Urban Impact Of Dissolved Metals In The Paso Del Norte Segment Of The Rio Grande

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URBAN IMPACT OF DISSOLVED METALS IN THE PASO DEL NORTE SEGMENT OF THE RIO GRANDE

Environmental Science and Engineering Program

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Dedication

For

Mom, Dad and my loved ones,

I dedicate to you

the joy and rejoicing of my successful work
URBAN IMPACT OF DISSOLVED METALS IN THE PASO DEL NORTE SEGMENT OF THE RIO GRANDE

by

SUMAYEH AHMAD FREIWAN, B.S., M.S

DISSERTATION

Presented to the Faculty of the Graduate School of
The University of Texas at El Paso
in Partial Fulfillment
of the Requirements
for the Degree of

DOCTOR OF PHILOSOPHY

Environmental Science and Engineering Program
THE UNIVERSITY OF TEXAS AT EL PASO
August 2013
Acknowledgements

For the past four years of my doctoral study, my strength is renewed from my lord, ALLAH. At this time, I am happy to express my gratitude to ALLAH for mercifully blessing me to complete this work. Foremost, I would like to express my sincere gratitude to my advisor Dr. W. Shane Walker for the continuous support of my Ph.D. study and research, for his patience, motivation, enthusiasm, and immense knowledge. His guidance helped me in all the time of research and writing of this dissertation. I would like to gratefully and sincerely thank Dr. John Walton for his guidance, understanding, patience, and most importantly, his friendship during my graduate studies.

In addition to my advisors, I would like to thank the rest of my dissertation committee: Dr. Wen-Yee Lee, Dr. Anna Szynkiewicz, and Dr. Arturo Woocay for their encouragement, insightful comments, and hard questions.

Before his encouragement and assistance, I did not consider pursuing a Ph.D.; I would like to thank Dr. Omar Al-Qudah for his help and advice through my study. And my sincere thanks also go to Sandra Aguirre-Covarrubias and Yvonne Lopez, for offering me the summer scholarship opportunity.

This research was produced through efforts of many people; I would like to thank EPWU staff for helping me through my research – mainly I mention here John E. Balliew and Elizabeth DeMoultrie. I would like to thank Mr. Cesar Boisselier, Mr. Alejandro Luna, and Mr. Gilbert Anaya from IBWC, and Dr. Michael Landis from US Bureau of Reclamation.

The team work was essential to completing my research work; at this moment I am glad to mention my colleagues, Sami Al-Haddad, César Bezares, Noe Ortega, Isaac Campos, and all
CIDS staff. César was a critical partner in this research, and without his selfless help in sampling, this work would not have been completed.

My time at UTEP was made enjoyable in large part due to the many friends and groups that became a part of my life. I am grateful for time spent with friends and the Islamic community at the Islamic Center of El Paso.

Lastly, I would like to thank my family for all their love and encouragement. For my parents, who raised me with a love of science and supported me in all my pursuits. For the presence, love, support, and encouragement of my brothers – Mohammad, Hassan, and Muath. For the warm prayers and kindness of my sisters – Aida, Fayza, and their husbands. I never forgot my lovely nephews and nieces and their nice words of missing me being with them.

Thank you

Sumayeh Freiwan

July, 2013
Abstract

The Paso del Norte segment of the Rio Grande experiences two seasons per year; the (wet) irrigation season and the (dry) non-irrigation season. The goal of this study was to improve the understanding of occurrence and contribution of dissolved metals in this region during the non-irrigation season. The objectives of this study were to (1) evaluate the impact of anthropogenic sources of metals on the Rio Grande water quality during the non-irrigation season, and (2) estimate the metal loads carried by the flow to the downstream region of El Paso. In order to evaluate the surface water quality of the Paso del Norte region, the sampling points investigated several major water discharges including agricultural drainage, stormwater runoff, and municipal wastewater treatment plants. For two sequential dry seasons of the period from 2011 to 2013, water samples were collected weekly and analyzed by IC and ICP-OES. The detection limits for ICP-OES were less than the EPA drinking water maximum contaminant limits (MCLs), except for Hg, Pb and Se.

The mean pH ranged from 7.1 in treated wastewater to 8.4 for the Rio Grande water, and variation between the two sampling dry seasons was insignificant. The stormwater runoff provided the Rio Grande with the lowest mean electrical conductivity (161 µS/cm) and mean alkalinity (44.7 mg/L as CaCO$_3$), and diluted the higher concentrations of major ions within the river system. The agricultural water in Montoya Drain discharged the maximum mean EC (4175 µS/cm) and mean concentrations of Na$^+$ (758 mg/L), Ca$^{2+}$ (156 mg/L), and Cl$^-$ (719 mg/L). The maximum concentrations of Mg$^{2+}$ (78 mg/L) and SO$_4^{2-}$ (724 mg/L) were observed in the Rio Grande at the international boundary. The maximum mean concentrations of K$^+$ (17 mg/L) and NO$_3^-$ (19 mg/L) were observed in treated wastewater effluent. The mean F$^-$ concentrations in all samples were all less than 1.35 mg/L. The highest mean concentrations of
Cd, Ni, Pb, and W, were 1.1, 11.3, 10.9 and 18.6 µg/L, respectively in the Rio Grande, observed downstream of Sunland Park and upstream of the Montoya Drain. The maximum mean concentration of Li (508µg/L) was observed in the Montoya Drain. The greatest mean concentrations of As, Ba, Mