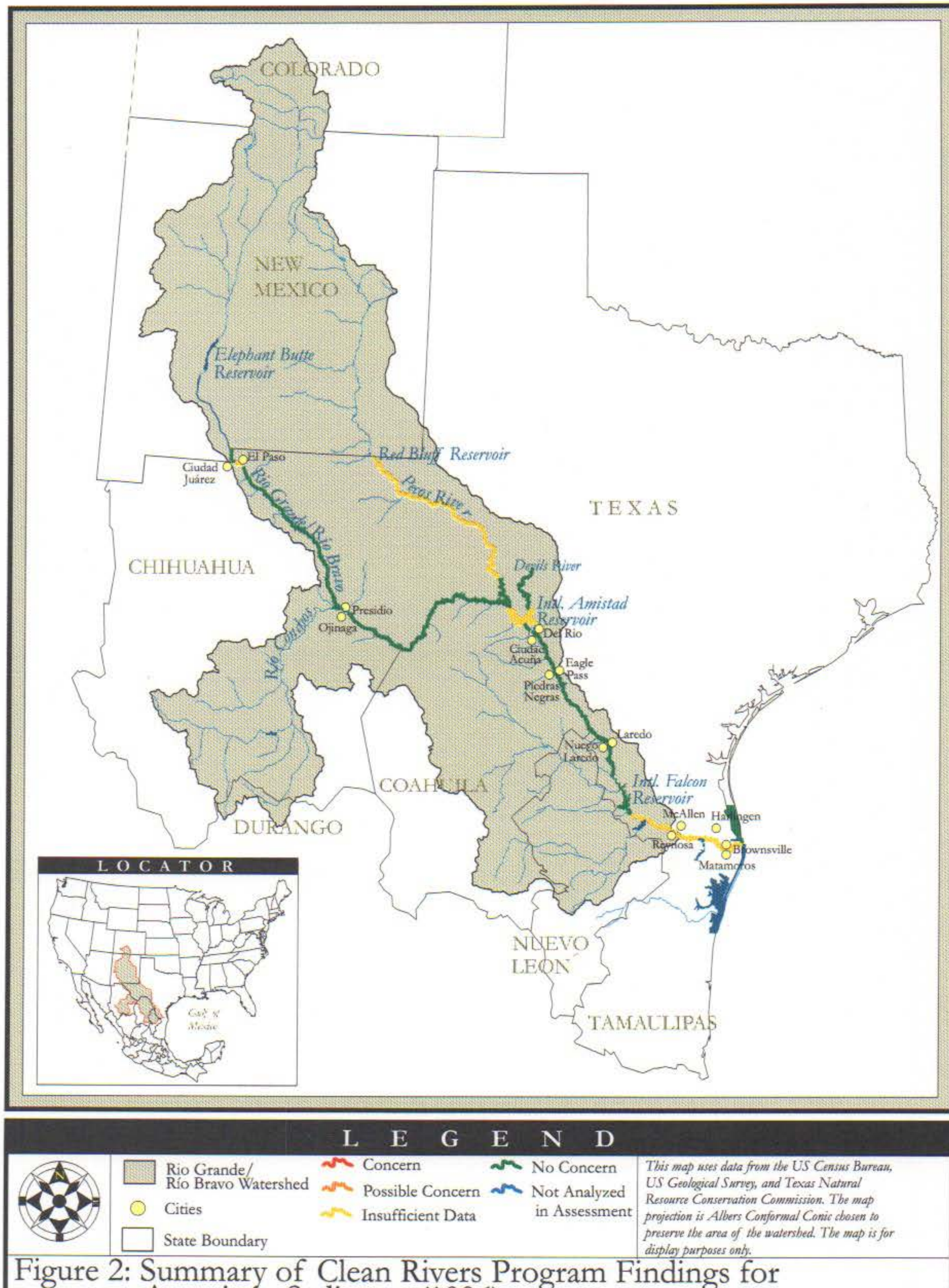

Figure 2: Summary of Clean Rivers Program Findings for Arsenic in Sediment (1996)

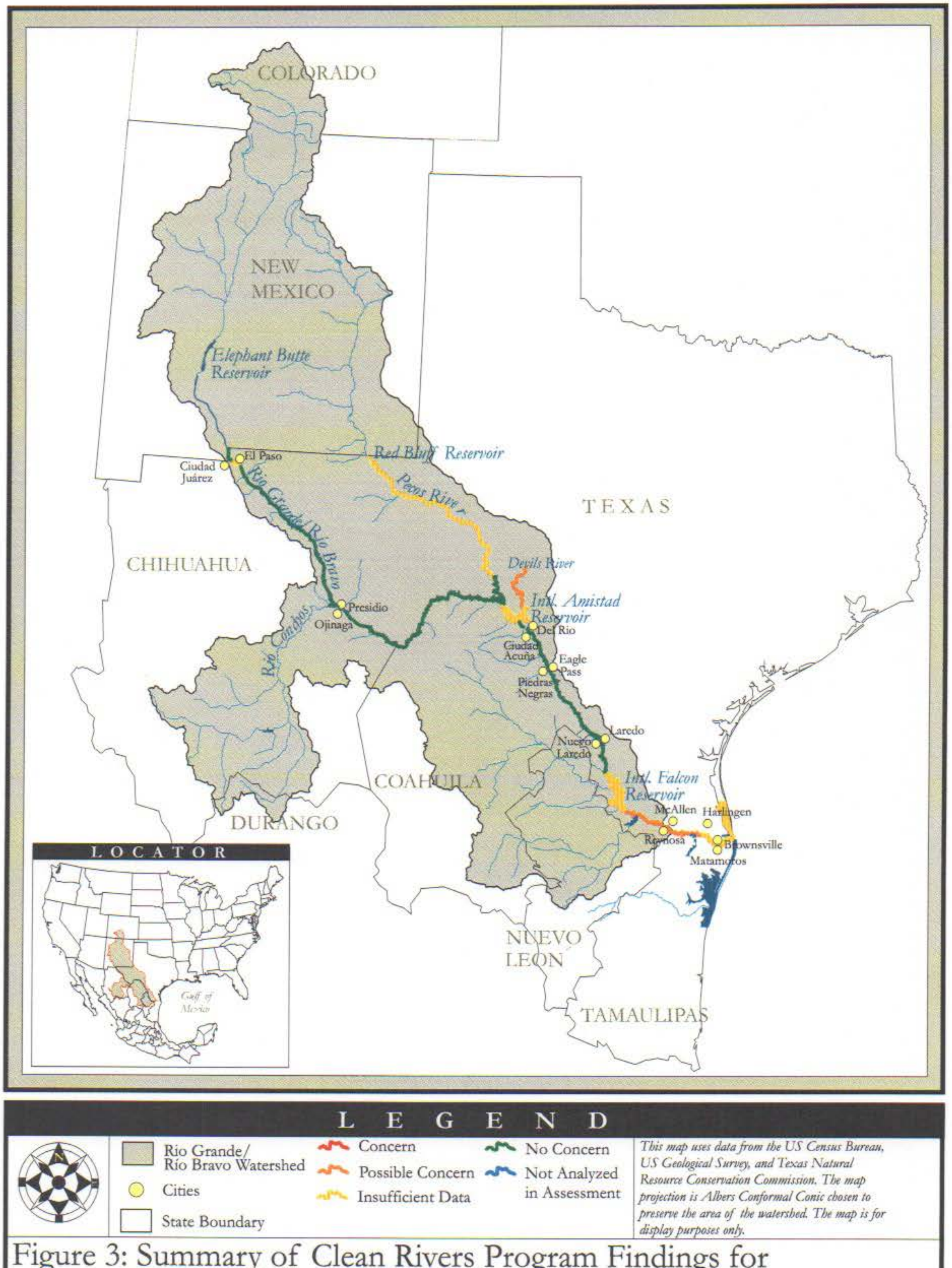

Figure 3: Summary of Clean Rivers Program Findings for Lead in Sediment (1996)

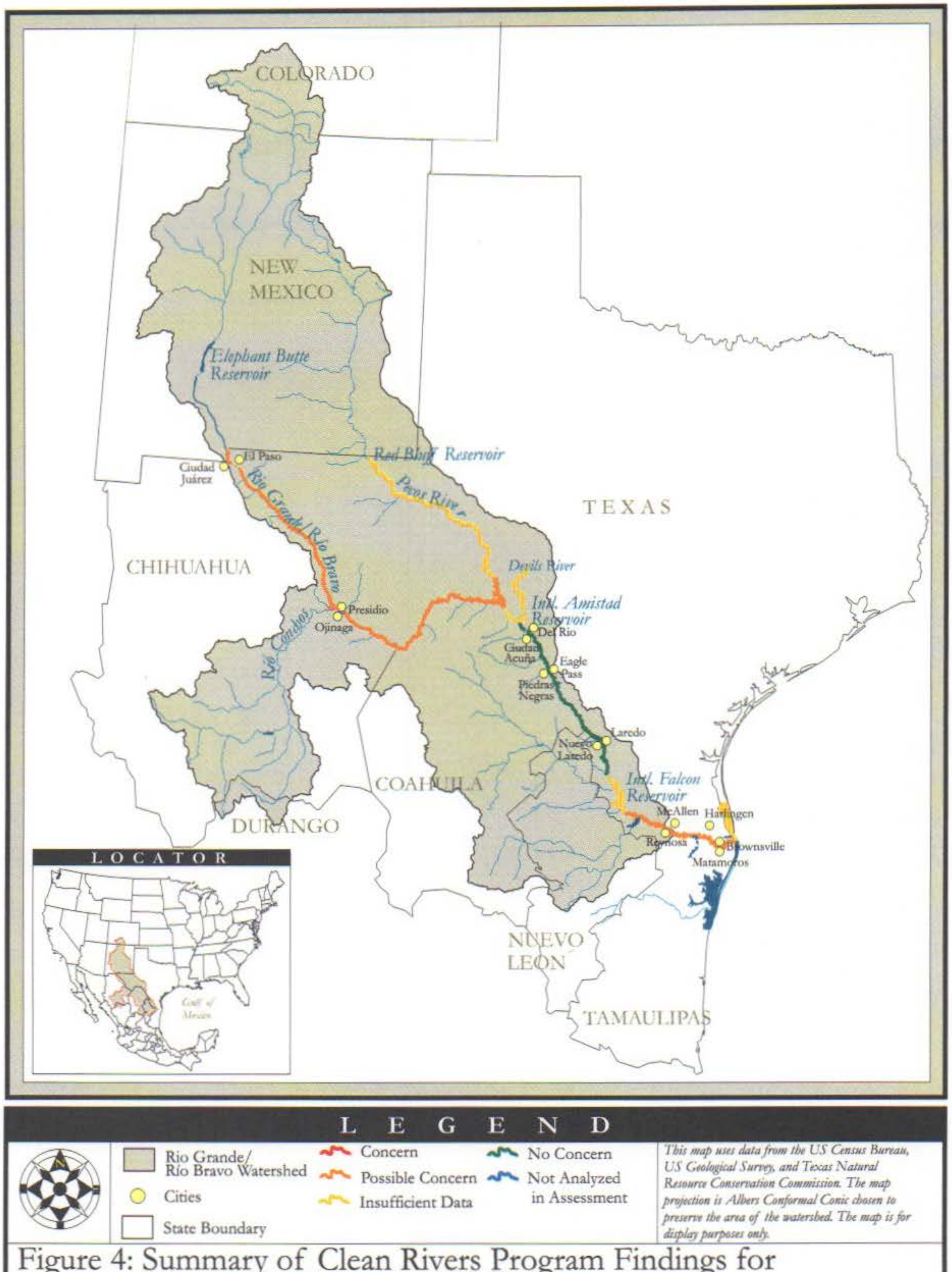

Figure 4: Summary of Clean Rivers Program Findings for Mercury in Sediment (1996)

Binational Toxic Substances Study Phases I and II

The TNRCC, IBWC, CILA, and USEPA conducted two phases of a multi-phased study, called the Binational Toxic Substances Study (BTTS), to assess the impact of toxic chemicals in the Rio Grande basin. TNRCC led the effort by coordinating all of the fieldwork and analysis. The TNRCC performed the fieldwork for Phase I of the analysis between November 1992 and March 1993, and resampled for Phase II between May and December 1995. The environmental analysis included water, sediment, fish tissue, biological, and toxicity testing. The two phases of the Toxic Substances Study compiled a good first level screening analysis of the conditions in the basin. The analysis of the samples showed several instances of arsenic, lead, and mercury exceeding state and federal water and fish tissue standards, and several sediment samples exceeded proposed sediment standards (TNRCC, 1998). Table 1 shows the sites that exceeded standards.

Table 1: Summary Sites from Toxic Substances Study Phase I and Phase II Exceedances[3]

	Phase I									Phase II								
	Water			Sediment			Fish			Water			Sediment			Fish		
Site	As	Hg	Pb	As	Hg	Pb	As	Hg	Pb	As	Hg	Pb	A s	Hg	Pb	As	Hg	Pb
0.5-Montoya Drain (El Paso)										✓					✓			
1-Rio Grande at Courchesne Bridge (El Paso)										✓					✓			
1.1-Rio Grande upstream of Haskell wastewater outfall										✓			✓	✓	✓			
1a-Haskell wastewater outfall (El Paso)	✓									✓								
2-Rio Grande at Zaragosa Bridge (El Paso)				✓	✓	✓			✓	✓					✓			
2a- Discharge Canal (Ciudad Juárez)				✓	✓					✓			✓	✓				
3-Rio Grande at Rio Conchos confluence				✓						✓			✓					
3a-Rio Conchos .2km upstream from confluence with Rio Grande	✓			✓				✓					✓		✓			
3a.1-Rio Conchos 25km upstream from confluence w/ Rio Grande										✓			✓					
3b-Alamito Creek (Presidio)	✓																	
4-Rio Grande downstream of Rio Conchos	✓			✓				✓		✓			✓		✓			
5-Rio Grande at Santa Elena Canyon (Big Bend)	✓			✓				✓		✓			✓					
5a-Terlingua Creek				✓														
5b-Rio Grande at Lozier Canyon				✓														
6-Rio Grande near Langtry								✓										
6a-Pecos River																		
6b-Devils River																		
6.1-Amistad Reservoir in Rio Grande Arm										✓			✓				✓	
6.2-Amistad Reservoir in Devils River Arm										✓			✓			✓		
7-Rio Grande upstream of Del Rio/Ciudad Acuña								✓										
7a-Arroyo Las Vacas (Ciudad Acuña)																		
7b-San Felipe Creek 1.8km upstream from confluence with Rio Grande								✓										
7b.1-San Felipe Creek in Del Rio													✓					

[3] Shaded boxes show sites not sampled during the phase. Checkmarks indicate sites which exceeded either state, federal or proposed standards. At the time of drafting, the second phase of the BTTS was in final revision at TNRCC.

	Phase I									Phase II								
	Water			Sediment			Fish			Water			Sediment			Fish		
Site	As	Hg	Pb	As	Hg	Pb	As	Hg	Pb	As	Hg	Pb	As	Hg	Pb	As	Hg	Pb
7b.2-San Felipe Creek 6km upstream from confluence with Rio Grande																		
8-Rio Grande downstream of Del Rio/Ciudad Acuña																		
8a-Pinto Creek																		
8b-Rio San Diego																		
8c-Las Moras Creek																		
8d-Rio San Rodrigo																		
8e-Maverick Canal																		
9-Rio Grande upstream of Eagle Pass/Piedras Negras							✓	✓	✓									
9a-Unnamed Tributary downstream of Piedras Negras	✓									✓								
9b-Rio Esscondido							✓	✓										
10-Rio Grande downstream of Eagle Pass/Piedras Negras							✓			✓			✓			✓		
10a-Manadas Creek										✓			✓		✓			
11-Rio Grande at Laredo/ Nuevo Laredo																✓	✓	
11a-Zacate Creek (Laredo)										✓			✓		✓			
11b-Chacon Creek (Laredo)										✓			✓		✓			
11b.1-Zacate Creek wastewater outfall (Laredo)										✓								
11b.2-Southside wastewater outfall (Laredo)										✓								
11b.3-Riverside wastewater collection system (Nuevo Laredo)										✓								
11c-Arroyo el Coyote (Nuevo Laredo)	✓									✓			✓	✓	✓			
12-Rio Grande in Laredo/ Nuevo Laredo 13.2 km downstream of US 81								✓		✓					✓			
12.1-Rio Grande in Laredo/Nuevo Laredo 25km downstream of US 81										✓								
12.2-Falcon Reservoir at headwaters										✓			✓		✓			✓
12.3-Falcon Reservoir at dam										✓					✓			
12a-Rio Salado																		
12b-Rio Alamo (Ciudad Mier)																		

Site	Phase I									Phase II								
	Water			Sediment			Fish			Water			Sediment			Fish		
	As	Hg	Pb	As	Hg	Pb	As	Hg	Pb	As	Hg	Pb	As	Hg	Pb	As	Hg	Pb
12c-Rio San Juan (Camargo)																		
12d-Arryo Los Olmos (Rio Grande City)										✓								
12e-Puertecitos Drain (Ciudad Dias Ordaz)																		
13-Rio Grande upstream of Anzalduas Dam								✓		✓			✓		✓			
14-Rio Grande downstream of Anzalduas Dam				✓				✓		✓			✓		✓			
15-Rio Grande in Reynosa								✓		✓			✓		✓			
15a-Anhelo Drain	✓									✓								
16-Rio Grande downstream of Las Milpas								✓		✓			✓					
17-Rio Grande in San Benito								✓		✓			✓		✓			
18-Rio Grande downstream of Brownsville/ Matamoros										✓			✓		✓			
C1-Rio Grande downstream of Brownsville/ Matamoros (100m from 18)								✓										
C2-Mouth of Rio Grande	✓																	
C3-Gulf of Mexico in Rio Grande Delta	✓						✓											
C4-Laguna Madre at Brazos Santiago Pass	✓																	
C5-San Martin Lake near Brownsville Ship Channel	✓							✓										
C6-Arroyo Colorado near Port of Harlingen								✓										
C7-Arroyo Colorado near mouth	✓						✓		✓									
C8-North Floodway	✓																	

Toxicity tests conducted at several sites during the study demonstrated toxic effects from sediment at two sites: stations 2 (100% mortality) and 2a (70% mortality). While the toxicity tests did not isolate impacts from individual chemicals, it is important to note that lead exceeded proposed sediment standards at station 2, and mercury and arsenic exceeded the same standards at station 2a.

The BTTS classified all chemicals found in the samples in four priority groups: high (exceeded screening levels throughout basin in the Rio Grande), medium (exceeded screening levels at multiple tributary sites), low (exceeded screening levels at one site), and no priority (no screening level exceedances). Based on the priority scale, the BTTS classified arsenic, lead, and mercury as high-priority pollutants in the basin.

The TNRCC also collected biological samples at several sites along the mainstem of the Rio Grande and compared the observed impacts to the levels of water and sediment contamination. Several non-random changes in the biological community were noted, including a statistically significant negative correlation between the presence of arsenic in sediment and the impact to the benthic community.

While the BTTS did not provide sufficient information to determine trends, the first two phases did provide a good snapshot of the environmental conditions in the Rio Grande Basin.

USGS Sediment Coring

To look at the long-term trends in sediment quality in the Rio Grande, the USGS, TNRCC, United States Bureau of Reclamation, and the El Paso Water Conservation and Improvement District No. 1 conducted a sediment coring study of the three major reservoirs in the Rio Grande watershed. The USGS analyzed sediment cores from each of the reservoirs to determine long-term trends in sediment quality since the construction of the reservoirs.

The study included an analysis of both organic and inorganic toxic substances. The scientists dated the cores using a simple correlation with the trend in cesium over time and in the depth of the core. While the analysis demonstrated several interesting trends in chemicals in all three reservoirs, the elements of most interest to this thesis are the trends in Amistad Reservoir. The study showed statistically significant increasing trends in concentration in the sediment core for arsenic, lead and mercury (Spearman's rank correlation of 95-percent confidence) in the Rio Grande arm of the reservoir. Arsenic and mercury also showed increasing trends in the Devils River arm of the reservoir; however, lead in this section decreased over time. The USGS attributed the decreasing lead concentrations to the cessation of use of leaded gasoline in United States in the 1970s. It is important to note, however, that the decreasing trend in lead is not as significant as those observed in other reservoirs across the nation. The USGS attributed this difference between Amistad Reservoir and other domestic reservoirs to the continued use of leaded gasoline in Mexico (VanMetre, 1997).

While the levels of mercury in Amistad Reservoir did not exceed the proposed USEPA sediment standards, the USGS noted that the trend in mercury both increased over time and correlated well with the development of industries in the basin. Specifically, the trends in mercury changed substantially at the same time the coal burning Carbon I and Carbon II plants came online in Mexico. The USGS did not assert that these coal-burning facilities directly caused the mercury trends, merely that significant changes in the mercury trends occurred at the same time each of these plants opened.

The USGS study also investigated the rate of sedimentation in the reservoirs. The rate of sediment deposition in Amistad Reservoir is nearly ten times the national average for other reservoirs. Therefore, the estimated life expectancy of Amistad Reservoir will be significantly less than its design without future dredging.

USGS Sediment Study

In 1996, USGS conducted a second study to complement their sediment coring analysis. Using data from 1976 through 1996, the USGS screened monitoring samples for the presence of toxic substances throughout the Rio Grande Basin. Because most toxic chemicals adhere to suspended sediments and eventually settle onto riverbeds or on the bottom of reservoirs, the USGS limited their study to sediment quality. For sediment samples that exceeded screening levels, the USGS also conducted preliminary trend analyses (Table 2) (Lee, 1997).

Table 2: Results of USGS Sediment Analysis
Temporal Trends in Arsenic, Lead, and Mercury

Location	Arsenic	Lead	Mercury
Rio Grande at El Paso	⇧		⇧
Rio Grande Below El Paso	⇧		
Rio Grande at Fort Quitman	⇧	⇧	
Rio Grande at Río Conchos	⇩	⇩	
Rio Grande above Amistad Reservoir			⇧
Pecos River at Red Bluff Reservoir			⇧
Pecos River below Red Bluff Reservoir			⇧
Amistad Reservoir			⇧
Rio Grande below San Felipe Creek			
Rio Grande at Eagle Pass			⇧
Rio Grande at Laredo		⇧	⇧
Falcon Reservoir	⇩		
Rio Grande near McAllen			⇧
Rio Grande at Brownsville			⇧

The USGS investigated all trace elements for which they observed values over detection limits. Of the trace elements, arsenic, lead, and mercury measurements above the detection limit were the most prevalent in the basin. The USGS study provided the impetus for selecting arsenic, lead, and mercury for further investigation by screening all trace elements for those with the most usable and extensive data.

This thesis partially replicates the study conducted by USGS by re-screening all samples for arsenic, lead, and mercury. However, this thesis goes one step further by performing several analyses for correlation between sediment values and other constituents and by relating the observed values to a sediment transport model.

Rio Grande Modeling Studies

A review of the literature revealed few applicable modeling studies in the Rio Grande basin. In general, most studies in the basin were instream models designed to simulate the transport and decay of contaminants within the stream itself – not throughout the basin. One model was particularly applicable to this thesis: a basinwide Soil and Water Assessment Tool model performed by the Texas Agriculture Experiment Station.

The Texas Agriculture Experiment Station (TAES) worked with the TNRCC to compile the data necessary for running the Soil and Water Assessment Tool (SWAT) model in the Rio Grande basin. The university worked with the Mexican Institute of Water Technology (Instituto Mexicano de Tecnología del Agua (IMTA) and Mexico's National Research Institute for Forestry and Agriculture (Instituto Nacional de Investigaciones Forestales y Agropecuarias (INIFAP) to compile many of the basic GIS layers necessary for running the SWAT model. These layers included soils, elevation, and land use.

Preliminary results from the SWAT model illustrate many of the difficulties with using such a comprehensive model in an international and large watershed (see the section titled "Existing Sediment Transport Models" for further discussion of the SWAT model). The most important lesson from the TAES's inability to complete the SWAT model for the Rio Grande is the difficulty in comparing data between the United States and Mexico. For example, the TAES attempted to define a homogeneous soils data set between the two countries by redefining the Mexican soils classified with the Food and Agricultural Organization's (FAO) classification into the STATSGO classification. This process involved many assumptions with the data that added significant error to the model, including assuming certain levels of porosity, erodibility, and water content with the FAO classification. The modelers also assumed pesticide application rates associated with certain land uses and vegetative cover. Because the SWAT model is so comprehensive, these assumptions dramatically swayed the model's results and prohibited the scientists from developing an accurate picture of the dynamics of the basin.

The studies performed by the USGS, TNRCC, and TAES laid the foundation for conducting sediment transport modeling in the basin; however, they did not completely fulfill this mission. Instead, each of the above-mentioned studies highlights the difficulty in assessing an international watershed.

Health Effects and Exposure Routes

Given the difficulty in assessing sediment quality in large, international watersheds, it is important to understand the motivation for performing such complicated and expensive analyses. The ultimate reason for analyzing metals in the environment is to tie the presence of the metals to potential environmental or human impacts. Even in the presence of potential environmental consequences, regulatory agencies rarely perform rigorous monitoring and assessment of situations without potential health effects to humans.

To emphasize the importance of sediment monitoring and modeling, this thesis focuses on three metals that are known to cause health effects as a result of chronic or acute exposure. Generally, federal and state regulations are designed to limit potential impacts from pollutants entering the environment; however, sediment standards do not currently exist in the United States. Therefore, the health effects noted in the following discussion are those typically associated with chronic or acute exposure, not health effects due to sediment contamination.

Toxicological Assessment of Arsenic, Lead, and Mercury

For regulatory purposes, scientists tend to assess the toxicological impact of chemicals in two phases: the impact of chemicals on the environment and the impact of the chemicals on humans. While several metals contribute to the proper functioning of organisms at low levels, all metals become toxic at high concentrations. As noted by Luoma, many species live on the fine line between healthy and toxic doses of metals:

> *For a number of metals, the difference between the required concentration and the toxic concentration is very small. Many aquatic organisms live perilously close to the threshold of trace metal toxicity, even in environments unperturbed by man (Luoma, 1985).*

Because many species thrive on a delicate balance of metals in their environment, determining the impact to the aquatic environment from metals contamination in sediment can be difficult.

Health Effects-Aquatic Life

Two primary mechanisms exist for determining the impact of chemicals found in sediment on the surrounding environment: toxicity testing and biological assessment. Simply determining bulk sediment chemistry measures does not indicate levels of toxic effects. For example, the USEPA discusses the relationship between toxicity and binding behavior in their *National Sediment Inventory*:

> *Similar concentrations of a chemical can produce widely different biological effects in different sediments. This discrepancy occurs because toxicity is influenced by the extent to which chemical contaminants bind to other constituents in sediment. The other sediment constituents, such as organic ligands and inorganic oxides and sulfides, are said to control the bioavailability of accumulated contaminants (EPA, 1997).*

USEPA's proposed sediment criteria rely heavily on toxicity testing to assess the actual impact from sediment contamination rather than simply assessing the concentration of a chemical in sediment. Toxicity testing requires agencies to expose an indicator organism like fathead minnows to water mixed with the sediment sample. Mortality of the indicator species is then measured after a certain period. The mortality of the indicator species relates directly to the expected impact on aquatic and benthic communities from the sediment contamination.

Biological assessment provides significant insight into the impact of sediment contamination on the surround aquatic and benthic communities. Scientists will evaluate the diversity of species, analyze the contaminate levels in the organisms, and observe any birth defects or lesions. The combination of the biological assessment with the analysis of sediment contamination effectively demonstrates the impact of sediment contamination on the aquatic community.

Many aquatic species spend a significant portion of their life living in or on aquatic sediments. By feeding on the sediments, these organisms provide a pathway for chemicals to be consumed by higher aquatic life and wildlife, avian species, and humans (Adams, 1992). Some aquatic health effects related to sediment contamination from arsenic, lead, and mercury include loss of species diversity, lesions, birth defects, and decline in number of bottom-dwelling fish (TNRCC, 1998).

Health Effects-Public Health

The primary public health concern from metals in sediment is the bioaccumulation of these metals in fish tissue. As fish feed on the bottom of a riverbed or reservoir they inadvertently consume metals in the vegetation, sediment, or in smaller animals. These metals accumulate in the fishes' tissue over time and then can pass to human tissue where they can again accumulate. To date, no study directly linked a particular concentration of metal in the sediment with a particular concentration of metal in human tissue, so no direct correlation can be made between the two. However, health effects from consuming metal-contaminated fish have been documented (VanMetre, 1997; USEPA, 1997).

The biologic cycle for metals in sediment includes bioconcentration of metals by vegetation and bioaccumulation of metals by animals. For persons in the general population, food sources represent the primary exposure to metals in sediment (Klaassen, 1986). Most sediment-related human exposure to contaminants is through indirect routes that involve the transfer of pollutants out of the sediments and into the water column or aquatic organisms (EPA, 1992).

Toxicity of Arsenic

Arsenic negatively impacts mitochondrial enzymes and impairs tissue respiration. Large doses of arsenic may be acutely fatal. The symptoms of acute arsenic exposure include fever, anorexia, hepatomegaly, melanosis, and cardiac arrhythmia with electrocardiograph changes that may signal eventual cardiovascular failure. Acute exposure also manifests respiratory, peripheral neuropathy, gastrointestinal, cardiovascular, and hematopoietic effects. Chronic exposure injures the liver (from jaundice to cirrhosis and ascites). Peripheral vascular disease (gangrene) may also result (Klaassen, 1986).

Studies demonstrated that chronic exposure to arsenic through drinking-water has resulted in tumors on the liver and lesions (Popper, 1988). People who inhale arsenic at work through arsenic-containing pesticides and copper smelts demonstrate increased lung cancer mortality. Chronic arsenic exposure is also linked to skin cancer and lung cancer (Klaassen, 1986). Arsenic also interferes with DNA repair mechanisms in dermal cell cultures. No reproductive effects in humans have been found.

Toxicity of Lead

Unlike other toxic metals, lead is not a necessary part of the biological cycle. This is particularly interesting since lead is the most prevalent of all of the toxic metals. Most acute exposures to lead are environmental, including indoor lead-paint, combustion of lead-containing gasoline and other combustibles, and industrial emissions. According to studies, lead is so common that most food and drinking water now contain it (Klaassen, 1986).

The nervous system is the most commonly affected part of the human body as a result of chronic or acute lead exposure. Acute exposure to lead can result in motor dysfunction, encephalopathy or peripheral neuropathy in the central nervous system. People suffering from encephalopathy also experience cerebral edema, an increase in cerebral spinal fluid pressure, and/or proliferation and swelling of endothelial cells in capillaries and arterioles.

Lead-induced anemia induces hemotologic effects. The renal (kidney) effect is two-fold: reversible renal tubular dysfunction as a result of acute exposure, and irreversible chronic interstitial nephropathy as a result of lead toxicity.

Studies also indicate that lead induces cancer in rodents when they are directly fed significant volumes of lead; however, evidence that lead is carcinogenic in humans is limited (Klaassen, 1986).

Severe lead toxicity leads to sterility, spontaneous abortion, and neonatal morbidity and mortality. Lead toxicity is also enhanced by dietary deficiencies in calcium and iron and possibly zinc. Given the diets commonly associated with the poorer communities in the Rio Grande basin, it is reasonable to assume a lack of calcium, iron, and zinc in the communities' diets.

Toxicity of Mercury

Exposure to mercury causes diverse toxicological effects. Mercury appears in three forms: elemental, inorganic, and organic. Metallic mercury can be oxidized to inorganic divalent mercury, particularly in the presence of an aquatic environment. Divalent mercury can convert to dimethyl mercury by anaerobic bacteria and diffuse into the atmosphere. This will return to earth as deposition, and can be taken up by fish.

Inorganic mercury attacks the kidneys and organic mercury attacks the brain. The most common exposure route to mercury is as mercury vapor, however, ingestion of methyl mercury is the most likely exposure route for mercury bound to sediments. The major consequences of ingestion of mercury include degenerative impacts to the cerebral cortex and lesions in the central nervous system (Klaassen, 1986).

Bioavailability

The fact that not all metals in sediment are available for uptake by organisms complicates the task of setting standards for regulation of sediment quality. This effect of "bioavailability" means that high concentrations of metals do not necessarily signify a high chance of contamination in benthic organisms (Rood, 1995). The chemical composition of the sediment, the iron content of water, and the pH of the digestive tract of the organisms feeding on the sediment all contribute to the availability of the metal to the feeding organism.

> *More subtly, organisms also appear to generally avoid the geochemical forms of trace metals that are most abundant, employing the geochemical complexity of metal reactions in aquatic environments as a buffer to avoid the potential toxic effects of those metals. Because many biological systems exist at the margin of metal toxicity, the physical and geochemical redistribution of metals in aquatic environments by human activities has a strong potential to disrupt aquatic ecosystems (Luoma, 1985).*

In addition to the effects of environmental conditions, the nature of the metals also affects bioavailability. Metals that exchange rapidly (e.g. arsenic) are accumulated by organisms less efficiently than metals that exchange slowly (e.g. mercury). The effect of the metal on the organism also depends on whether the metal is essential or not. The uptake of nonessential metals correlate more with the concentration of the metal in sediment than do essential metals (Luoma, 1985).

Exposure Routes and Mechanisms of Uptake

Many benthic and invertebrate organisms uptake metals in sediment through diffusion. The metal interacts with a carrier molecule and is absorbed into the organism. Diffusion is especially effective with metals that are lipid-soluble (e.g., mercury). Other organisms uptake by endocytosis (engulfment)—a process similar to digestion. Endocytosis works particularly well with lead. Other digestive processes can contribute to uptake, relying on amino acids to transport metals throughout the organism. One important factor in digestion of metals is the pH of the organism's digestive tract:

> *Lower pH, longer digestive times, and great digestive efficiency might be expected in upper trophic level and air-breathing organisms (since the latter must rely on food for calcium). High concentrations of some metals (e.g., mercury) occur in large predatory fish and in air-breathing animals linked to aquatic food chains. However, biomagnification through several trophic levels, which could result from rigorous extraction of metals during digestion, has not been observed for most metals (Luoma, 1985).*

Studies show positive relationships between the age of fish and invertebrates and the concentration of metals in the organism. Many fish and invertebrates possess metal-specific binding proteins that encourage uptake of metals. In mammals, metallothionein synthesis has been shown to stimulate metal uptake.

For humans, two main exposure routes to metals in sediment predominate: ingestion of exposed organisms and consumption of drinking water containing re-suspended particles. Consumption of fish represents the more significant risk for arsenic, lead and mercury. Each of these metals tends to not only bioaccumulate, but also biomagnify, up the food chain. Therefore, ingestion of exposed fish – usually older fish in a subsistence fishing community – presents a significant health risk for those people in the Rio Grande basin relying on fish from the river as their primary source of protein. Also because many people in the colonias rely on the river as a source of drinking water they are also exposed to re-suspended metals that are not removed during a water-treatment process.

Sediment Criteria

Usually the USEPA promulgates criteria and standards that protect the environment and humans from the impacts of contamination. Unfortunately, no formal program for managing sediment quality exists at the national level. USEPA performed a National Sediment Inventory in 1997; however, this inventory relied primarily on data retrieved from the STORET database. This database does not reflect all studies performed on sediment in Texas, and does not comprehensively represent the studies across the United States. Additionally, Texas's sediment-sampling program focuses primarily on locations where contamination is expected, and even this sampling has been limited by lack of motivation.

In general, TNRCC's approach to water-quality monitoring is to target areas where known problems exist and monitor the changes in those problems over time. In some instances, routine monitoring sites look at ambient conditions; however, because funds are limited and because the focus of the program has been standards compliance, most monitoring sites simply reflect municipal or industrial monitoring. In the absence of a federally-mandated sediment standard, the TNRCC will likely continue to limit sediment monitoring to the occasional special study[4].

For the Rio Grande, few representative "background" or reference sites for sediment exist. In fact, the TNRCC considers only the monitoring site upstream of International Amistad Reservoir on the Devils River

[4] The BEAT at the TNRCC did initiate a Middle Basin Monitoring Plan in conjunction with several federal, state, and local entities in the basin that included sediment monitoring at several sites in the watershed. With the demise of the BEAT, however, TNRCC's commitment to implement the negotiated and accepted plan is questionable. Should the plan become practice in the basin, the Rio Grande will be the first watershed in the state with comprehensive and consistent sediment monitoring.

to be an ecological reference site. Unfortunately, this site is not representative of all ecoregions in the Rio Grande watershed. It is itself impacted and therefore does not represent true background conditions.

Regulation

Current water-quality standards strive to protect the quality of water in the water column, not the sediment quality; therefore, because arsenic, mercury, and lead tend to adsorb to sediments, restrictive water-quality regulations by themselves do not protect sediment quality. While neither USEPA nor the State of Texas has promulgated standards for sediment quality, other regulatory models do exist. Canada and the State of Washington instituted standards in the late 1980s in an attempt to control continued degradation of sediment quality.

EPA is working to develop Sediment Quality Criteria (SQC) using the Equilibrium Partitioning Approach instead of drafting sediment standards. These criteria would combine chemical measurements with biological assessments to determine both the chemical composition of sediment and the impact on the biological community of different levels of sediment contamination.

> *Considerable published data indicate that total metal concentrations on sediments are not good estimators of the 'free' and bioavailable fraction of the total chemical present. Different sediments can differ by a factor of 10 or more in toxicity for the same total metal concentration. To use toxicity estimates based on chemical measurements there needs to be a way to estimate the bioavailable fraction of the total present. A number of approaches to determine metal bioavailability associated with sediments have been review or tried, including carbon normalization and sorption or metals in oxic freshwater desegments to particulate carbon and the oxides of iron and manganese (Adams, 1992).*

Table 3 compares the proposed USEPA guidelines for sediment quality criteria with those used by Texas and Environment Canada. The Environment Canada guidelines tend to be more conservative than those proposed or used by Texas and USEPA. This is not surprising since Environment Canada tends to be more restrictive in all environmental regulatory guidelines than the United States agencies.

Table 3: Sediment-Quality Guidelines (mg/kg)

Agency	Type of Effect	Arsenic	Lead	Mercury
EPA	Threshold	8.2	46.7	0.15
	Probable	70	218	.71
Environment Canada	Threshold	5.9	35	.17
	Probable	17	91.3	.49
TNRCC	Statewide 85th Percentile	19	60	.12

Potential Sources of Metals in Environment

Metals accumulate in the environment as a result of both natural and human activities. Metals occur naturally in rock and soil. Rain erodes soils and breaks-down rocks, introducing metals into the hydrologic cycle. In the hydrologic cycle, the metals bind to suspended sediment and eventually settle out. Volcanic activity also releases a substantial amount of metals into the atmosphere and onto the ground. The metals then transport in the air until they rain deposits them, where they also enter the hydrologic cycle.

Human activities compound metal inputs from the natural environment. Farming and ranching disturbs the soil and increases erosion. Over-harvesting of forests—especially the practice of clear-cutting trees and underbrush—removes the vegetative cover and increases erosion potential. Mining activities further disturb the soil and rock and generate increased metals loading. Nonpoint source pollution from human activities also increases the metals loading to the environment, especially runoff from crop irrigation and city streets.

Commercial, Industrial, and Agricultural Sources of Metals

Human impacts on the natural environment are not the only sources of metals contamination from human activities: commercial, industrial, and agricultural uses of chemicals also contribute metals to the hydrologic cycle.

The agriculture industry uses arsenic as a leaf desiccant and insecticide. Heavy industry generates arsenic as a by-product of glass-making and the semiconductor manufacturing. The commercial industry relies on arsenic as a wood preservative.

Mercury is widely used in the preparation of chlorine and caustic soda. Electrical components and industrial control instruments (e.g. switches, thermometers, and barometers) also contain mercury. The paper industry uses mercury in the manufacturing of pulp and paper products.

Of the three metals in this study, lead is the most prevalent. Until the 1970s, lead was widely used as an additive to gasoline in the United States and Mexico still allows lead in gasoline. Lead is used in pipe, as a liner for containers used for corrosive gases and liquids, and as part of alloys in metallurgy. Lead is also often found in paint pigments, ceramics, batteries, electronic devices, and plastics.

One major activity that releases arsenic, lead, and mercury simultaneously is the burning of fossil fuels—primarily coal. The continued use of coal as a source of heat and electricity, especially in lower-income regions, provides dramatic inputs of metals into the atmosphere that rain eventually deposits. Studies of the Great Lakes region dramatically illustrate the significant impact of atmospheric transport of metals from coal-burning facilities in the Ohio Basin (Ongley, 1994).

Trends in Metals in Environment

Human activities do not simply increase the metals loading to the environment, they redistribute the entire environmental balance of metals. For millions of years nature went through a cycle of creating rock, eroding rock, depositing rock, and starting again; since the industrial age, however, man significantly increased the movement of metals through the hydrologic cycle:

> *The role of human activity in redistribution of metal is demonstrated by the 200-fold increase in lead content of Greenland ice beginning with a "natural" low level (about 800 BC) and a gradual rise in lead content of ice through the evolution of the industrial age, followed by a nearly precipitous rise in the lead corresponding to the period when lead was added to gasoline in the 1920s (Ng, 1981).*

As humans began removing vegetation, disrupting soil, paving over land, and channeling rivers and streams, metals contamination increased in magnitude, coverage, and rate. To better understand the impact of human activities on the contamination of sediments, one can use a model to simulate the movement of metals through the environment.

Available Sediment Transport Models

Models, when applied appropriately, can predict the movement of contaminants through watersheds. By combining theories of sediment transport with historical observations, models simulate the concentration or loading of contaminants over a period of time. The existing sediment transport models use a variety of approaches to simulate the changing environmental conditions. Some evaluate changes over an entire year, while others meticulously analyze daily timesteps. Many models use a combination of data about land uses and land covers, while others rely more on the relationship of one metal to another.

The information required to operate the models is often very extensive. In most cases, a minimum of flow, climate, and historical observations are required. For models that use GIS, land use and elevation are also required.

Models for sediment transport fall into one of three categories: non-GIS, GIS-integrated, and GIS-native models. The following sections describe commonly-used models investigated for applicability to the Rio Grande watershed.

Non-GIS Models

Non-GIS models tend to be older and more established than those integrated with or native to GIS. Because they have not traditionally been integrated with GIS, many non-GIS models focus on the dynamics of sediment transport only within the river channel. Inputs to the river channel are assumed.

Watershed Assessment Program

The Watershed Assessment Program (WASP), developed by the USEPA, is widely available and commonly used. The model simulates transport and transformation of toxic pollutants in the water column and in sediments. WASP does not, however, include the capacity to model sediment transport without specifying specific parameters like shear stress, settling, resuspension, and burial. It is intended to be a long-term, screening-level model. A major limitation of WASP is that it can simulate only three contaminants at a time; therefore it is not able to fully investigate the interaction of several chemicals together.

Hydrologic Engineering Center-6 Model

The Hydrologic Engineering Centers' Model number 6 (HEC-6) was developed by the United States Army Corps of Engineers (COE). HEC-6 simulates the capability of a stream to transport sediment given the upstream sources of sediment. The model includes both bed and suspended sediment load based on Einstein's Bed-Load Function. The COE designed HEC-6 partially to address some of the limitations of WASP.

HEC-6 is an extremely robust system, requiring a significant number of measurements and other inputs for appropriate model runs:

> *HEC-6 is computationally intense, requires large laboratory and field data sets, lacks well-developed components for computing contaminant transport, and is not particularly suited for screening-level applications prior to fine-scale study (Velleux 1996).*

As presented by Velleux, "robust" models often mean data-intensive and complex systems.

In-Place Pollutant Export Model

The In-Place Pollutant Export Model (IPX) developed by the Wisconsin Department of Natural Resources (Velleux, 1994) identifies and evaluates the extent of contamination, pathways for fate and transport, and the different remediation scenarios associated with sediment transport. IPX represents more of a screening level study than a complex model. Because the model is relatively simple to use, it is useful for evaluating long-term simulations and for managers.

IPX modifies WASP4 to handle sediment transport through a screening process. It expands on WASP4 by including processes for sediment aging, decreased sediment resuspendability with increasing age, and resuspension of freshly deposited sediments as a function of water velocity. It expands the contaminant transport capabilities. It also overcomes a major limitation of WASP by allowing an unlimited number of contaminants in the model.

GIS-Integrated Models

Several sediment transport models combine the benefits of GIS with external models to estimate sediment transport. These tools use the GIS to provide input into the models, then return the results of the model-run to the GIS for display. GIS-integrated models tend to be simultaneously complex and simple: the model itself retains all of the functionality of the non-GIS tools while the GIS component is distilled to a simple form. For example, many of the GIS-integrated models limit the number of analyzed watersheds to a small number, limit the analysis region to a small area, or restrict the output to one storm event instead of over time.

Agricultural Nonpoint Source Pollution Model

The Agriculture Nonpoint Source Pollution Model (AGNPS) is a single storm-event based simulation. The model requires that the watershed be divided into a finite number of subwatersheds. The GIS inputs to the model include the definition of and relationship between subwatersheds, topography, location of streams, types of soil, land use, land cover, and point sources. From this data the model returns runoff and peak flow, expected sedimentation/erosion, and concentration of nutrients.

AGNPS computes results for a single rainfall event. In the model, the sediment runoff is calculated from modified universal soil loss equation (USLE). Typically AGNPS is limited to watersheds not larger than 200 km^2 due to the amount of information required to run the model. Some scientists run the model using very large cell sizes to increase size of watershed analyzed; however, studies have shown AGNPS to be very sensitive to the size of the cell so large cells cause an unacceptable level of error and promote unsubstantiated conclusions (Vieux, 1993).

Simulator for Water Resources in Rural Basins

The Simulator for Water Resources in Rural Basins (SWRRB) operates similar to AGNPS. SWRRB improves on AGNPS by generating a daily time-step for calculations of sediment yield, flow routing, and pesticide and nutrient runoff. The model also uses subwatersheds, topography, streams, soils, land use, and land cover and adds crop differentiation and weather. SWRRB also relies on the USLE to predict sediment transport. SWRRB limits the analysis area to a maximum of 800 square kilometers (Pavel, 1996).

Hydrological Simulation Program-FORTRAN

The Hydrologic Simulation Program-Fortran (HSPF) model builds on SWRRB—it is a continuous timestep model requiring even more intensive data. HSPF integrates GIS with

FORTRAN programs to perform analysis. The model performs all calculations external to the GIS and returns the results to the GIS. HSPF predicts the results of management activities and scenarios on irrigation return-flow. The tool simulates both hydrology and water quality.

The model requires soils, land use, and crop definition information. It also requires continuous weather data, evapotranspiration measurements, and air temperature as inputs. With this data, the model all phases of sediment transport, handling silt, clay, and sand sediment movement, erosion, sedimentation, and re-suspension of particles.

Unlike SWRRB, HSPF divides the watershed into segments instead of subwatersheds. Segments are then linked together to provide an in-stream model. The model can simulate interactions in basins up to several thousand square kilometers.

Chemicals, Runoff, and Erosion from Agricultural Management Systems

The U.S. Department of Agriculture-Agricultural Research Service developed the Chemicals, Runoff, and Erosion from Agricultural Management Systems (CREAMS) to simulate the impact of differing land use practices on water quality. Like HSPF, CREAMS is a continuous simulation model requiring continuous precipitation and air temperature information. Soil and crop type data are also provided as inputs. The model distinguishes between several different agricultural practices, including tillage, pesticide use, aerial spraying, etc.

CREAMS calculates daily erosion, sediment yield, and chemical concentrations based on runoff volume, peak flow, infiltration, evapotranspiration, soil water content, and percolation.

One model, Opus, modified CREAMS to be a true watershed model. Opus simulates sediment transport, chemical transport, carbon and nutrient cycles in soil microbial decay, flow of heat in soil, and growth of crops. Opus relies heavily on algorithms from other models: weather conditions are simulated by a daily weather generation model (WGEN), daily runoff is calculated from a modified Soil Curve Number approach, and soil erosion is modeled using the USLE (Saunders, 1996).

Both CREAMS and Opus are hybrid tools, relying on the GIS as simple input into the model instead of relying on the GIS to run the model.

Better Assessment Science Integrating Point and Nonpoint Sources Model

In 1997, USEPA expanded on the available modeling toolset by creating the Better Assessment Science Integrating Point and Nonpoint Sources Model (BASINS). BASINS uses HSPF integrated with a GIS software called ArcView to perform nonpoint source pollution analysis.

BASINS was designed for use by state agencies as a simple-to-use mechanism for nonpoint source pollution modeling. BASINS comes pre-packaged with data for ease-of-use. The tool provides a graphical interface to three background models: the Nonpoint Source Model (NSPM), Enhanced Stream Water Quality Model (QUAL2E), and TOXIROUTE. NSPM is a modification of HSPF that estimates nonpoint source pollution loads at a subwatershed scale. Within the BASINS tool, subwatersheds correspond to the hydrologic unit areas defined at a national scale by the USGS.[5] QUAL2E is an in-stream model that simulates sediment transport through the stream channel. TOXIROUTE performs dilution/decay calculations at the watershed level. The combination of the three models provides a detailed analysis of environmental conditions for one subwatershed at a time.

The second release of basins provided tools to subdivide a standard subwatershed into smaller units; however, it does not allow the user to aggregate the watersheds into larger units.[6] At this time, BASINS operates on subwatersheds of approximately 250,000 square meters.

Native GIS Models

Because the Rio Grande watershed spans such an extensive area, the major non-GIS and GIS-integrated models do not offer a simple solution to handle the entire watershed. Models that reside in a GIS offer a better opportunity to combine the best of the previously-discussed models with the geographic coverage necessary to comprehensively assess the Rio Grande watershed.

GIS models rely on a mathematical approach called "map algebra" to perform most of their calculations. This means that they tend to require more mathematical steps to accomplish what several of the other models can do in a few iterations. Therefore, in addition to requiring more powerful computers to operate, GIS-based models tend to require more time to generate model runs and more hard drive space to store intermediate results.

Aerial Nonpoint Source Watershed Environment Response Simulation

The Aerial Nonpoint Source Watershed Environment Response Simulation (ANSWERS) model was one of the first to operate entirely in a GIS. ANSWERS is based on grid approach and fully utilizes map algebra. The model simulates erosion and sediment transport for a river basin by

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[5] BASINS relies on the most-commonly used hydrologic unit areas – the 8-digit areas. These areas contain approximately 250,000 square meters and are defined across the United States.

[6] BASINS included a tool in the second release that built on a TNRCC/Environmental Systems Research Institute (ESRI) program called the "Watershed Delineator." This delineator functions completely in the GIS, while the rest of the modeling capabilities execute in FORTRAN programs outside the GIS environment.

evaluating runoff, erosion, sediment transport, and phosphorous loading for individual subwatersheds.

ANSWERS requires the several types of information to run the model: slope, aspect, porosity, moisture content, field capacity, infiltration capacity, erodibility, and crop delineation. The model defines channels and calculates information in relationship to the defined channels, for example sedimentation and water quality. Studies have compared results from ANSWERS to AGNPS and the Soil and Water Assessment Tool (DeRoo 1993 and Engel 1993) and demonstrated that the results were comparable between the models. Unfortunately, because ANSWERS is so comprehensive and requires such extensive information, it is intended for subwatersheds of up to only 200 square kilometers (Pavel, 1996).

Limburg Soil Erosion Model

The Limburg Soil Erosion Model (LISEM) is a physically-based, hydrological and soil erosion model intended for conservation and planning. The model incorporates raster data in GIS to simulate erosion. LISEM resides completely within the GIS and requires no external processing. LISEM builds on the ANSWERS model by covering a larger basin area and by including more functions associated with the transport of sediment. The model uses rainfall, interception[7], surface storage, infiltration (direct throughfall and leaf drainage and overland flow from uphill areas provide water available for infiltration), vertical movement of water in the soil, overland flow, channel flow, detachment by rainfall and throughfall, detachment by overland flow, and transport capacity of the flow to ultimately simulate erosion and sediment yield (DeRoo, 1994).

Because LISEM is more comprehensive than ANSWERS it requires more incidental data than ANSWERS. It also requires a significant number of historical observations to calibrate the model.

Soil Water and Assessment Tool

The Soil Water and Assessment Tool (SWAT) is similar to SWRRB except it operates fully within a GIS. SWAT requires data related to weather, hydrology, erosion potential, soil temperature, crop growth, nutrients, pesticide application, subsurface flow, and agricultural management practices to simulate sediment yield. The model produces a daily time step simulating up to 100 years of data. SWAT is limited, however, to using only 10 watersheds.

The Texas Agricultural Experiment Station (TAES) combined SWAT with QUAL2E to simulate both the in-stream and runoff conditions. Even with the QUAL2E modifications, SWAT

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[7] Interception is the measurement of vegetation intercepting flow before it touches soil.

was primarily intended for analysis of crop management and resulting nutrients loads--not sediment transport. SWAT looks primarily at standard regulatory constituents (including nutrients, aquatic vegetation and chemical oxygen demand). SWAT was intended for large river basins (Srinivasaan, 1995).

Nonpoint Source Pollution Assessment Model

Another approach to using GIS to model sediment transport is one used by the Center for Research in Water Resources at the University of Texas. This model, coined the Nonpoint Source Pollution Assessment Model (NSPAM), operates under the assumption that complex transport calculations are not necessary to create "screening-level models". Instead, NSPAM relies on the analysis of observed runoff concentrations for particular land use types that are then applied across the entire river basin.

In 1995 Saunders applied the NSPAM approach to the San Antonio-Nueces Coastal River Basin in Texas. Based on estimated mean concentrations (EMC) of pollutants for each major land use in the basin, Saunders calculated a predicted annual average load of the pollutant for each cell in the basin. From this calculation, loads could then be calculated for each subwatershed in the basin.

Because NSPAM relies simply on digital elevation models, EMCs from observed values, land use, and precipitation, creation of a NSPAM model for any river basin in the United States is simply a matter of determining the appropriate EMC values for the basin. While this model does not produce intricate time step calculations nor predict instantaneous concentrations, it does provide a simple, cost-effective approach toward targeting monitoring and assessment efforts within a large river basin.

Midwest Agrichemical Transport Model

In 1996, Pavel developed a GIS-based model for the Upper Mississippi, Upper Missouri, and Ohio River Basins called the Midwest Agrichemical Transport Model (MAT). MAT was developed to address the needs of large-scale basins. The model decomposed the river basins into drainage areas of about 25 square kilometers. While the model focuses primarily on chemical transport instead of sediment transport, it sets the foundation for future GIS-based models. Unlike in the NSPAM model, the important issues of flow, decay, and transport dynamics are interpreted in MAT.

Summary of Existing Sediment Transport Models

The review of the existing models illustrated three types of model deficiencies for this study: 1) the model does not reside in a GIS and therefore will not take advantage of GIS functionality; 2) the model handles small river basins and is not designed for a watershed the size of the Rio Grande; or 3) the model requires too much incidental information. Table 4 illustrates the differences between the reviewed models, and the deficiency of each for analyzing sediment transport in the Rio Grande basin.

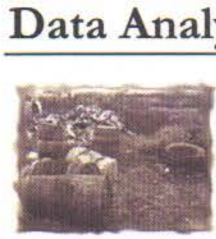
Table 4: Summary of Reviewed Sediment Transport Models

Model	Intent	Watershed Size	Deficiency
WASP	Basic transport of toxic pollutants in water and sediment	Large	Not in GIS; only three constituents
HEC-6	In-stream sediment transport	Large	Too data intensive; not in GIS
IPX	Screening level model, In-stream sediment transport	Small	Not in GIS
SWRRB	Sediment yield model that relies on universal soil loss equation	Small	Watershed size too small for basin
AGNPS	Designed to assess impact of land management activities on medium sized watersheds	Medium	Watershed size too small for basin
HSPF	In-stream analysis of sediment transport	Medium	Watershed size too small for basin
CREAMS	Rigorous model to assess impact of agriculture acitivities in watersheds; predicts erosion potential	Medium	Watershed size too small for basin
BASINS	Comprehensive assessment tool for regulatory agencies; includes nonpoint source model, in-stream model, and decay model	Medium	Watershed size too small for basin
ANSWERS	Designed to assess impact of agricultural land practices on in-stream conditions	Medium	Watershed size too small for basin
LISEM	Comprehensive soil erosion model	Medium	Watershed size too small for basin
SWAT	Robust sediment transport model designed to assess impact of land management activities	Large	Number of subwatersheds limited to 10; too data intensive
SWAT-QUAL2E	Integrates SWAT with in-stream model of sediment transport	Large	Number of subwatersheds limited to 10; too data intensive
NSPAM	GIS nonpoint source pollution model for nutrients	Large	Models nutrients and not sediment
MAT	GIS nonpoint source pollution model for nutrients	Large	Models nutrients and not sediment

The ideal model for analyzing sediment and associated contaminant transport in the Rio Grande basin will require a small amount of data, few flow gaging stations, and will minimize the effects of using data generated by two different countries and several different monitoring entities. Therefore, the majority of the models reviewed in the literature will not suffice for this analysis.

The data analysis section will provide further details regarding the quality of data available for developing model for the Rio Grande Basin.

Data Analysis



The Data Analysis chapter discusses the monitoring and analysis methods used to collect data in the Rio Grande basin, preliminary screening results, detailed screening results, and trend analyses.

Monitoring and Analysis Methods

Depending on the constituents being analyzed, sampling protocols vary among agencies that monitor sediment quality. For the data set analyzed in this thesis, the sediment sampling protocols included: sampling using a stainless steel Eckman dredge, grab samples using Teflon scoops, and other grab sampling protocols. In general the samples are composite with between two and eight samples mixed into one overall composite for each site.

Laboratory analytical methods for metals also vary among agencies. For the period of record, the primary analytical methods follow the USEPA sampling and analysis protocols listed in Table 5.

Table 5: Sediment Monitoring and Analysis Methods

Measurement	Preparation	Analytical Method	Description
Arsenic	EPA SW Method 3050	EPA 206.2	Graphite furnace atomic absorption (GFAA)
		EPA 200.4	Inductively Coupled Plasma Mass Spectrometry (ICPMS)
Lead	EPA SW Method 3050	EPA 239.2	GFAA
		EPA 200.4	ICPMS
Mercury	EPA SW Method 3050	EPA 245.5	Manual cold vapor
Grain Size			Fraction separation and gravimetric determination

Arsenic and Lead Analysis Procedures

All of the arsenic and lead analyses began with a "digestion" process. Labs use one of two digestion methods: total acid digestion or strong acid digestion. Total acid digestion releases mineral-bound metals (including those in crustal minerals) into solution for further analysis. The digestion uses either a combination of nitric, perchloric, and hydrofluoric acids (Method 200.4; USEPA 1983) or a combination of hydrofluoric acid and aqua regia (USGS, 1996)[8].

Strong acid digestion uses nitric acid and hydrogen peroxide (USEPA SW-846 Method 3050), but, unlike total acid digestion, does not break down all mineral (matrix) components. The strong acid digestion approach is newer than the total acid digestion method, which may account for subtle differences between older and newer measurements. The data used in this thesis did not include a reference to the particular digestion method employed during analysis; therefore, for the purposes of this analysis it is assumed that the differences between the two methods are statistically insignificant.

Following digestion of the sediment sample, the arsenic and lead in the resulting solution are analyzed by inductively coupled plasma mass spectrometry (ICPMS) or graphite furnace atomic absorption spectroscopy (GFAA).

In the GFAA method the analyst inserts a small sample of the digested solution in a graphite tube and heats it very rapidly to 1,500-2,600 degrees Celsius. Light with a wavelength and very narrow bandwidth specific to an element is projected down the tube. The amount of light absorbed by the atomized sample is proportional to its concentration in solution (West Coast Analytical Service, 1997).

In the ICPMS method the analyst sprays the digested solution into flowing argon and then passes it into a torch heated to approximately 10,000 degrees Celsius. This process atomizes and ionizes the gas which then forms a plasma. Positive ions in the plasma are focused down a quadrapole mass spectrometer. Chemistry and concentration of the sample may then be determined by the mass spectrum of the plasma.

Mercury Analytical Methods

Because bacteria in sediment can transform inorganic mercury into the more bioavailable form of methyl mercury, scientists use two different approaches to determining the concentration of mercury in sediment: analysis of methyl mercury and of inorganic mercury. Methyl mercury is generally analyzed using cold vapor atomic fluorescence (VAF). In this process, sediment samples are digested in a potassium hydroxide-methanol solution by heating at 60 degrees Celsius for 2-4 hours. After the solution cools, sodium tetraethylborate is added to form methyl-ethylmercury. This solution is then concentrated and finally added to a gas chromatography column (Bloom, 1989).

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[8] Occasionally the USGS employs a nondestructive method called X-Ray Fluorescence (XRF). This alternative to digestion involves freeze-drying a sediment sample, ball milling it to approximately 120 mesh, and pelletizing it. Typically, detection limits achievable with XRF are higher than those achievable with the digestion methods and analysis by GFAA and are lower than those obtained by ICP. While this process was documented in USGS materials, no documentation found during research indicated use of this method to analyze data in the Rio Grande basin.

The analysis of inorganic mercury in sediments requires a separate digestion procedure using potassium permanganate as the oxidizing agent, with analysis by cold vapor atomic absorption spectroscopy (CVAA) (USEPA, 1994).

Preliminary Screening of Sediment Quality

The preliminary screening of sediment quality data for the basin included subdividing the data set into arsenic, lead and mercury measurements, assessing each of the metals data sets, subdividing the data into watersheds, and then determining which stations collected sufficient information to generate trend analyses.

The data set for monitoring of metals in sediment contains a total of 273 arsenic, 273 lead, and 274 mercury measurements. While the data set contains information dating to 1966, the subset of arsenic, lead, and mercury contains measurements dating from1973. The costs associated with measuring metals in sediment far exceed those for measuring water quality, so it is no surprise that few measurements for metals in sediment exist in the data set. Table 6 provides basic descriptive statistics for the data set.

Table 6: Basic Statistics for Metals in Sediment Measurements (mg/kg) (1966-1996)

Metal	Valid N	Mean	Median	Min.	Max.	Variance	Std.Dev.	Skewness	Kurtosis
Arsenic	273	5.66	4.10	0.5	49	34.98	5.91	4.06	19.65
Lead	273	12.42	9.70	1	93	98.33	9.92	3.11	17.28
Mercury	274	0.14	0.045	0.01	6.00	0.32	0.57	9.21	88.67

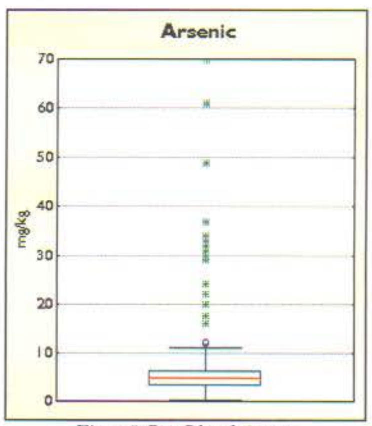


Figure 5: Box Plot of Arsenic

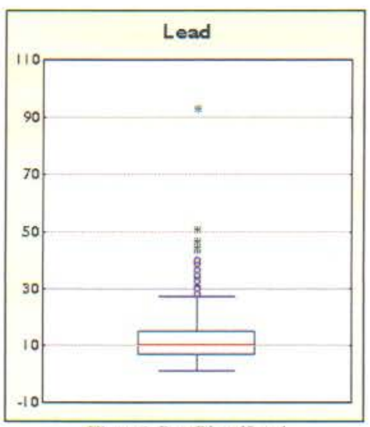


Figure 6: Box Plot of Lead

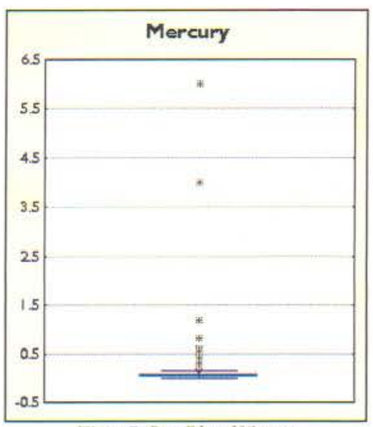


Figure 7: Box Plot of Mercury

One important characteristic of the metals data set illustrated in Table 6 is the lack of normality in the data. This positive skew to the sediment-quality measurements is common to most environmental data sets because no negative values can exist. Positively-skewed data is also typical of all metals monitoring because true minimums cannot be measured (values below minimum analytical limits cannot be measured).

The difference between the means and medians in the data set demonstrates the effect of extreme measurements on the data: the means for all three metals are significantly higher than the medians, showing that a few extremely high measurements within each subset are pulling the mean values higher. This effect is particularly evident in the mercury data where the majority of measurements seem to fall between 0 and 0.5 mg/kg, with a few very high extremes at 6.0 mg/kg. Frequency distributions further demonstrate this phenomenon.

Table 7 shows the frequency distribution and associated histogram of frequencies for arsenic in sediment. The frequency distribution confirms the impact of extreme values on the mean – 96% of the measurements are within two standard deviations of the mean. The remaining values fall as many as six standard deviations away.

Table 7: Frequency Distribution of Arsenic in Bottom Deposits (mg/kg)

Value	Count	Cumulative Count	Percent of Cases	Cumulative Percent of Cases
0	0	0	0.00	0.00
>0-5	176	176	64.47	64.47
>5-10	80	256	29.30	93.77
>10-15	4	260	1.47	95.24
>15-20	3	263	1.10	96.34
>20-25	2	265	0.73	97.07
>25-30	2	267	0.73	97.80
>30-35	4	271	1.47	99.27
>35-40	1	272	0.37	99.63
>40-45	0	272	0.00	99.63
>45-50	1	273	0.37	100.00
Missing	0	273	0.00	100.00

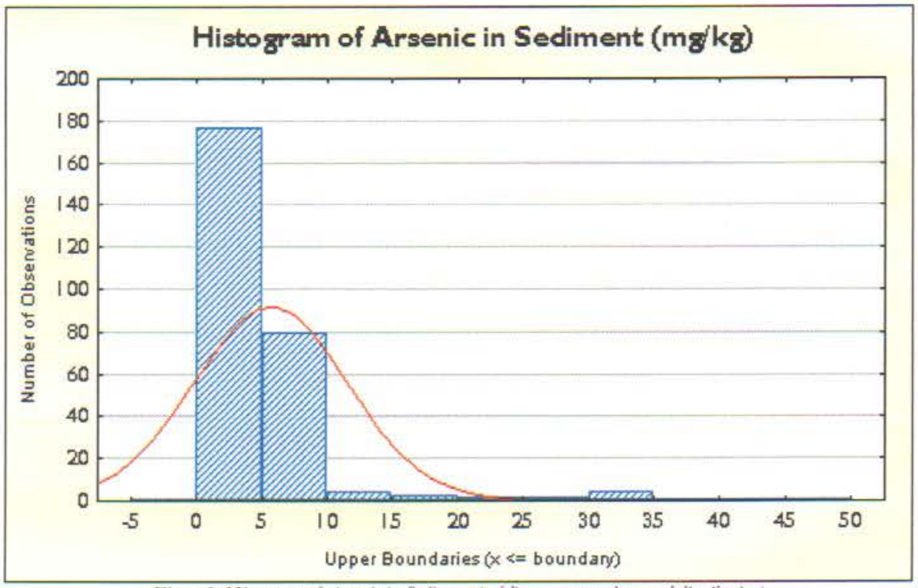


Figure 8: Histogram of Arsenic in Sediment (red line = expected normal distribution)

To better understand the spread of values in the majority of the arsenic data, Table 8 demonstrates the consequence of removing the values greater than two standard deviations from the median from the data set. The mean and median are much closer together, however the distribution is still positively skewed.

Table 8: Frequency Distribution of Subset of Arsenic in Sediment Values (mg/kg)
(0<Value<=10 mg/kg, mean=4.42, median=3.91)

Category (mg/kg)	Count	Cumulative Count	Percent of All Cases	Cumulative Percent of Cases
0	0	0	0.00	0.00
>0-1	5	5	1.95	1.95
>1-2	25	30	9.77	11.72
>2-3	41	71	16.02	27.73
>3-4	61	132	23.83	51.56
>4-5	44	176	17.19	68.75
>5-6	25	201	9.77	78.52
>6-7	20	221	7.81	86.33
>7-8	14	235	5.47	91.80
>8-9	14	249	5.47	97.27
>9-10	7	256	2.73	100.00
Missing	0	256	0.00	100.00

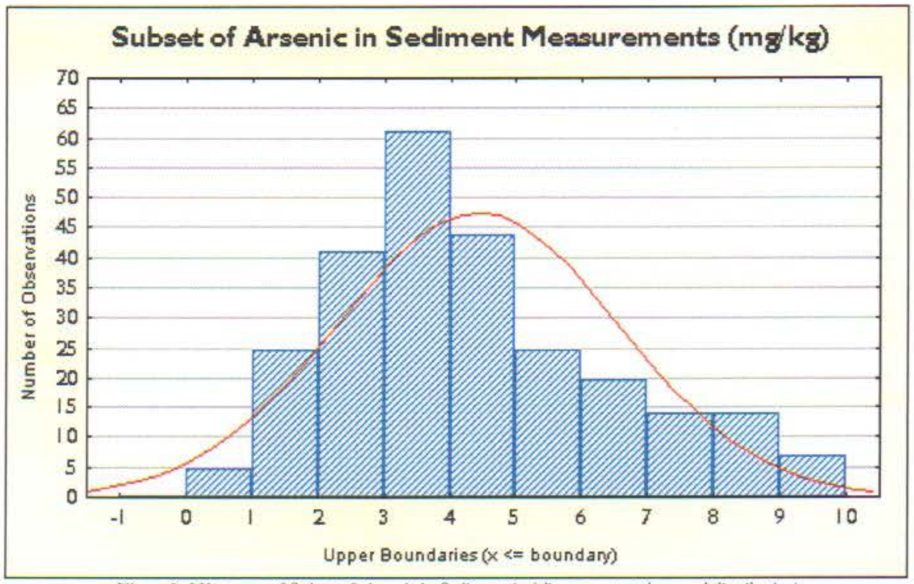


Figure 9: Histogram of Subset of Arsenic in Sediment (red line = expected normal distribution)

Table 9 shows the frequency distribution and associated histogram for lead in sediment. The patterns within the lead data mirror those from the arsenic data, with a significant positive skew to the data. Table 10 examines a subset of the data at the lower values to demonstrate the lack of normality in the data even without extreme values in the data set.

Table 9: Frequency Distribution of Lead in Sediment Values (mg/kg)

Category (mg/kg)	Count	Cumulative Count	Percent of All Cases	Cumulative Percent of Cases
0	0	0	0.00	0.00
>0 – 5	23	23	10.75	10.75
>5 – 10	57	80	26.64	37.38
>10 - 15	58	138	27.10	64.49
>15 - 20	33	171	15.42	79.91
>20 – 25	24	195	11.21	91.12
>25 – 30	11	206	5.14	96.26
>30 – 35	2	208	0.93	97.20
>35 – 40	4	212	1.87	99.07
>40 – 45	1	213	0.47	99.53
>45 – 50	0	213	0.00	99.53
>50 – 55	0	213	0.00	99.53
>55 – 60	1	214	0.47	100.00
Missing	0	214	0.00	100.00

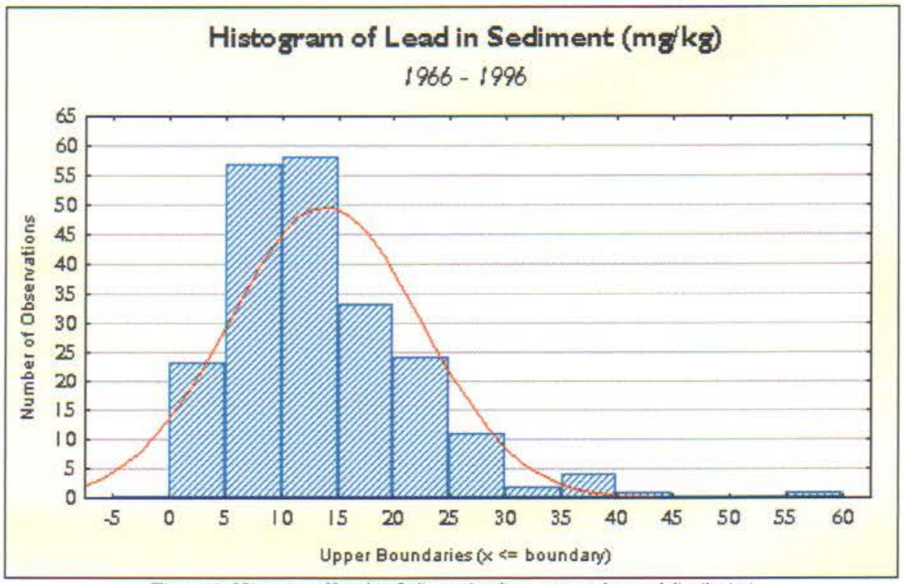


Figure 10: Histogram of Lead in Sediment (red line = expected normal distribution)

Table 10: Frequency Distribution for Subset of Lead Values (0.0 < Value < 50.0) (mg/kg)

Category (mg/kg)	Count	Cumulative Count	Percent of All Cases	Cumulative Percent of Cases
0	0	0	0.00	0.00
>0-5	42	42	15.79	15.79
>5-10	99	141	37.22	53.01
>10-15	63	204	23.68	76.69
>15-20	32	236	12.03	88.72
>20-25	17	253	6.39	95.11
>25-30	6	259	2.26	97.37
>30-35	4	263	1.50	98.87
>35-40	3	266	1.13	100.00
Missing	0	266	0.00	100.00

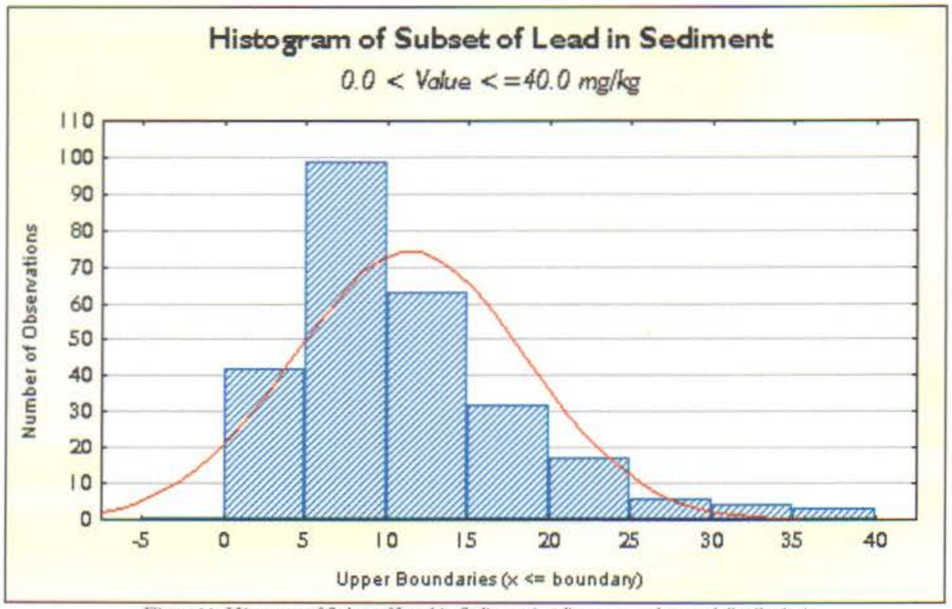


Figure 11: Histogram of Subset of Lead in Sediment (red line=expected normal distribution)

The impact of extreme values on the metals data is readily apparent in the mercury measurements. The majority of the measurements, over 96%, are less than 0.5 mg/kg, with values ranging as far as 11 standard deviations away from the 0.14 mg/kg mean (Table 11).

Table 11: Frequency Distribution of Mercury in Sediment (mg/kg)

Category (mg/kg)	Count	Cumulative Count	Percent of All Cases	Cumulative Percent of Cases
0	0	0	0.00	0.00
>0-0.5	265	265	96.72	96.72
>0.5-1.0	5	270	1.82	98.54
>1.0-1.5	1	271	0.36	98.91
>1.5-2.0	0	271	0.00	98.91
>2.0-2.5	0	271	0.00	98.91
>2.5-3.0	0	271	0.00	98.91
>3.0-3.5	0	271	0.00	98.91
>3.5-4.0	1	272	0.36	99.27
>4.0-4.5	0	272	0.00	99.27
>4.5-5.0	0	272	0.00	99.27
>5.0-5.5	0	272	0.00	99.27
>5.5-6.0	2	274	0.73	100.00
Missing	0	274	0.00	100.00

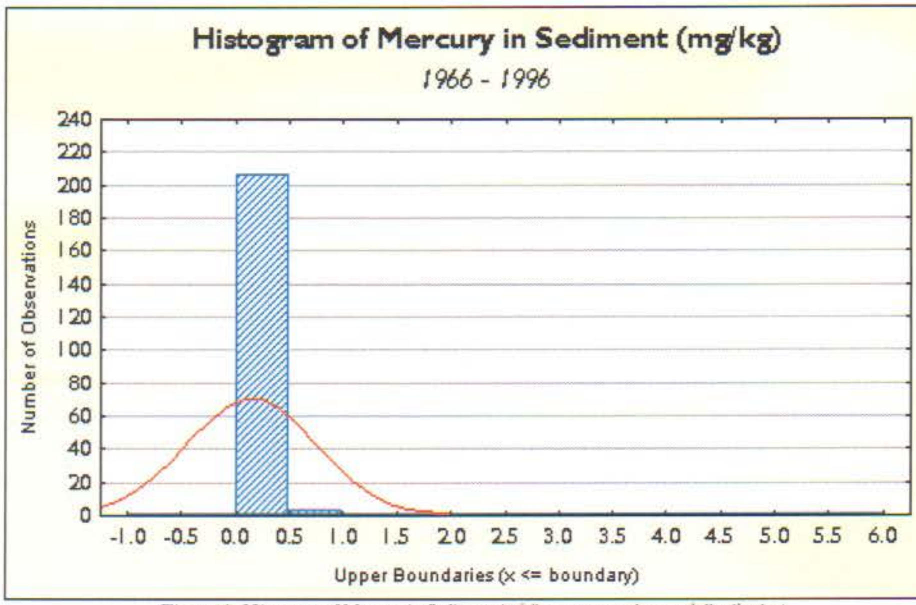


Figure 12: Histogram of Mercury in Sediment (red line = expected normal distribution)

Table 12 illustrates the impact on the mercury data by removing the extreme values. An examination of the frequency distribution and histogram of the frequency of values less than 0.5 mg/kg still shows a significant positive skew to the data set; however, the values are more evenly distributed.

Table 12: Frequency Distribution of Subset of Mercury in Sediment (Values Between 0.00 – 0.5 mg/kg)

Category (mg/kg)	Count	Cumulative Count	Percent of All Cases	Cumulative Percent of Cases
0	0.00	0.00	0.00	0.00
>0-0.02	42	42	15.85	15.85
>0.02-0.04	85	127	32.08	47.92
>0.04-0.06	55	182	20.75	68.68
>0.06-0.08	21	203	7.92	76.60
>0.08-0.10	32	235	12.08	88.68
>0.10-0.12	4	239	1.51	90.19
>0.12-0.14	4	243	1.51	91.70
>0.14-0.16	2	245	0.75	92.45
>0.16-0.18	2	247	0.75	93.21
>0.18-0.20	1	248	0.38	93.58
>0.20-0.22	3	251	1.13	94.72
>0.22-0.24	2	253	0.75	95.47
>0.24-0.26	2	255	0.75	96.23
>0.26-0.28	0	255	0.00	96.23
>0.28-0.30	0	255	0.00	96.23
>0.30-0.32	3	258	1.13	97.36
>0.32-0.34	3	261	1.13	98.49
>0.34-0.36	1	262	0.38	98.87
>0.36-0.38	1	263	0.38	99.25
>0.38-0.40	0	263	0.00	99.25
>0.40-0.42	2	265	0.75	100.00
Missing	0	265	0.00	100.00

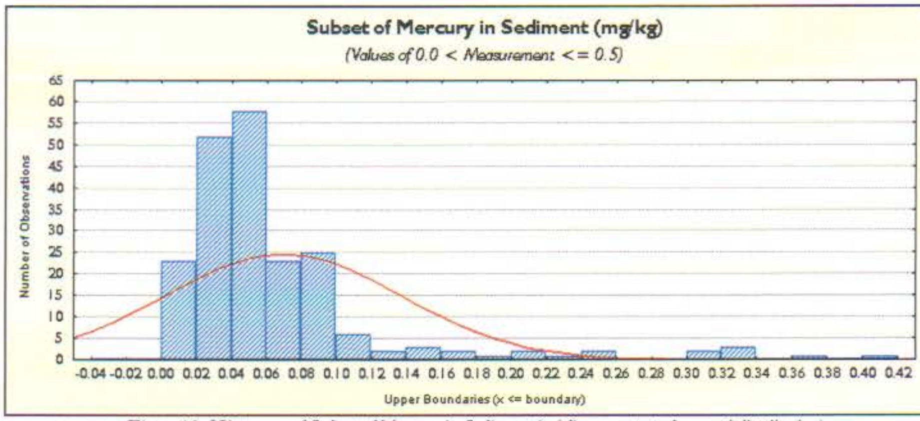


Figure 13: Histogram of Subset of Mercury in Sediment (red line = expected normal distribution)

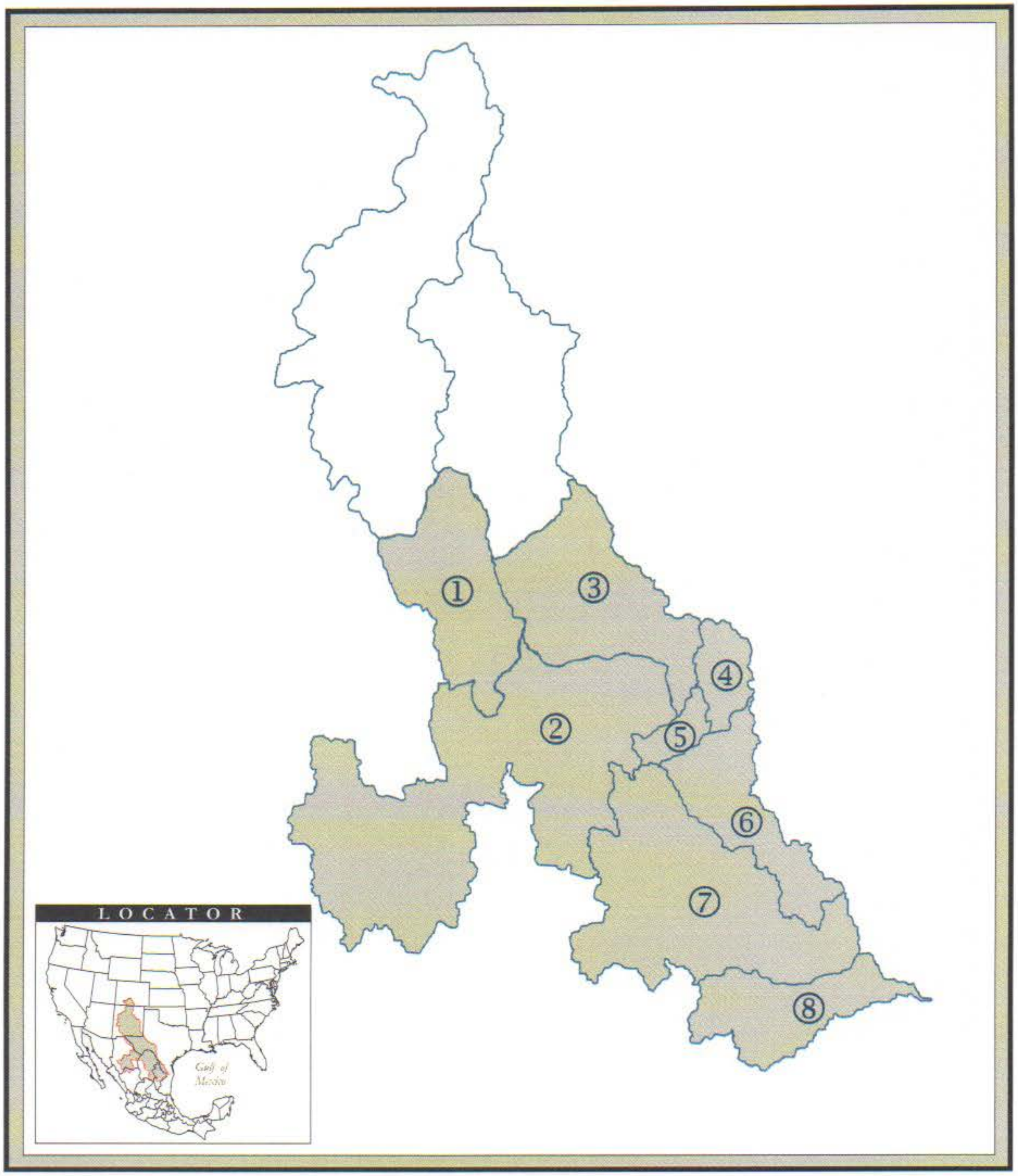
Analysis of Metals by Watershed

The data may be further analyzed by subdividing it into watersheds. Within the study area, eight large watersheds may be easily delineated: 1) from the dam at Elephant Butte downstream to the point at which the Rio Conchos joins the river; 2) the Rio Grande and Rio Conchos downstream to Amistad Reservoir; 3) the Pecos River; 4) Devils River; 5) Amistad Reservoir; 6) Rio Grande between Amistad and Falcon Reservoirs; 7) Falcon Reservoir; and 8) Rio Grande below Falcon Reservoir (Figure 14).

The segregation of data into watersheds demonstrates the change in sediment quality with varying environmental conditions within the basin. Table 13 illustrates the difference in arsenic values between the major watersheds. The area of the basin with the highest arsenic values is in Amistad Reservoir. This result is predictable because the watershed is a reservoir and therefore offers a greater opportunity for sediment and associated contaminants to settle to the bottom, and because Amistad Reservoir receives more than ten times the sediment load per year of the average United States reservoir. Amistad Reservoir filters so much sediment from the water that Falcon Reservoir downstream receives a much smaller sediment load. The arsenic values for Falcon Reservoir are also substantially lower than those found in Amistad Reservoir.

Because no sediment standards currently exist, to determine the screening criteria for metals in sediment the TNRCC and USEPA use an 85th percentile of all observed measurements throughout Texas[9]. For arsenic, the screening levels are: 6.7 mg/kg for freshwater, 6.9 mg/kg for tidal streams, 6.2 mg/kg for estuaries, and 18.3 mg/kg for reservoirs. Using this screening approach, only one watershed has a median value above the screening level (Rio Grande/Rio Conchos), while all of the watersheds except the Devils River and Falcon Reservoir have some measurements that exceed the screening levels.

[9] The TNRCC described screening approaches in both the Texas Clean Rivers Program Guidance and the State of Texas Water Quality Inventory for 1994 and 1996. This process aggregates all measurements for a particular metal under one of four hydrological conditions (freshwater, reservoir, tidal stream, and estuary) and determines an 85th percentile of the measurements as a screening level. For measurements evaluated at less than the detection limit for the metal, 50 percent of the detection limit was used. Any measurement exceeding this screening level in any watershed is then reported as a "possible concern" or as an exceedance.



LEGEND

Subwatershed Boundary

Subwatershed Boundary (not in study area)

① Upper Rio Grande
② Rio Grande/Río Conchos
③ Pecos River
④ Devils River
⑤ Amistad Reservoir
⑥ Middle Rio Grande
⑦ Falcon Reservoir
⑧ Lower Rio Grande

This map uses data from the US Census Bureau, US Geological Survey, and Texas Natural Resource Conservation Commission. The map projection is Albers Conformal Conic chosen to preserve the area of the watershed. The map is for display purposes only.

Figure 14: Major Watersheds in the Rio Grande Basin

Table 13: Basic Statistics for Arsenic in Sediment by Watershed (mg/kg)

Watershed	Valid N	Mean	Median	Minimum	Maximum	Std.Dev.	Skewness
Rio Grande above Rio Conchos	67	3.56	2.80	0.69	22	3.12	3.60
Rio Grande and Rio Conchos	38	8.00	7.00	2.60	49	7.31	5.04
Pecos River	31	5.60	3.63	0.50	29	6.73	2.94
Devils River	2	3.31	3.31	1.61	5	2.40	--
Amistad Reservoir	14	16.08	9.50	4.80	37	12.03	0.86
Rio Grande below Amistad	58	5.50	4.20	2.30	32	4.87	4.07
Falcon Reservoir	10	3.75	3.18	2.30	5.9	1.39	0.59
Lower Rio Grande	53	4.55	4.10	2.30	10.3	1.66	1.48

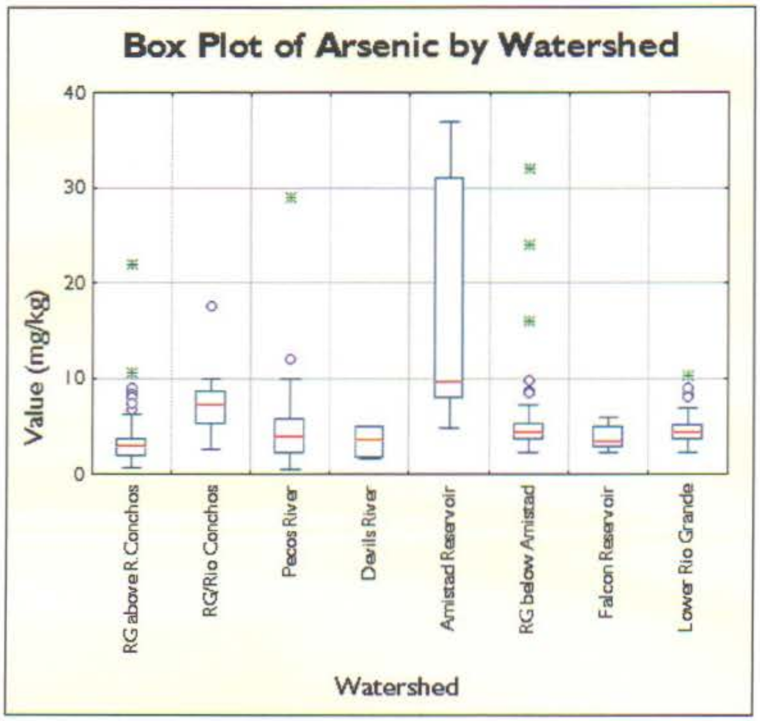


Figure 15: Box Plot of Arsenic in Sediment by Watersheds

Table 14 shows the basic statistics for lead in sediment subdivided into watersheds. Upon first glance, it seems apparent that the arsenic and lead measurements were gathered in similar fashion. The percent of measurements within each watershed is consistent between the two data sets.

The pattern of screening values for lead follow a different pattern than arsenic: 50 mg/kg in freshwater, 95 mg/kg in tidal streams, 60 mg/kg in reservoirs, and 30 mg/kg in estuaries. None of the median values exceed the respective screening levels and only the Rio Grande below Amistad and the Lower Rio Grande watersheds have any measurements that exceed the screening levels.

Table 14: Basic Statistics for Lead in Sediment by Watershed (mg/kg)

Watershed	Valid N	Mean	Median	Minimum	Maximum	Std.Dev.	Skewness
Rio Grande above Rio Conchos	67	14.78	11.00	1.90	44.46	10.31	1.08
Rio Grande and Rio Conchos	38	13.43	11.50	6.00	43.8	7.66	2.52
Pecos River	31	8.83	8.10	1.00	21	5.70	0.48
Devils River	2	4.14	4.14	3.27	5	1.22	--
Amistad Reservoir	14	13.75	14.00	1.00	21	4.84	-1.15
Rio Grande below Amistad	58	13.18	9.05	2.10	93	13.87	3.89
Falcon Reservoir	10	9.50	10.30	1.60	17	6.29	-0.10
Lower Rio Grande	53	10.53	8.12	1.00	47	8.42	2.95

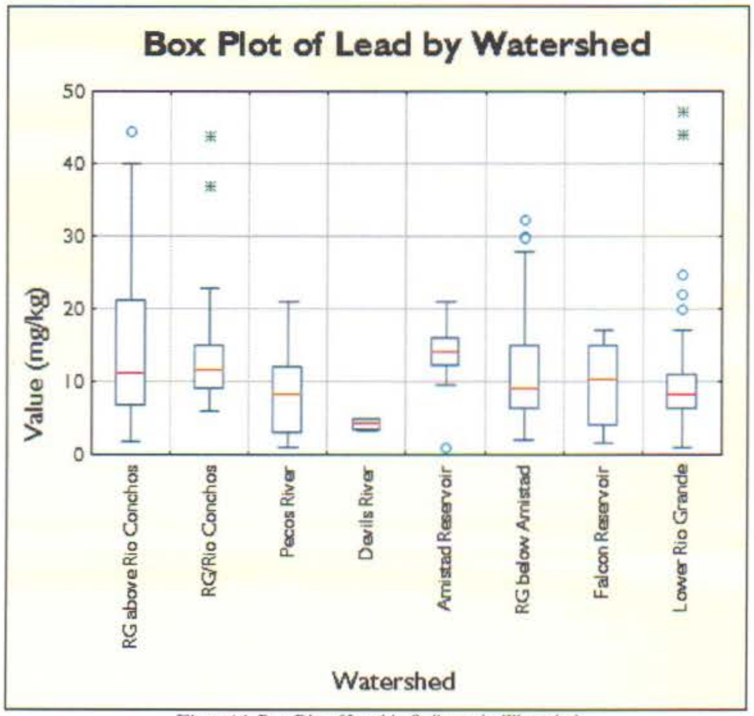


Figure 16: Box Plot of Lead in Sediment by Watershed

The mercury measurements (Table 15) are also consistent with the same sampling pattern as both arsenic and lead. The screening levels for mercury are 0.09 mg/kg in freshwater, 0.28 mg/kg in tidal waters, 0.22 in reservoirs, and 0.12 in estuaries. None of the medians exceed the screening levels; however, every watershed except Amistad Reservoir and the Lower Rio Grande watershed have values that exceed the screening levels.

Table 15: Basic Statistics for Mercury in Sediment by Watershed (mg/kg)

Watershed	Valid N	Mean	Median	Minimum	Maximum	Std.Dev.	Skewness
Rio Grande above Rio Conchos	68	0.21	0.04	0.01	6	0.86	5.97
Rio Grande and Rio Conchos	40	0.06	0.05	0.01	0.226	0.05	2.35
Pecos River	22	0.17	0.04	0.02	1.19	0.28	2.72
Devils River	2	0.06	0.06	0.03	0.09	0.04	--
Amistad Reservoir	14	0.06	0.06	0.03	0.1	0.02	0.22
Rio Grande below Amistad	57	0.21	0.05	0.01	6	0.79	7.15
Falcon Reservoir	10	0.10	0.04	0.02	0.6	0.18	3.06
Lower Rio Grande	52	0.06	0.05	0.01	0.211	0.04	1.71

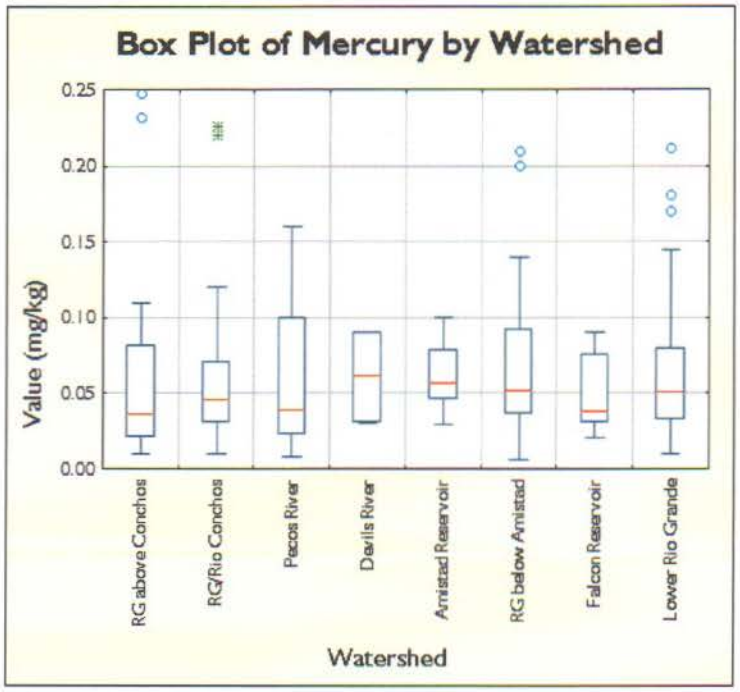


Figure 17: Box Plot of Mercury in Sediment by Watershed

The preliminary screening merely gives details about the nature of the data—the variability of the data, the coverage of the data by watershed, whether the data is normal, and whether it exceeds screening levels at any point. The preliminary screening of the sampling data from 1966 through 1996 shows fundamental information about metals in sediment in the Rio Grande:

- Arsenic, lead, and mercury were sampled intermittently.
- In general, the reservoirs contain higher measurements for metals in sediment that the river beds.

Detailed Analysis of Sediment Quality Data

The detailed analysis determined the correlation between arsenic, lead, and mercury, and measurements of other constituents, including total suspended sediment, total dissolved solids, and pH. It also investigated the data set for potential normalization approaches, including iron, aluminum, total organic carbon, and grain size, and determined the trend in metals in sediment over time.

Trends and Correlations

One of the most important aspects of environmental analysis is to answer questions regarding trends in contamination. Trends and correlation between parameters provide significant insight into the behavior of contaminants in the environment. Anecdotal evidence suggests that contamination in the Rio Grande basin has drastically increased over the last twenty years. This relationship of metals concentration in sediment to time becomes important during the modeling phase as significant trends over time can skew the model results. Therefore, one goal of the detailed analysis was to determine changes in metal concentrations in sediment during the twenty-year period of record.

Temporal Trend in Metals in Sediment

Both nonparametric and parametric tests demonstrate no trend over time in any of the three metals. Of the three metals, however, it is somewhat surprising not to see a downward trend in lead. With the switch from leaded to primarily unleaded gasoline in the United States in the late 1970's and the regulations on leaded paint, one might expect sediment samples to show significant decreasing trends over time, especially during the period between 1966 and 1996. However, several other lead sources could contribute to a lack of a significant trend: Mexico still relies on leaded gasoline to fuel the majority of the nation's vehicles, large coal-burning plants came online in the basin in the early 1980s, and lead continues to be extensively used for piping and industrial applications.

The scatterplots of the metals measurements over time illustrate an increase in the sampling activity during 1992 and 1993 (Figures 18-20). This increased sampling reflects activity related to the BTTS. (Please see the "Literature Review" chapter for details about the BTSS). The BTSS sampled at routine monitoring sites, but also expanded sampling into tributaries; therefore, more measurements exist even though the sampling was not significantly more frequent during 1992 and 1993. The additional measurements in the tributaries do not seem to have a significant effect on overall trend in the arsenic and lead graphs. During 1993 several outliers occurred in the mercury measurements. These mercury outliers do seem to affect the trend line for changes in mercury over time, but the Pearson's coefficient (R) is small enough both with and without the outliers that it is still possible to state that no trend exists in mercury over time.

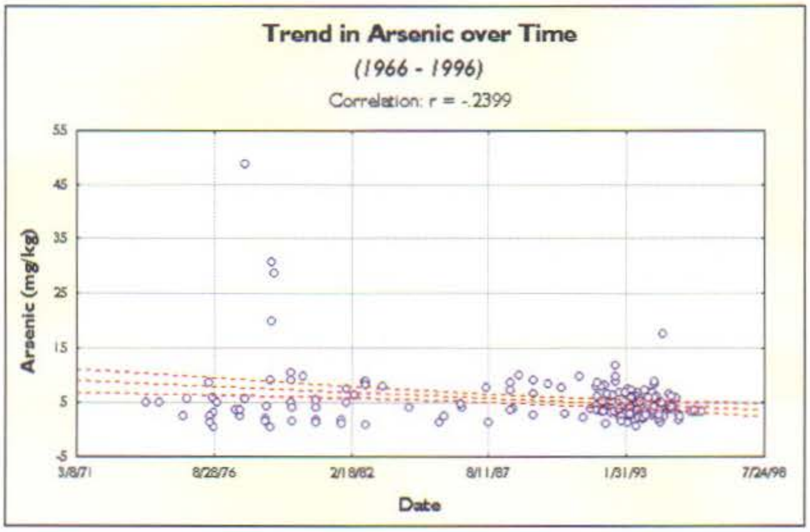


Figure 18: Temporal Trend in Arsenic in Sediment

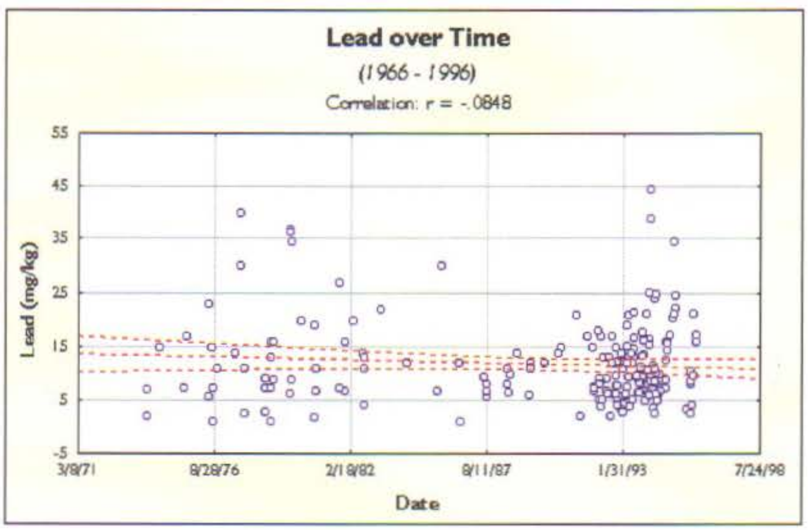


Figure 19: Temporal Trend in Lead in Sediment

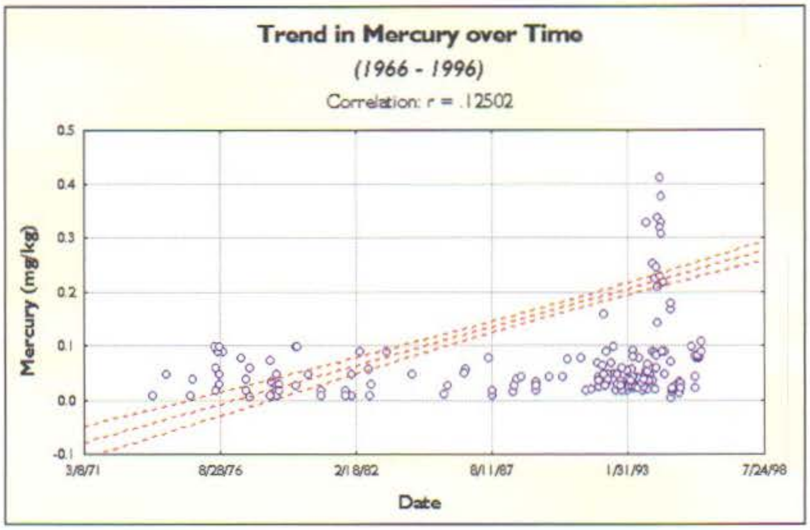


Figure 20: Temporal Trend in Mercury in Sediment

Correlation between Metals and other Water-Quality Parameters

From the preliminary screening of the data, it is apparent that relatively few measurements of metals in basin sediment exist. To handle this problem, modelers will often choose other correlated parameters to develop the dynamics of the model. By determining relationships between water quality and sediment quality, it becomes possible to use the water-quality data to predict changes in the sediment-quality data.

To accomplish this goal of determining suitable substitute parameters for modeling, the metals in sediment data were compared against other constituents. The approach for this comparison consisted of choosing matched pairs of data – data obtained at the same site and at the same time. This condition further limited the data, sometimes to as few as fifteen pairs throughout the period of record for the entire river basin.

Because the comparisons were performed on small data sets, nonparametric statistics were used to determine the correlation between parameters. Nonparametric statistics determine relationships in situations when little is known about the variable in comparison to the rest of the population and in situations with small (n <100) data sets. Nonparametric statistics do not rely on the mean and the standard deviation as a way to describe the distribution of measurements away from the expected function. Therefore, nonparametric statistics, while less powerful than parametric statistics, can be appropriate for lower-quality data sets.

The nonparametric version of the correlation coefficient demonstrates the relationship between two different parameters. For this study, the Kendall-Tau test represents the nonparametric correlation coefficient.

The monitoring data used for the study includes measurements for over 3,400 constituents and contained data related to water, fish tissue, biological, and sediment data. Because the model requires a correlated parameter with an extensive amount of data, the constituents were limited to only those for which more than 1,000 measurements exist in the database or those for which data could be simulated using other models. This criteria limited the data set to 18 parameters plus the dissolved metal, total metal, and metal in fish tissue measurements for each metal. The parameters were then paired with the metals data and analyzed for correlations. Tables 16-18 represent the results of the analysis.

Fecal coliform is the only water-quality parameter with a significant number of measurements in the database and with a statistically significant relationship to arsenic. This relationship may be partially explained by the affinity both constituents have for adhering to sediment and settling out of the water column. It is also evident that both arsenic and fecal coliform can enter the water through nonpoint source runoff from agricultural land uses. In fact, a further investigation of the data shows that the relationship between fecal coliform and arsenic in sediment remains valid in subwatersheds with predominately agricultural land uses, but in subwatersheds with predominately urban land uses the relationship between parameters disappears. Therefore, while fecal coliform may be used as a surrogate for arsenic in sediment in agricultural watersheds, it is not appropriate for urban watersheds.

Aluminum concentrations also correlate with arsenic measurements. This relationship is often observed in water-quality data sets. Aluminum can serve as a normalizing agent for arsenic, demonstrating the "naturally-occurring" concentrations of arsenic. Insufficient measurements for aluminum exist in the database to serve as a surrogate for arsenic.

The parameters with the best relationship to arsenic in sediment are the percent of silt and clay in the sample. This relationship is also expected because arsenic tends to bind to sediment particles of a particular size. Unfortunately, few measurements for percent clay and silt exist in the database since this parameter was measured only under the BTSS.

Table 16: Nonparametric Analysis for Arsenic in Sediment versus other Constituents

Arsenic Correlation Parameter	Valid N	Kendall Tau	Z	p-level
Percent of Clay	59	0.406	4.539	0.00001
Percent of Silt	59	0.398	4.456	0.00001
Aluminium	74	0.314	3.953	0.00008
Dissolved Arsenic	102	0.240	3.580	0.00034
Fecal Coliform	31	-0.291	-2.300	0.02146
Phosphate	17	-0.260	-1.458	0.14486
pH	29	0.151	1.151	0.24954
Alkalinity	33	-0.119	-0.972	0.33119
Nitrate	38	0.110	0.969	0.33276
Sulfate	40	0.105	0.953	0.34063
Phosphorus	40	-0.104	-0.943	0.34578
Total Suspended Solids – Volatile	38	-0.088	-0.777	0.43715
Dissolved Oxygen	44	0.074	0.709	0.47824
Nitrogen as Ammonia	40	-0.069	-0.627	0.53082
Total Dissolved Solids	70	0.049	0.601	0.54773
Total Suspended Solids	40	-0.036	-0.330	0.74104
Arsenic in Fish Tissue	83	0.019	0.256	0.79768
Flow	26	-0.031	-0.223	0.82367
Total Organic Carbon	90	0.013	0.178	0.85861
Turbidity	15	-0.011	-0.055	0.95585
Chloride	40	0.001	0.012	0.99061

A comparison of lead in sediment to other parameters also shows a significant correlation between lead and aluminum and lead and percent of clay and silt. Unlike arsenic, however, lead also correlates with pH and ammonia nitrogen. The Kendall Tau value of lead versus pH shows that as the pH value increases, the value of lead decreases. It also shows that as ammonia nitrogen increases the value of lead increases. Fortunately, thousands of measurements for pH and ammonia nitrogen exist in the database, providing an opportunity to use two commonly-measured parameters to predict values of lead.

Table 17: Nonparametric Analysis for Lead in Sediment versus other Constituents

Lead Correlation Parameter	Valid N	Kendall Tau	Z	p-level
Percent Silt	56	0.437	4.753	0.00001
Aluminium	74	0.348	4.381	0.00001
Percent Clay	56	0.353	3.841	0.00012
pH	28	-0.282	-2.104	0.03536
Ammonia Nitrogen	39	0.197	1.767	0.07719
Total Organic Carbon	90	0.117	1.628	0.10361
Lead in Fish Tissue	83	-0.113	-1.510	0.13113
Phosphorus	39	0.167	1.494	0.13516
Total Suspended Solids-Volatile	37	0.156	1.356	0.17519
Total Lead	24	0.194	1.326	0.18473
Total Suspended Sediment	39	0.127	1.136	0.25607
Phosphate	58	0.084	0.928	0.35335
Dissolved Lead	102	0.044	0.656	0.51206
Alkalinity	32	-0.065	-0.523	0.60087
Chloride	39	-0.056	-0.499	0.61801
Total Dissolved Solids	69	-0.039	-0.471	0.63735
Fecal Coliform	28	0.051	0.380	0.70402
Sulfate	42	0.014	0.134	0.89354
Turbidity	14	0.022	0.111	0.91136
Biological Oxygen Demand	3	--	--	--
Dissolved Lead	2	--	--	--

Statistically-significant correlations exist between mercury and the physical parameters of total suspended solids, total suspended solids-volatile, and percent clay. Studies have shown that mercury has become such a wide-spread problem that it can be measured in nearly every reservoir and riverbed in the world. Of the three metals analyzed, mercury is most likely to move through the air to eventually be deposited in rain. Therefore, since mercury is so prevalent in soil and in as a component of air deposition, logically it would correlate well with the measurements of soil in water (total suspended sediment).

Phosphorus also correlates with mercury measurements. The most likely explanation for this correlation is that both mercury and phosphorus can be components of nonpoint source pollution from agricultural sources. Since agricultural practices contribute to erosion potential for soils, logic would also dictate that as farmers fertilize and irrigate their crops, nonpoint source runoff will carry both sediments and nutrients into rivers and streams. This would imply that both phosphorus and mercury naturally correlate with suspended sediments, but perhaps not with one another. This question may be further explored using multiple regression.

Table 18: Nonparametric Analysis for Mercury in Sediment versus other Constituents

Mercury Correlation Parameter	Valid N	Kendall Tau	Z	p-level
Total Suspended Solids-Volatile	37	-0.330	-2.872	0.00408
Percent Clay	59	0.250	2.800	0.00511
Total Suspended Sediment	39	-0.307	-2.753	0.00590
pH	112	-0.163	-2.547	0.01088
Phosphorus	39	-0.284	-2.545	0.01093
Percent Silt	59	0.205	2.290	0.02203
Aluminium	73	0.130	1.630	0.10314
Total Dissolved Solids	72	-0.130	-1.614	0.10652
Ammonia Nitrogen	39	0.163	1.458	0.14485
Nitrate	39	0.163	1.458	0.14485
Phosphate	17	-0.212	-1.188	0.23478
Turbidity	17	0.166	0.931	0.35173
Total Mercury	41	0.095	0.876	0.38117
Dissolved Mercury	83	-0.065	-0.864	0.38750
Chloride	39	0.063	0.561	0.57462
Alkalinity	32	-0.067	-0.540	0.58927
Dissolved Mercury	81	-0.032	-0.428	0.66874
Mercury in Fish Tissue	81	-0.032	-0.428	0.66874
Sulfate	42	0.014	0.134	0.89354
Fecal Coliform	28	-0.014	-0.104	0.91744
Total Organic Carbon	85	0.005	0.073	0.94150
Flow	28	0.005	0.041	0.96725
Biological Oxygen Demand	3	--	--	--

Multiple Regression Analysis of Metals in Sediment

Further investigation of the relationship between parameters and metals in sediment requires multiple regression analyses. Multiple regression can distinguish between the correlated parameters to determine the impact of each of the independent parameters on the dependent variable.

Unfortunately, the lack of depth in the database again becomes apparent when attempting multiple regression analysis. For the analysis of arsenic in sediment, percent of clay, percent of silt, and fecal coliform were never measured simultaneously; therefore, it is impossible to quantify the impact of each of these constituents on arsenic in sediment using multiple regression techniques.

For the analysis of lead in sediment, ammonia nitrogen and pH were measured simultaneously with lead in sediment and percent clay and percent silt were measured simultaneously. However all four parameters were not measured simultaneously with lead. The analysis shows that ammonia nitrogen and pH together explain less than half of the residual variability of lead in sediment (Table 19). More simply stated, ammonia nitrogen and pH together are not sufficient to predict the value of lead in sediment. Through the regression analysis it becomes clear that the parameters ammonia nitrogen and pH are themselves related and therefore that the unique contribution of ammonia nitrogen to the value of lead in sediment becomes a very small number when analyzed with jointly with pH. Figure 21 graphically illustrates how a few outliers can influence the determination of a relationship between parameters: without three of the measurements, no relationship between ammonia nitrogen and lead in sediment would exist.

Figure 22 shows a discernable relationship between pH and lead in sediment. Figure 23 illustrates the results of the multiple regression analysis showing a significant portion of the residuals fall far outside of the 95% confidence bands.

Table 19: Regression Summary for Dependent Variable Lead

	BETA	Standard Error of BETA	B	Standard Error of B	t(25)	p-level
Intercept			94.009	54.433	1.727	0.096
Ammonia Nitrogen	0.105	0.220	1.477	3.088	0.478	0.637
pH	-0.339	0.220	-10.363	6.717	-1.543	0.135
$R= .407$ $R^2= .165$						

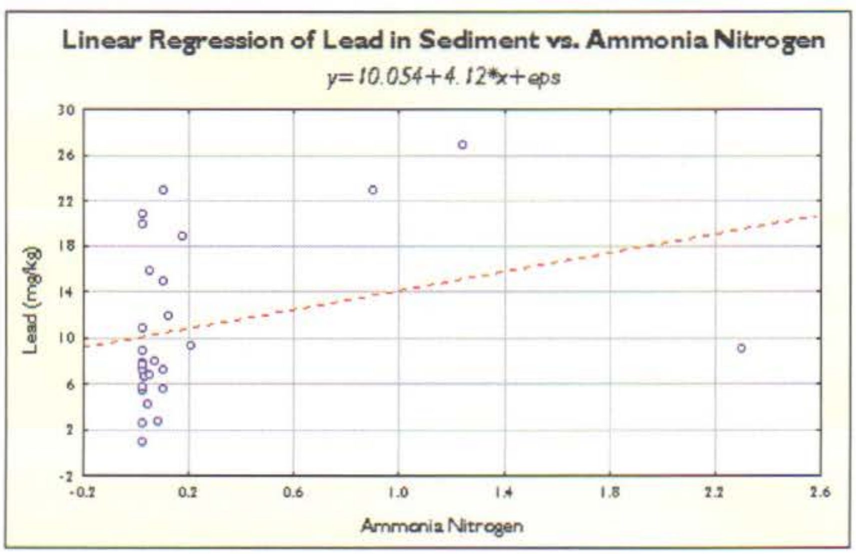


Figure 21: Regression of Lead in Sediment vs. Ammonia Nitrogen

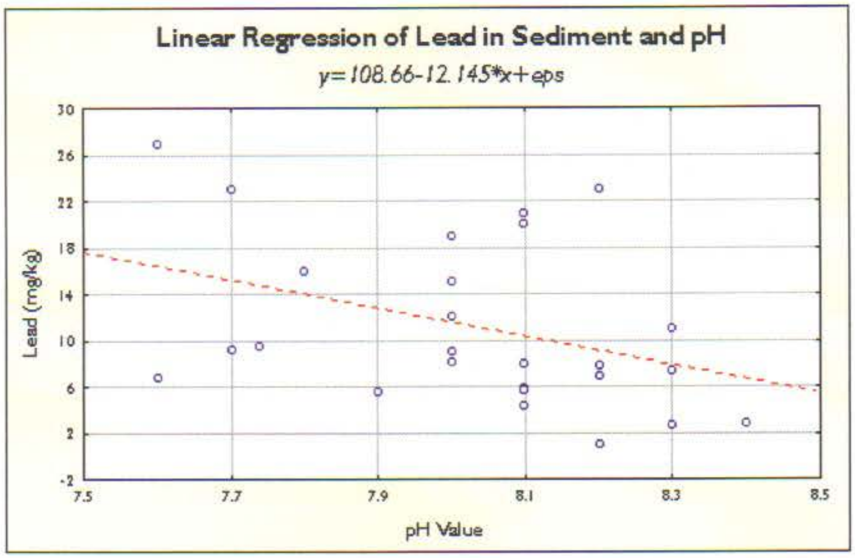


Figure 22: Regression of Lead in Sediment vs. pH

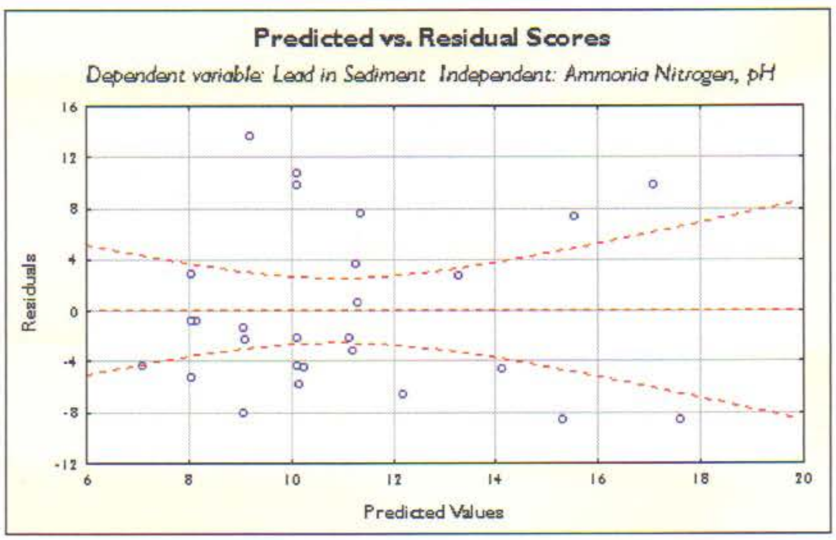


Figure 23: Multiple Regression of Ammonia Nitrogren and pH to Predict Lead in Sediment with 95% Confidence Bands

The analysis of percent clay and percent silt versus lead in sediment shows that only 38% of the measurements of lead in sediment can be explained by clay and silt content of the samples (Table 20). Again, the parameters clay and silt demonstrate a relationship between one another that then reduces the impact of the combination of the parameters on the value of lead in sediment. Figures 24 and 25 illustrate the relationship of clay and silt with lead in sediment, and figure 26 shows the analysis of predicted values versus residuals from the combination of clay and silt on lead in sediment. The figures clearly illustrate similar regression results from each of clay and silt, and the impact of considering both parameters against lead. The residual analysis in particular illustrates that while there is a discernable relationship between the parameters, a significant portion of the residuals fall far outside of the 95% confidence bands.

Table 20: Regression Summary for Dependent Variable Lead

	BETA	Standard Error of BETA	B	Standard Error of B	t(53)	p-level
Intercept			5.944	2.230	2.665	0.010
Percent Clay	0.163	0.161	0.164	0.162	1.011	0.316
Percent Silt	0.257	0.161	0.109	0.068	1.599	0.116
R= .380 R^2= .144						

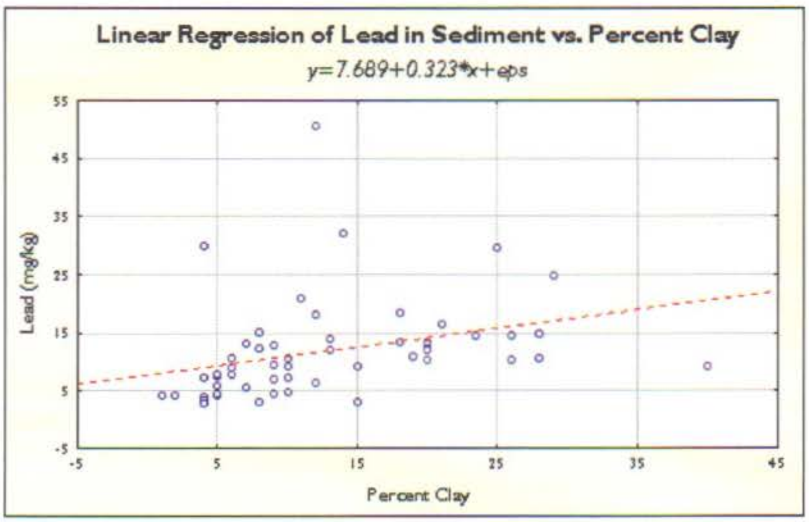


Figure 24: Regression of Lead in Sediment vs. Percent of Clay in Sample

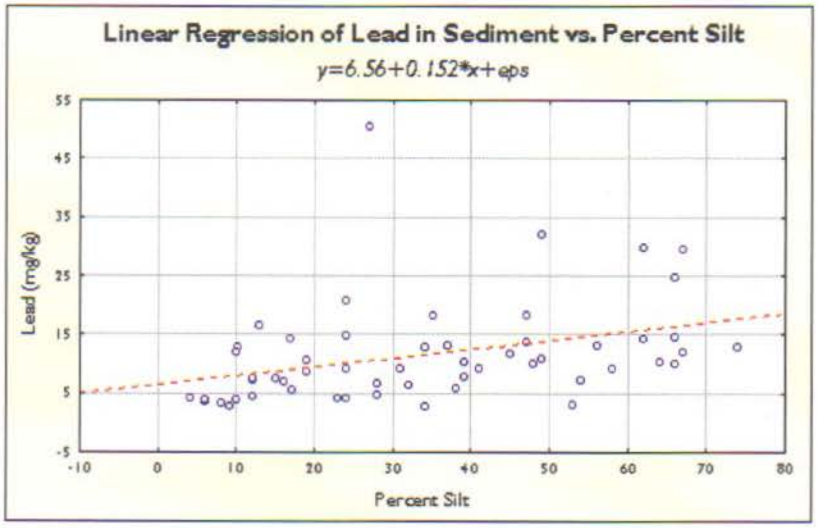


Figure 25: Regression of Lead in Sediment vs. Percent of Silt in Sample

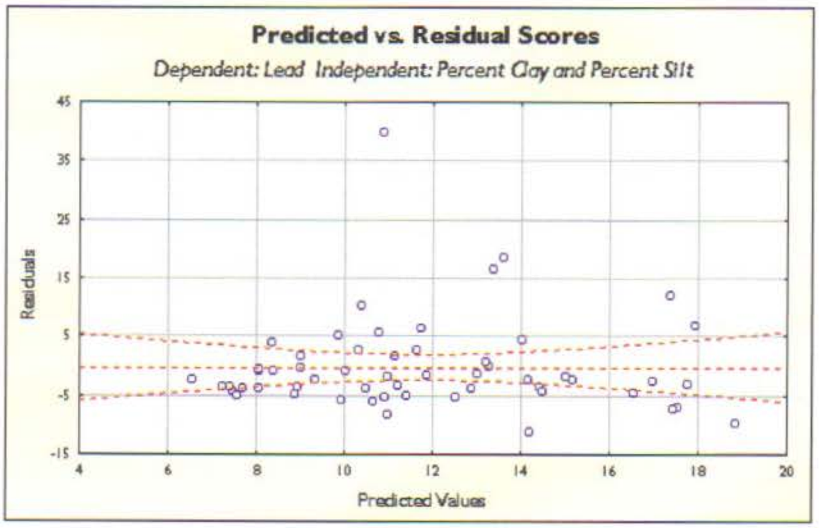


Figure 26: Analysis of Residuals vs. Predicted Values of Lead in Sediment Particle Size from Independent Variables Percent Clay and Percent Silt

Perhaps the most significant conclusion from the multiple regression analysis of the independent variables clay and silt is that they do not predict a zero value for lead nor a value near the minimum analytical limit. A further investigation of the data indicates that all of the samples where percent clay and percent silt were measured simultaneously with lead in sediment were from the BTTS. These sampling stations were purposely located in areas where sediment contamination from point and nonpoint source pollution would be expected. Therefore, no measurements in the sample data set show relationships between these three parameters in ambient conditions. If the model relied solely on the values of percent clay and percent silt to predict lead, the predictions throughout the basin would likely be significantly high.

The multiple regression analysis for mercury in sediment uses four parameters to predict the concentration: TSS, TDS, pH, and phosphorus. Together these parameters account for 40% of the variability of mercury in sediment (Table 21). Individual plots of the parameters versus mercury in sediment (figures 27 through 31) show more detail than the simple numbers convey. For example, Figure 27 shows that while there may be a relationship between phosphorus and mercury in sediment, the relationship is almost a flat line and therefore not a substantial predictor of the value of mercury. TDS and pH contribute the largest influence on the value of mercury in sediment.

However, it is important to note that while the nonparametric analyses for each of the independent variables showed a statistically significant relationship with mercury in

Table 21: Regression Summary for Dependent Variable Mercury and Independent Variables TSS, TDS, pH, and Phosphorus

	BETA	Standard Error of BETA	B	Standard Error of B	t(21)	p-level
Intercept			0.475	0.295	1.609	0.123
TSS	-0.112	0.235	0.000	0.000	-0.478	0.638
TDS	-0.402	0.240	0.000	0.000	-1.677	0.108
pH	-0.386	0.269	-0.052	0.036	-1.434	0.166
Phosphorus	-0.319	0.286	-0.023	0.021	-1.117	0.277
R= .408 R^2= .167						

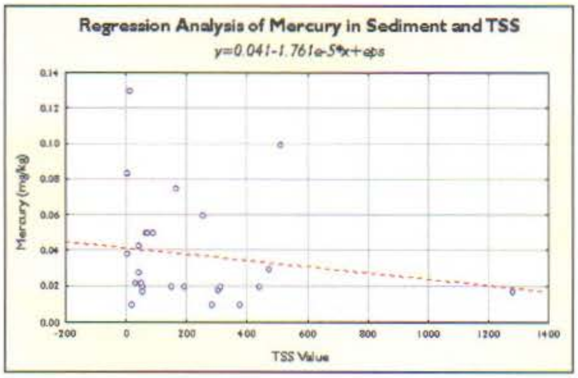


Figure 27: Regression Analysis of Mercury in Sediment and TSS

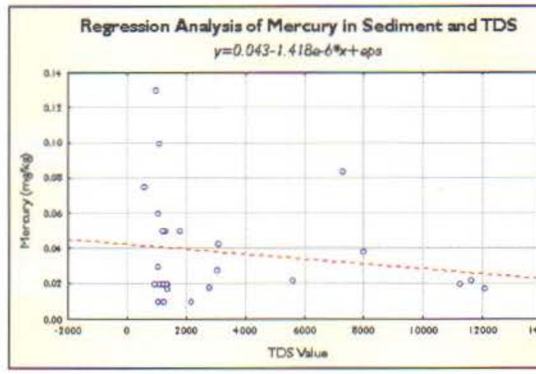


Figure 28: Regression Analysis of Mercury in Sediment and TDS

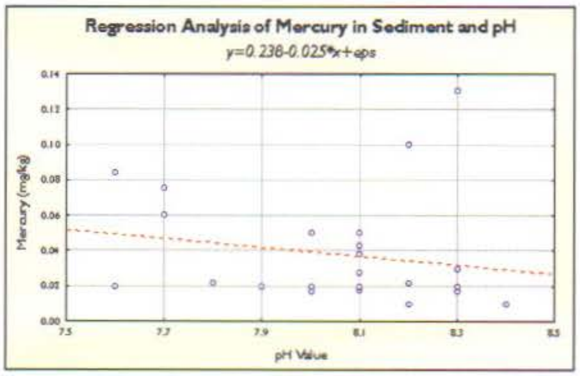


Figure 29: Regression Analysis of Mercury in Sediment and pH

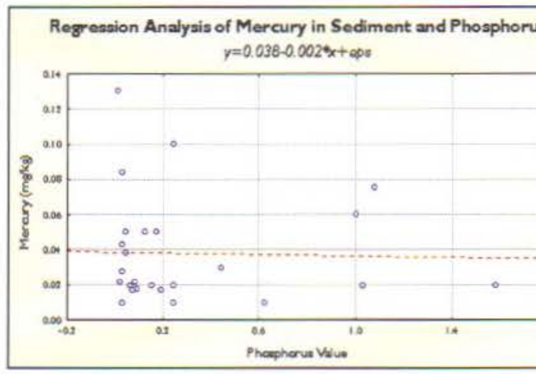


Figure 30: Regression Analysis of Mercury in Sediment and Phosphorus

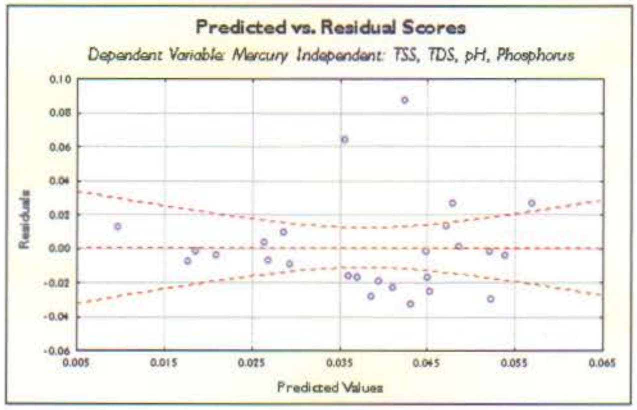


Figure 31: Analysis of Residuals vs. Predicted Values of Mercury in Sediment from Independent Variables TSS, TDS, pH, and Phosphorus

sediment, the multiple regression analysis shows a p-level greater than .1, and therefore does not indicate a statistically significant relationship. A review of the beta values from Table 21 and figures

27 and 30 might lead one to the conclusion that removing TSS and phosphorus from the multiple regression analysis would generate better results. Table 22 demonstrates that in fact the analysis becomes even less reliable in predicting mercury values, accounting for less than 30% of the variability with a p-level of greater than .2. Therefore, it is not appropriate to use the independent parameters TSS, TDS, pH, and phosphorus to reliably derive a model for mercury in sediment.

Table 22: Regression Summary for Dependent Variable Mercury and Independent Variables TDS and pH

	BETA	Standard Error of BETA	B	Standard Error of B	t(21)	p-level
Intercept			0.289	0.222	1.306	0.205
TSS	-0.214	0.204	0.000	0.000	-1.049	0.305
TDS	-0.228	0.204	-0.030	0.027	-1.115	0.277
$R = .280$ $R^2 = .079$						

Normalization of Metals Data

To understand the impact of man's activities on the environment with respect to metals, it is important to first determine the concentration attributable to naturally-occurring conditions. Normalization with another metal presents an opportunity to determine this contribution. Scientists use several different parameters to represent the normalization factor: Aluminum, Iron, Lithium, Total Organic Carbon, and grain size. Of these constituents, Aluminum is most often used because it naturally occurs in high concentrations, is generally present in sediment, and it is a major component of clay soils (Daskalakis, 1995).

In the Rio Grande, a nonparametric analysis of Aluminum's relationship to the three metals during the thirty-year analysis period demonstrates positive correlations for arsenic (Kendall Tau = .314, $p<.000077$, $n=74$) and lead (Kendall Tau=.348, $p<0.00001$, $n=74$), and no relationship for mercury (Kendall Tau=.130, $p<.103$, $n=73$). Using these relationships, it is possible to determine the contribution of metals in sediment from natural sources and to use the 474 aluminum measurements in the data set to predict values of arsenic and lead in sediment.

One important note is that all of the applicable normalization measurements occur during either Phase I or Phase II of the BTTS and do not coincide with other sampling events. In total, only 74 samples were taken with both aluminum and other metals in sediment measured simultaneously, and almost no measurements for Total Organic Carbon and grain size are taken other than those in the BTTS. The data analysis is further restricted by the absence of sufficient measurements in the data set.

Geostatistical Analysis of Sediment-Quality Data

Just as the detailed statistical analysis of the data revealed a serious lack of ability to generate conclusions from the data, a geostatistical analysis also emphasizes the data's lack of depth. The most apparent conclusion is that the overwhelming majority of monitoring sites are clustered near urban areas along the main river (Figure 32). While this might be acceptable for a regulatory agency that restricts itself to conclusions about point source pollution in urban situations, a thorough sediment screening should distribute monitoring sites to obtain sufficient information about a variety of land use and flow conditions.

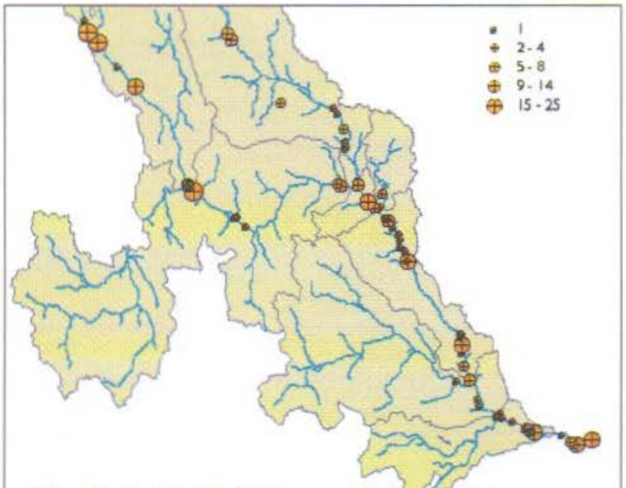


Figure 32: Analysis of Spatial Frequency of Sediment Monitoring

Figure 32 illustrates patterns in sampling. In isolated cases, the monitoring entities clearly attempted to develop a profile of an entire stretch of river or stream. At points along the river the sampling stations are clustered within a very small area – for example, three monitoring stations on Manadas Creek in the Laredo/Nuevo Laredo area. However, large portions of the basin remain unsampled for sediment. Figure 32 clearly shows the difference in frequency of sediment monitoring in highly populated areas (the large circles near El Paso/Juárez, Laredo/Nuevo Laredo, Harlingen/Reynosa, and Brownsville/Matamoros) versus rural or agricultural areas. One interesting conclusion from figure 32 is the large number of samples at the confluence of the Río Conchos with the Rio Grande. This site is not located immediately downstream from a major urban area, but it is positioned to determine the contribution of contaminants from the largest Mexican tributary to the Rio Grande.

The most basic of geostatistical analysis is to display simple images of monitoring sites that exceed screening levels. This type of screening analysis assists researchers in limiting their focus for further study and regulators in targeting their assessment and remediation activities. It is also the first step toward understanding the potential sources of contamination. Figures 33-35 show monitoring sites with different colors to highlight those stations where the mean value exceeds screening levels for arsenic, lead, and mercury in sediment.

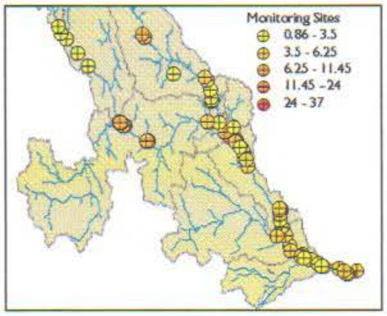


Figure 33: Analysis of Arsenic by Monitoring Site

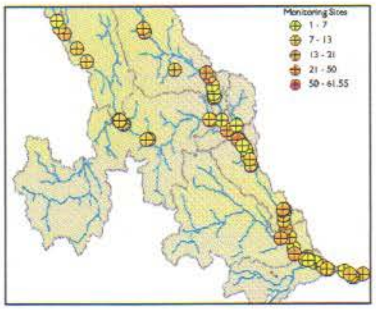


Figure 34: Analysis of Lead by Monitoring Site

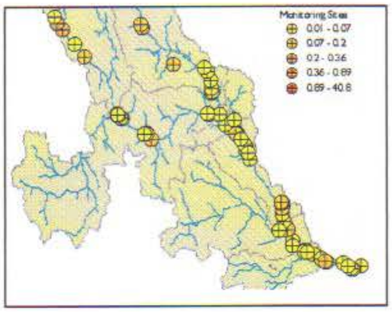


Figure 35: Analysis of Mercury by Monitoring Site

Figure 33 shows the spatial analysis for arsenic in sediment. From a simple picture it is apparent that the areas of the basin that immediately merit concern are Amistad Reservoir and Devils River. However, the upper portion of the Pecos River and the upper portion of the Rio Grande at the confluence of the Río Conchos also show potential problems with arsenic. Figure 34 shows that lead measurements are high in Amistad Reservoir, and are also significant in the upper and middle reaches of the Rio Grande. Figure 35 shows sporadic elevated mercury throughout the basin, with the highest mean values occurring in the upper reaches of the Rio Grande and Pecos Rivers.

Summary of Data Analysis

The results of the data analyses were somewhat less than originally anticipated. Given the size, importance, and perceived magnitude of water-quality problems in the basin, it was expected that the sediment monitoring data would be plentiful and wide-spread throughout the basin. Instead, the data analysis demonstrated a lack of sufficient long-term sediment-monitoring data for metals. The analysis also indicated that the agencies tasked with tracking water quality do not necessarily do so in a way that provides sufficient information from which to draw conclusions and develop transport models.

Of particular concern is the lack of supporting or incidental information gathered simultaneously with sediment samples. By gathering flow, pH, TSS, TOC, Aluminum, and biological data with sediment samples agencies would lay the foundation for developing indicators and simulators for certain metals in sediment. They would also provide data to supplement their ability to rely more heavily on sediment samples as a substitute for other routine monitoring. The use of indicators can assist agencies with better targeting their ever-dwindling resources toward areas with conditions suitable for metals contamination.

However, indicators and simulators are never a substitute for adequate field collection. Unfortunately the agencies performing monitoring in the Rio Grande basin have elected to perform point-source compliance monitoring exclusively—relying on the indicator of "urban land use" or "permitted discharge" to site sampling locations. The data analysis reflects this preference for urban monitoring. This approach limits the agencies' ability to eventually rely on other indicators for targeted monitoring. This approach also seriously limited efforts to develop a sediment transport model for the basin. The next chapter—Sediment Transport Analysis using GIS—illustrates the difficulties encountered in relying on the existing monitoring data to develop the model.

Sediment Transport Analysis using GIS

This chapter discusses both the preparation of Geographic Information System (GIS) data and use of GIS to further analyze sediment quality in the Rio Grande basin. It also recommends changes to the existing monitoring strategies in the basin based on the results of the modeling effort.

GIS Data Types

GIS uses two different types of data - raster and vector. Raster data generally consist of either imagery or continuous data (e.g. elevation) divided into cells or a grid. A grid is evenly spaced over the data set and the GIS then presents information that characterizes each cell within the grid. For example, each cell on an elevation grid will contain one number representing the meters above sea level within the cell. The smaller the cells in the grid, the more detailed the resolution of information will be.

Vector data are comprised of points, lines, and polygons. Each of the objects represents some entity, e.g. a point can represent a monitoring site, a line can show a river, and a polygon can symbolize a lake. Vector data uses a much smaller amount of information to represent objects than raster data.

Generally, GIS-based models reside in the raster realm where they rely on a series of "map calculations" to process the data. Fundamentally, map calculations perform algebraic and logical functions on data within each cell of the grid and return a new grid with the results of the equation. Depending on the intricacy of the calculations, the data may expand exponentially in order to accommodate the calculations.

Selection of a Modeling Approach

Recently, researchers at University of Texas (UT) in Austin developed GIS-based models that operate in both the vector and raster arenas[10]. GIS models that combine the advantages of each realm—the continuous coverage of the raster side and the economy of the vector side—tend to provide the greatest flexibility to researchers. The UT models use a simple approach to performing the analysis that relies on data that is generally available over Internet for most of the United States. Based on the availability and accessibility of data in previous UT modeling studies and on the review of models during the literature search, the UT methodology proved the simplest, least data-intensive, and most likely to be successfully applied in the Rio Grande Basin.

[10] The UT studies include: Saunders, 1995; Pavel, 1996; Reed, 1997; and Maidment, 1994.

The data required to create a model for the Rio Grande basin following the protocols of the UT studies include layers for elevation, precipitation, land use, and soils. The following sections describe the processed followed during the attempt to replicate the UT model for the Rio Grande watershed.

Preparation of GIS Data

The GIS data used in this thesis included both raster and vector data that often required extensive manipulation before use.[11] Because the Rio Grande is an international watershed, obtaining the data necessary for performing even the simplest GIS analysis frequently proved extremely difficult. During the incipient stages of thesis development (1994) much of the GIS data did not exist for the Rio Grande watershed. As the discussion will make apparent, even the creation of data by large, international teams did not always prove effective.

The fundamental GIS data sets required for sediment transport analysis include topographic, geological, hydrological, and demographic data. The most important GIS coverages[12] included: elevation, soil types, precipitation, land use, land cover, hydrology, population density, and geology. From these baseline coverages new data layers were created, including erosion potential, slope, and estimated runoff concentrations.

All GIS data were processed using either a Sun UNIX workstation with ArcInfo 7 software or with a Pentium 200 MHz personal computer running ArcView GIS 3 and SpatialAnalyst software. Because the Rio Grande basin covers such a large area, the scale chosen to represent the basin was very coarse to minimize the processing time. In general, raster data was resampled to a grid of either 100 –meter or 1-kilometer cells. All vector data was generated from either 1:250,000 or 1:100,000 maps. All coverages were projected into a modified Albers Conformal Conic projection optimized for the middle of the Rio Grande. The Albers projection was chosen to preserve the area instead of the shape of objects in the basin.[13]

Preparation and Analysis of Elevation Data

The most fundamental data used in the GIS analysis was elevation (Figure 36). The elevation data used for analysis was originally compiled from two different data sources: the United States data was generated by the USGS and the Mexican data was generated by the National Institute of Statistics and Geography (INEGI). The data was resample to 100-meter cells for hydrological analysis. Figure 36 shows a shaded relief of the elevation data called a "hillshade." The lighter regions represent high elevation and the

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[11] Please see Appendix B for sources of GIS and water quality data.

[12] The terms "coverage", "layer", and "theme" are GIS terms used interchangeably to represent one type of data. For example, data representing land uses in the Rio Grande watershed may be called a "land use coverage", a "layer of land uses", or a "theme of land uses".

[13] Metadata for all GIS coverages is available on the CD-ROM included with the thesis.

darker regions represent lower elevations. The elevation in the basin varies from sea level to as high as 4,068 meters in both Colorado and Coahuila.

Analytical procedures followed during the preparation of the elevation data follows a standard watershed analysis methodology used by Dr. David Maidment at the University of Texas (Maidment, 1994, Saunders, 1995, and Pavel, 1996). This methodology has long been recognized as the standard approach to stream and watershed delineation. Historically, processing the data for the hydrological analysis would have required a robust UNIX system running expensive ArcInfo software; however, to demonstrate the relative simplicity of newer software packages, the majority of the watershed delineation work was processed on a personal computer running Avenue scripts in ArcView.[14]

The first step in processing the elevation data is to fill the unnatural depressions in the data. This process, called "filling the sinks" ensures that during the hydrological analysis water continues to move downstream instead of collecting in small basins or sinks. Often sinks result from either miss-entered data or from errors between data sets and cause erroneous streams and subwatersheds to appear in the data if not corrected. The corrected elevation data became the foundation for further steps in developing the model.

The second step determined which direction water will flow from each cell in the elevation grid. The direction analysis is based on the presumption that water will flow along the path of least resistance, which in general should be to the neighboring cell with the lowest elevation. The resulting grid, called a "flow direction" grid, contains numerical data representing the direction from the current cell to to neighboring cell with the lowest elevation value (Figure 37).

Figure 36: Elevation Data

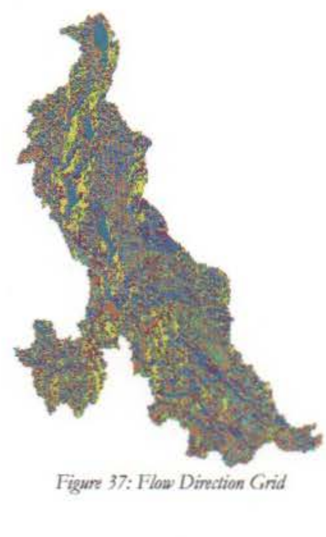

Figure 37: Flow Direction Grid

Figure 38: Flow Accumulation Grid

[14] The author worked with the software vendor Environmental Systems Research Institute (ESRI) and Dr. Maidment at UT through a TNRCC and USEPA project funded to create programs within ArcView that performed the same hydrological functions as the more robust software. The project, title "Watershed Delineator", created program extensions to ArcView that allowed users to performed standard hydrological processes and modeling. To the greatest extent possible, this thesis demonstrates the utility of ArcView for extensive and sophisticated GIS analysis.

From the flow direction grid the network of cells that eventually became streams and rivers was created. For each cell in the grid, the analysis determined how many cells would be upstream from it. This upstream analysis produces a "flow accumulation" for each cell in the grid. Figure 38 shows the resulting flow accumulation grid. In the flow accumulation grid, the darker cells represent those receiving the greatest accumulation of upstream cells flowing into it. Another way
to say this is that as water moves through a watershed and flows into larger rivers it joins water flowing from other parts of the watershed. The largest rivers in a basin represent the largest downstream accumulation of water from other parts of the watershed.

By setting a threshold of flow accumulation required to be considered a stream, it was possible to then convert the flow accumulation grid to a grid representing the larger streams and rivers in the Rio Grande watershed (Figure 39). Figure 39 simply shows cells that receive flow from 5,000 or more cells upstream. To create the network of streams in the basin, it was necessary to further process the stream grid to identify the stream order and the link between streams. The stream order (Figure 40) and link grids formed the foundation for delineating the associated subwatersheds. Figure 41 shows the subwatersheds created by delineating the drainage area associated with the junction between two different streams throughout the river basin. Finally, to facilitate the analysis of metals in sediment based on hydrologic areas, eight "outlet" drainage points were chosen to represent major watersheds in the basin. The resulting eight subwatersheds are illustrated in Figure 42.

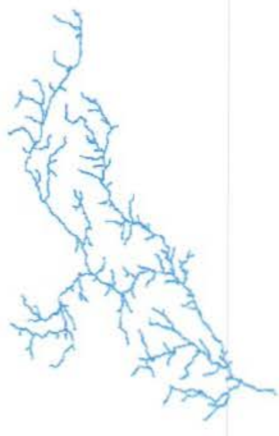

Figure 39: Streams Delineated from Elevation

Figure 40: Stream Order Determined from Streams

Figure 41: Subwatersheds Delineated from Streams

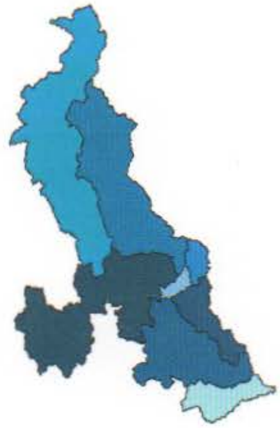

Figure 42: Eight Major Subwatersheds for Study Area

Land Cover, Population, and Land Use

One of the more significant issues in this thesis was obtaining a usable coverage of land use for the Rio Grande watershed. Land use is one of the most important data sets used to model the basin—especially when the model relies on Estimated Mean Concentrations of metals associated with each type of land use. Unfortunately, even for small watersheds, obtaining accurate land use data can be extremely expensive.

In the United States, the entity primarily responsible for creating land use coverages for the country is the USGS. The USGS created a GIS coverage of land use for the United States in the early 1980s. Other sources of land use information exist, however, the USGS provides the only continuous coverage of land use for the entire Unites States portion of the watershed. Obtaining a corresponding Mexican coverage is not possible: Mexico uses different definitions of land use, different scales, and distributes information under different policies than in the United States.

The difficulty in obtaining land use information led to the creation of a new GIS coverage that combines several data layers. The TAES study provided the most consistent land data available for the basin. The TAES created the land cover data in conjunction with the TNRCC, IMTA, and INIFAP from satellite data taken in 1995.[15] Because the TAES focuses on agricultural studies, however, the data created for their study contained only "land cover" (Figure 42).[16] Land cover generally describes the vegetation covering the land in the watershed.

The original TAES coverage distinguishes between 205 different vegetation types in the watershed. To create Figure 43, the 205 classes were aggregated into 17 major vegetative categories. Figure 43 shows the land cover within the watershed to be predominantly one of three categories: grassland, scrubland or cropland (the large light and medium green portions of the watershed).

Figure 43: Land Cover Data

Figure 44: Population Density

Figure 45: Final Land Use/Land Cover

[15] The data was created under a project funded and lead by the Border Environmental Assessment Team at the TNRCC.

[16] The TAES relied upon an automated procedure to create the land cover data. This procedure scans satellite imagery for reflectance, heat (infrared), and color intensity. TAES relied on existing studies to determine the vegetation type indicated by the combination of color measurements.

The most important data type missing from the land cover layer is the urban category. Again, Mexico and the United States approach the definition of the urban land use category differently; therefore, little compatible information on urban land uses between the two countries exists. To compensate for this deficiency, a population database was chosen to simulate the urban portions of the watershed. The raw population data was converted to a grid representing population density within the basin. Figure 44 shows the result of the population analysis, with the progressively darker colors representing more densely populated areas in the basin.

From Figure 44, the most populous portions of the watershed are easily apparent, with Albuquerque and El Paso/Juárez in the northern most portion of the basin and the sister cities along the border at the southeastern portion easily discernable.

To create the final land use coverage, the population density grid was resampled for only those areas with more than 50 people per square kilometer. This grid was then overlaid with the land cover grid. Where the two grids shared common cells, the values for land categories in the land cover data were replaced with a new "urban" code. Finally, the new land cover data was reclassified into just seven land use categories: cropland, grassland/scrubland, forest, wetlands, barren, water, and urban. This reclassification of data greatly simplifies the land use coverage for the basin (Figure 45).

While this data represents the most comprehensive information found during the study for the entire watershed, the land use coverage is seriously limited in its ability to serve as the foundation of a water and sediment transport model. The most apparent problem remains the coverage's lack of detail regarding urban land uses. A typical GIS-based transport model would distinguish between different types of land uses, including residential, commercial, and industrial. For very small, urban watersheds, models often rely on several different subcategories within the three main urban land use codes, e.g. light industrial, heavy industrial, landfill, etc.

Another unexpected limitation of the data was discovered while characterizing the land uses for each subwatershed in the river basin—the data was potentially affected by the drought in the basin during the 1990s. Table 23 shows the basic land use characteristics of each of the major watersheds in the basin. The two statistics pointing toward potential deficiencies in the data are the columns for percentage of wetlands and percentage of water in the subwatersheds. The combination of elevation, soils, and precipitation data indicates that the Lower Rio Grande watershed should have a significant wetlands component; however, no wetlands appear in the watershed. The Amistad Reservoir and Falcon Reservoir watersheds should also have a significant water component, which is also far below expected values. Because the drought had reached its third year by 1995, reservoirs were at least forty feet below normal and many wetlands were dry. Consequently, the land cover data shows far less wetlands and water coverage than during normal years. Reliance on the land use coverage created for this study would produce skewed results.

Table 23: Percentage of Watershed Covered by each Land Use Type

Land Use	Upper Rio Grande	Rio Conchos	Pecos River	Devils River	Amistad Reservoir	Middle Rio Grande	Falcon Reservoir	Lower Rio Grande
Cropland	14%	31%	47%	51%	72%	53%	42%	25%
Grassland/ Scrubland	61%	53%	43%	44%	17%	37%	45%	46%
Forest	20%	15%	10%	5%	8%	4%	10%	16%
Wetlands	0%	0%	0%	0%	0%	0%	0%	0%
Barren	1%	0%	0%	0%	0%	0%	0%	0%
Water	0%	0%	0%	1%	3%	0%	1%	0%
Urban	4%	1%	0%	0%	0%	5%	2%	13%

Precipitation Data

To determine the relationship between precipitation and runoff in the Rio Grande basin it was necessary to obtain a precipitation data set. This task became complicated because most comprehensive weather data in or near the basin contained only United States data. Review of the literature about precipitation modeling lead to the conclusion that the most appropriate data for modeling would be generated from the "Parameter-Elevation Regressions on Independent Slopes Model" (PRISM)[17]. The PRISM model creates a grid from a series of points representing weather stations. The grid cells between weather stations become populated through an interpolation process that places greater weight on weather stations under similar elevation, slope, and aspect conditions. This interpolation process generates data that more accurately represents actual weather patterns than more commonly used processes. Two barriers existed in the attempt to use PRISM data: the data was available only for the United States portion of the watershed, and the regression model and code are not currently available in the public domain.

To simulate the PRISM data using available information, it became necessary to generate a grid using standard interpolation processes. Data obtained from the National Climate Data Center (NCDC) formed the foundation of the precipitation analysis. The analysis used 199 weather stations in or near the Rio Grande watershed and evaluated data from 1971-1990 (figure 46). The output from the NCDC consisted of print files that each required conversion to database tables. These tables were then analyzed for inconsistencies, missing data, and inappropriate data, and stations were eliminated based on a lack of sufficient or suitable

[17] The Oregon Climate Center (OCS) at Oregon State University created PRISM as an alternative approach to creating gridded precipitation data. The program is still in development and is not available for use outside of the climate center. The model operates on data from the National Climate Data Center's national weather stations. The OCS is also currently testing use of NEXRAD data in the model. The OCS plans to eventually make the model commercially available.

information. The remaining 132 stations were imported into the GIS. To determine average annual rainfall at each station, the average monthly precipitation was calculated then the monthly values were summed.

Four different interpolation processes were evaluated: inverse distance weighting, spline, kriging, and trend. Each of the four interpolation methods creates a surface grid based on mathematical functions between the known points. The inverse distance weighting (IDW) method uses a linear function based on the distance between points and thus places a heavier emphasis on the points closest to the cell being evaluated. The spline method fits contours that must go through each known point and must minimize curvature of the function between the points. Trending uses a polynomial regression to fit a least-squares surface to the known points. Kriging creates a semi-variogram of the data and analyzes the data based on the assumption that the values should create the best linear, unbiased estimation (or that the mean residual and the variance of the errors should be minimized).

Results from each of the analyses were compared to the PRISM data to attempt to determine the data set that most accurately represented precipitation. None of the four analyses produced results comparable to PRISM's data. This conclusion is intuitive since the PRISM approach combines the IDW method with a weighting factor on the slope and aspect grids. This weighting factor influences the PRISM data significantly more than the model's IDW analysis, resulting in a grid that somewhat resembles elevation. Because PRISM relies on IDW as part of it's analysis, the results from the IDW interpolation were chosen as a foundation for precipitation in the basin (Figure 47).

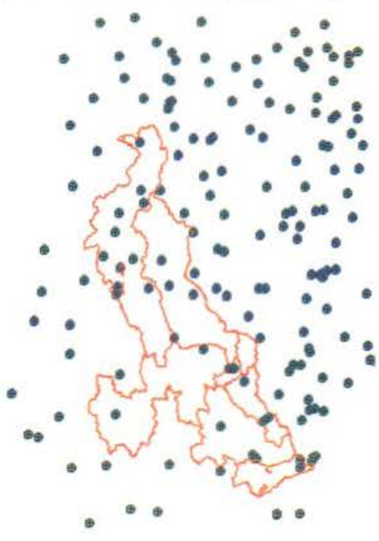

Figure 46: Weather Stations from NCDC Global Daily Summary

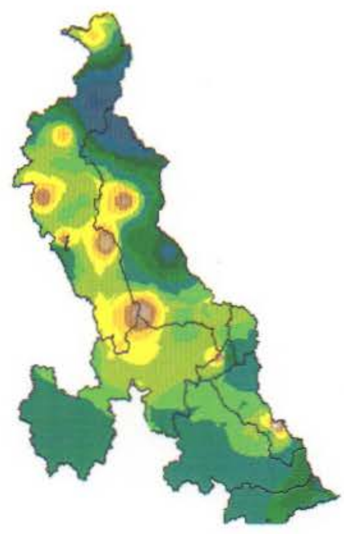

Figure 47: Precipitation Grid from IDW Interpolation

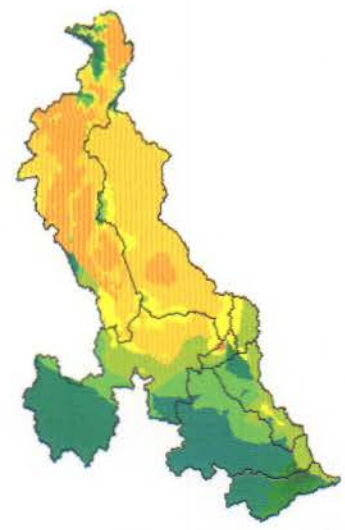

Figure 48: Combination IDW and PRISM Grid

To maximize the use of the PRISM data, the IDW and PRISM grids were combined to produce an overall mean annual precipitation grid (Figure 48). However, because the PRISM data cannot be deconstructed to daily precipitation values, a modified version of the IDW method became the interpolation method for the sediment modeling effort. An error factor was calculated for each cell in the grid between the PRISM annual precipitation grid and the IDW grid. This error factor was then applied to the model such that each daily measurement simulated results similar to those expected if PRISM were used to generate each daily precipitation grid.

Soil Data

The soil data also presented analytical challenges. The United States data is based on a national data set called the State Soil Geographic Database (STATSGO). This data is extremely comprehensive and includes information ranging from type of soil to water content, grain size, composition, erodibility, etc. It is based on county-level soil series performed by the Natural Resource Conservation Service.

Mexico bases its data on a second soil classification supported by the Food and Agriculture Organization (FAO). The FAO classification is an international classification and therefore inherently contains far less detail than the STATSGO data. To develop one consistent soils coverage for the Rio Grande watershed, the TAES created new STATSGO classifications for the Mexican data and provided very fundamental measurements like percent clay, silt, and sand, and potential to contain water.[18] Figure 49 shows the different STATSGO soil polygons for the watershed. Because the polygons are identified first by their state then by a sequential number, they do not themselves represent a particular type of soil. Rather, they link to a database of characteristics associated with the soil. For example, Figure 50 shows the four major groups

Figure 49: : STATSGO Soil Types

Figure 50: Soil Hydrological Groups

Figure 51: Susceptibility of the Soil to Water Erosion (darker equals more susceptible)

[18] The TAES designed the soil data in the watershed to be used in the SWAT model in GRASS—a different GIS than used in this thesis. The model uses STATSGO data from text files instead of from Dbase or INFO tables. Consequently, it was necessary to import the STATSGO state databases directly from tables provided by the United States Department of Agriculture for Texas, New Mexico, and Colorado. It was also necessary to import a text file for each Mexican soil type into the overall soils database.

for the soil's capacity to drain water. The lighter color represents sandy, freely-drained soil while the darker colors represent poorly-drained clay.

One of the more important analyses from the soils data is the determination of the soils susceptibility to water erosion, called the K-factor. The K-factor is one component of the STATSGO database that must be calculated as a weighted factor of all soils in the soil polygon. The resulting number is an index of the potential for soil to be eroded by rainfall. The higher the index, the more susceptible the soil is to erosion. Figure 51 shows the results of this analysis, with the lighter colors representing a low erodibility and the darker colors representing increasing susceptibility to erosion.

Flow Data

Of all of the data used in this thesis, the flow data is the most comprehensive and useful. Data was compiled for 19 USGS/IBWC gage stations in the basin for the full period of record (Table 24). While only data from 1966 – 1996 was considered in developing average monthly and annual flows, daily flow data ranging as far back as 1900 exists in the data set. The database was queried to determine an average monthly flow for the thirty-year analysis period at each gauging station. To determine average annual flows the monthly averages were summed.

Figure 52: Gage Stations and Associated Drainage Areas(Shaded Areas represent areas analyzed in this study)

Table 24: USGS Gauging Stations in the Rio Grande Watershed

Gage Number	Station Description	Drainage Area km^2
8365000	Rio Grande at El Paso	81,715
8370500	Rio Grande at Fort Quitman	88,966
8371500	Rio Grande at Presidio	97,612
8374200	Rio Grande at Rio Conchos	184,625
8374500	Rio Grande at Big Bend	2,984
8377200	Rio Grande above Del Rio	225,064
8447410	Pecos River at Amistad Reservoir	98,111
8449400	Devils River at Amistad Reservoir	11,047
8450900	Rio Grande at Amistad Reservoir	343,434
8455000	Rio Grande at San Felipe Creek	694
8458000	San Felipe Creek	354,190
8459000	Rio Grande at Laredo	369,747
8461300	Rio Grande at Falcon Reservoir	444,188
8464700	Rio Grande at Rio Grande City	486,278
8469200	Rio Grande at Hidalgo	491,159
8475000	Rio Grande at Brownsville	491,775
8407500	Pecos River at Red Bluff Reservoir	54,495
8361000	Rio Grande at Elephant Butte Res.	79,484

The gauging station locations were then imported into the GIS and converted from latitude/longitude measurements to the Albers projection. To eventually compare the flow measurements across the entire basin it became necessary to delineate the drainage areas associated with each of the gauging stations. By combining the gauging station locations with the flow accumulation and flow direction grids created during the elevation analysis it was possible to determine the watershed associated with each gauge (Figure 52). The watersheds represent the boundary of the cells from which water flows to the particular gauging station.

From the gaging station data and the associated drainage grid, it is theoretically possible to develop a runoff relationship between the calculated precipitation grid and the observed flow values. The process requires the development of a rainfall-runoff relationship between the flow predicted by a combination of the elevation and precipitation data and the flow observed at gaging stations in the basin. Three different methods exist for creating the rainfall-runoff relationship: using average annual measurements, using historical monthly measurements, or using daily data. The average annual method allows the modeler to generate predicted sediment loads for a typical year in the basin. The historical monthly approach would predict sediment loads in a monthly-time-step over the thirty-year analysis period. The daily approach provides the most detail and allows the modeler to simulate sediment loading with great precision.

Because the sediment-quality data for the basin is relatively sparse, it is not possible to calibrate either the daily or monthly time-step models. Therefore, the average annual method was chosen as most appropriate for the basin. To generate the rainfall-runoff relationship for the basin, the gaging station data were first queried to generate an average annual runoff value for the entire thirty-year analysis period. This average value smoothes any effects to the data caused by both drought and flooding during the period of record. The data were then associated with a grid by converting the gage point coverage to a grid and relating the observed runoff value to the grid. This process produced a grid without any values except in the cells occupied by gage stations.

A new grid was then created by generating a new flow accumulation grid that was weighted by the precipitation. This weighting process accommodates both the upstream flow and the new precipitation for each point in the basin – basically a water balance for the basin. This flow accumulation represents the predicted flow if all of the water were to move through the watershed without evaporation, groundwater recharge, diversion, or other sources of water depletion. To determine the relationship between the precipitation and the runoff values, the value in the flow accumulation grid is compared to the same cell in the gage grid. A simple regression analysis between the observed flow and predicted values should show the relationship between rainfall and runoff.

However, in the Rio Grande data, unlike in the studies reviewed to formulate the modeling strategy, the relationship between rainfall and runoff was not strong ($p<.12$). This lack of relationship between rainfall and runoff merited further study. A review of historical flow information published by the IBWC revealed that the dominant factor in determining in-stream flow in the Rio Grande was the controlled releases of the three major reservoirs in the watershed. A combination of factors led to the highly-regulated flow within the river: the water rights are apportioned based on an international treaty, the precipitation throughout the basin is very low and intermittent throughout the year, the basin is dominated by agricultural land uses—many requiring irrigation, and the entire flow of the Rio Grande is owned by either the Mexican government, domestic municipalities, or private owners. Because water is a commodity in this basin, it must be strictly released based on the needs of the water rights holders. Unfortunately this condition further limits the ability to create a GIS-based model for the region.

Reservoir Releases

An attempt was made to secure a data set of historical reservoir release information from a variety of sources, including the TNRCC and the IBWC; however, an adequate data set could not be found. The IBWC historically reported information related to the reservoir in terms of the capacity within the reservoir, not a measurement of the water released by the dam. A data set was acquired from the TNRCC, however the supporting documentation was insufficient to determine the nature of the data in the text file.[19] Without an adequate reservoir release data set, the modeling effort ceased.

Results of Modeling Effort

While a model that simulated the transport of sediment-bound metals throughout the watershed was not produced for the Rio Grande, the attempt to develop a model was productive for a variety of reasons. The most significant of the results from the analysis were the compilation of the basic data layers required to eventually model the watershed and a new understanding of the information still required to complete the analysis.

This thesis used a modeling approach previously proved in watersheds of comparable scale but in different regions of the United States. The attempt to replicate this proven modeling approach in the Rio Grande basin demonstrated the myriad difficulties that face researchers in working in an international watershed. The differences between data in the United States and Mexico, the lack of sufficient sediment-quality data, and the complex hydrologic conditions in the watershed, seriously restrict any researcher's ability to generate models for the Rio Grande Basin.

Since this project began, however, many successes were achieved. The creation of a seamless digital elevation model, development of a relationship between the two soil classification systems, and the production of a new land cover data set for the basin represent significant strides toward creating an effective model for the basin. This analysis also provides the first step toward understanding the potential sources of sediment contamination in the basin. By using the data developed in the modeling effort, it is possible to characterize each watershed in the basin. This characterization can provide insight about potential sources of contamination—both naturally-occurring and as a result of human activity. A characterization of the subwatershed between Amistad and Falcon Reservoirs demonstrates the utility of the data compiled for the GIS.

The review of the sediment-quality data indicated potential problems with both lead and mercury in sediment for the middle Rio Grande portion of the basin. A simple analysis of the GIS data for the middle Rio Grande subwatershed can contribute to understanding potential sources of sediment contamination. Figure 53 shows the location of the middle Rio Grande subwatershed, and Figures 54-58 show the GIS data clipped to just the subwatershed.

From Figure 54, it is apparent that the majority of the sediment sampling in the middle Rio Grande subwatershed was performed in and around the urban land uses (Figure 55). Several sites also appear at the river's confluence with streams entering the river from the Mexican portion of the watershed (Figure 54). Few monitoring sites exist in non-urban portions of the watershed. This sampling pattern remains consistent with the TNRCC's desire to sample to determine compliance with point source permits. Figure 56 shows that the precipitation patterns throughout the watershed area do not fluctuate drastically. Figure 57 illustrates the quickly-drained soils in the middle and lower portion of the watershed, while Figure 58 shows the southern half of the watershed to have a high potential for water erosion.

This characterization of the watershed using GIS provides greater insight into the sediment-quality data for the middle Rio Grande watershed. From the GIS data it is apparent that the locations with the highest lead and mercury measurements in the subwatershed appeared downstream of urban land uses, in areas with quickly-drained soils and in areas with highly erodible soils. By providing an understanding of the conditions in the Rio Grande watershed that are suitable for sediment contamination to occur, researchers can then target their assessment activities toward those regions with the highest potential for environmental impact.

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[19] The data obtained from the TNRCC was from the BEAT internet site. The data did not contain any explanation of the units of measurement, nor the source of the data. Therefore, it was decided that the data was inappropriate for use in developing a model.

Figure 53: Middle Rio Grande (Amistad to Falcon)

Figure 54: Monitoring Sites in the Middle Rio Grande

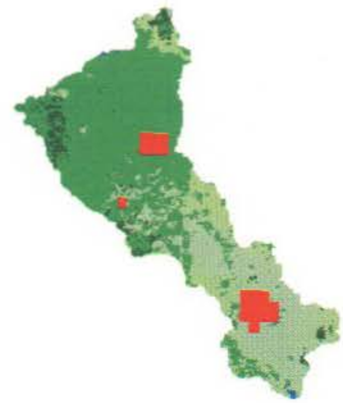

Figure 55: Land Use in Middle Rio Grande

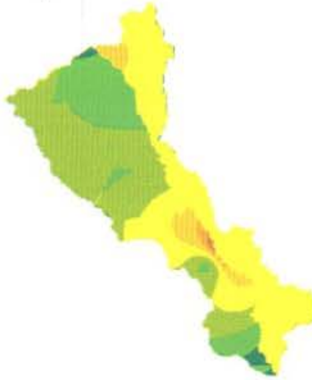

Figure 56: Precipitation in the Middle Rio Grande

Figure 57: Soil Type in the Middle Rio Grande

Figure 58: Erosion Potential in the Middle Rio Grande

While the study did not prove the utility of GIS for modeling sediment transport in the Rio Grande basin, it did produce results sufficient to deem the study a success. The analysis of the metals in sediment data highlighted potential problems with the monitoring methodologies used by the agencies tasked with protecting the basin's water quality. The attempt to build a simple model for the basin illustrated the difficulty in approaching an international watershed using domestic thinking. Finally, the study also completed work begun by several different agencies nearly six years ago.

Conclusions

This thesis set out to prove the utility of GIS in analyzing and modeling sediment transport and contamination in the Rio Grande watershed. In the incipient stages of the study, seemingly simple decisions were made—like the choice to focus on metals in sediment, and in particular arsenic, lead, and mercury in sediment—that eventually contributed to the difficulties in proving the utility of the GIS.

By focusing on metals that were found in previous studies in the basin, it was assumed that the potential for failure in this analysis would be reduced. However, the detailed analysis of the sediment-quality data in the Rio Grande watershed discovered serious impediments to completing a functional model. One of the obstacles was in the quality and quantity of the sediment-quality data. The previous studies used very small sampling sizes (sometimes as small as two to four samples) to establish trends. It was decided at the beginning of this study that no trends consisting of less than ten samples would be used. This decision seriously limited the researcher's ability to develop significant correlations between the metals in sediment and other contaminants in the water or sediment.

The most restrictive of the decisions during the study, however, was the choice of the Rio Grande watershed itself. By focusing on a watershed that is international, very large, and contains many remote areas, the job of gathering data to run the model became significantly more complicated than in other watersheds.

The failure to develop a model, however, does not mean a failure in the approach, assumptions, or in the possibility for future success. Instead, the process of attempting to create a model highlighted needed changes in the monitoring protocols for the basin and opportunities to improve data in the future. To effectively monitor, assess, and model the Rio Grande watershed, researchers must gather data in land use situations other than urban, and at locations beyond up and downstream of permitted discharges and irrigation return flows. Part of the assessment process should include developing an understanding of all major land uses in the basin. In particular, more monitoring to assess potential nonpoint sources should be performed in the basin.

One fundamental discovery during the data analysis was that when agencies performed special studies they more effectively gathered data than under routine monitoring conditions. Specifically, during special studies basic water quality analysis, biological monitoring, and occasionally toxicity testing, were also performed. Often during routine monitoring, however, little or no incidental information was gathered with the sediment samples. Therefore, while the sediment analysis itself provides significant insight into the environmental conditions in the basin, simple water chemistry and basic physical data like flow could have provided further understanding. Without routine monitoring like pH, TSS, TDS, TOC, flow, etc., it is impossible to form a thorough understanding of the chemical and physical interactions that lead to the contamination of sediment. Without some biological monitoring and toxicity testing, it is difficult to prove an impact as a result of sediment contamination.

Another important data void is the lack of consistent GIS data for the entire basin. Because Mexico and the United States approach the creation of GIS data differently, the GIS coverages were often incompatible. Having consistent land use, soil type, vegetation type, and geology coverages for the entire basin would improve the ability of both countries to assess and manage the water quality in the basin.

The failure to develop a simple screening model for the watershed also highlights the difficulty in attempting to apply methodologies developed in the United States to international watersheds. Most domestic models require extensive data not usually collected in other countries; therefore, in international watersheds many of the existing models are simply too intensive for practical use. Of the most commonly used models in the United States, not one discussed in this thesis could have effectively been applied in the Rio Grande given the current condition of the water, sediment, and GIS data.

Finally, this thesis demonstrates that while governmental agencies continue to monitor conditions in an attempt to protect human and environmental health in the Rio Grande watershed, they do not necessarily monitor in a way that provides sufficient information to answer complex questions about ecosystems. Despite over twenty-years of data collection and analysis, limitations in the utility of the data still exist.

Appendix A: Acronyms

The following table lists acronyms found in this document:

Acronym	Description
AGNPS	Agricultural Nonpoint Source Pollution Model
BASINS	Better Assessment Science Integrating Point and Nonpoint Source
BOD	Biological Oxygen Demand
BTSS	Binational Toxic Substances Study
CAN	Mexico National Water Commission
CILA	International Boundary and Water Commission (Mexican side)
COE	Corps of Engineers
CREAMS	Chemicals, Runoff, and Erosion from Agricultural Management Systems
CVAA	Cold Vapor Atomic Absorption
CWA	Clean Water Act
DO	Dissolved Oxygen
FAO	Food and Agricultural Organization
GIS	Geographic Information Systems
HEC	Hydrologic Engineering Center
HSPF	Hydrological Simulation Program-FORTRAN
IBWC	International Boundary and Water Commission
ICPMS	Inductively Coupled Plasma Mass Spectrometry
IDW	Inverse Distance Weighted
IMTA	Mexican Institute of Water Technology
IPX	In-Place Pollutant Export Model
MAL	Minimum Analytical Level
mg/kg	milligrams per kilogram
PRISM	Parameter-Elevation Regression on Independent Slopes Model
R	Pearson's Coefficient
STATSGO	State Soil Geographic Database
STORET	State Online Reporting Tool
SWRRB	Simulator for Water Resources in Rural Basins
TAES	Texas Agriculture Experiment Station
TCRP	Texas Clean Rivers Program
TDS	Total Dissolved Solids
TNRCC	Texas Natural Resource Conservation Commission
TSS	Total Suspended Solids
USEPA	United States Environmental Protection Agency
USGS	United States Geological Survey
USLE	Universal Soil Loss Equation
UT	University of Texas
VAF	Vapor Atomic Flourescence
WASP	Watershed Assessment Program
XRF	X-Ray Flourescence

Appendix B: Sources of Data

The data used for the analysis came from multiple sources, including federal, state, and international agencies. The following tables describe the sources and locations for obtaining copies of the original or updated data.

Water Data

Data Set	Description	Location
Routine Water-Quality Data	1966-1996 Monitoring Data for the Rio Grande Basin. Compilation of data from major monitoring entities, including Texas Natural Resource Conservation Commission, International Boundary and Water Commission, and the United States Geological Survey	Originally compiled by the Border Environmental Assessment Team, Texas Natural Resource Conservation Commission, PO Box 13087, Austin, TX 78711-3087 http://beat.riogrande.org/
Toxic Substances	Monitoring data from Phases I and II of the Binational Toxic Substances Study. Represents simultaneous monitoring by the Texas Natural Resource Conservation Commission, International Boundary and Water Commission, Comisión Internacional de Límites y Aguas, Comisión Nacional del Agua	By request of the Surface Water Quality Monitoring Team at the Texas Natural Resource Conservation Commission, PO Box 13087, Austin, TX 78711-3087
Flow Data	Monthly gauge information from permanent monitoring stations installed by the United States Geological Survey and maintained by the International Boundary and Water Commission.	Combination of hand-entered from Annual Reports of the International Boundary and Water Commission and by request of the Texas Natural Resource Conservation Commission, PO Box 13087, Austin, TX 78711-3087. Temporarily available at http://beat.riogrande.org/
Reservoir Release Data	Monthly accounting of releases from Elephant Butte, Amistad, and Falcon Reservoirs from 1960 – 1995.	Originally compiled by the Border Environmental Assessment Team, Texas Natural Resource Conservation Commission, PO Box 13087, Austin, TX 78711-3087 http://beat.riogrande.org/

Geographic Information System Data

Land Cover	Grid of different land cover types based on automated classification scheme from AVHRR data. Classification performed in conjunction with EROS Data Center	Blackland Research Center Temple, Texas http://brc.tamu.edu
Elevation Data	Grid of average elevation above sea level recorded in meters using 100-meter cells. Data compiled and resampled to consistently represent entire watershed. Original data sources are USGS and INEGI.	Blackland Research Center Temple, Texas http://brc.tamu.edu
Population Density	Grid of the density of human population per 1 kilometer cell. Original data resampled and clipped to Rio Grande Watershed.	Consortium for International Earth Science Information Network http://www.ciesin.org
Rainfall	Raw rainfall data for 199 stations covering the entire Rio Grande watershed. Data is daily precipitation information.	National Climate Data Center "Global Daily Summary: 1977-1991" CD-ROM ordered through: http://www.noaa.gov/
Soils	Polygons of soil types based on STATSGO methodology. Data from Mexico reclassified from FAO structure to STATSGO structure.	Blacklands Research Center Temple, TX http://brc.tamu.edu
Geology	Polygons of soil type digitized and compiled from USGS and INEGI maps.	United States Geological Survey Cameron Road Austin, TX 78751

Appendix C: Data

The CD-ROM included in this appendix contains the data used to develop the thesis. It includes the historical water-quality, sediment-quality, rainfall, gage, land use, land cover, elevation, population, and soil data discussed in the thesis. It also includes an ArcView project that displays the GIS data in the formats used to generate all maps and graphics in the thesis.

The CD-ROM must be read using an Intel-based computer using Windows 95, Windows 98, or Windows NT, and running ArcView GIS 3.0a or greater and SpatialAnalyst 1.2 or greater. To view the water-quality, sediment-quality, rainfall, and soils data, the user must have Microsoft Access 97 or greater (or a program that can import such a file).

All images used in the thesis and a version of the thesis in Adobe Acrobat are also included on the CD-ROM. To view the GIS data in ArcView, open the program then open the file \thesis\thesis data\gis\riogrande.apr.

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VITA

Angela Kay Smith Miller was born in Cincinnati, Ohio on June 22, 1966, the daughter of Timothy Roland Smith and Betty Irene Smith. Ms. Miller graduated in the top 5 percent of Littleton, Colorado's Heritage High School in 1984. During her collegiate career, Ms. Miller also worked in a professional capacity for Cominco America, Oxbow Geothermal, and Homestake Mining, generating maps and graphics for the companies. Ms. Miller received a Bachelor of Arts in English and Economics from Rice University in Houston, Texas in 1989.

Ms. Miller began her graduate studies at the University of Texas School of Public Health in 1990. During the next eight years, she worked full-time while attempting to complete her masters degree in Environmental Science. She worked as an environmental paralegal for the law firm of Mayor, Day and Caldwell in Houston, Texas for over a year. She then started her own firm – Acappricio Consulting – during 1991. Her firm specialized in matching information technologies to the needs of law firms. She also worked part time for an environmental consulting firm, participating in site assessments, soil borings, and remediation activities.

In 1992 Ms. Miller married Kelly Brian Miller, moved to Austin, Texas, and began a five-year career with the Texas Natural Resource Conservation Commission (TNRCC). It was at the TNRCC that her passion for mapping and analysis saw fruition. At the TNRCC, Ms. Miller initiated and managed several projects using Geographic Information Systems (GIS) to perform water-quality analysis. She eventually managed the Rio Grande Assessment of Water Quality. In this capacity she managed several projects that used GIS in the Rio Grande watershed, help set policies for the use of GIS both at the TNRCC and at the state level, and initiated several cooperative projects with local, state, and federal governments, non-governmental organizations, and Mexican and Canadian partners. She also published and/or presented over ten papers related to GIS. In 1997, Ms. Miller transferred to the Texas General Land Office where she had the opportunity to direct the development of several GIS tools for the agency and the state.

This thesis was typed by Angela K. Smith.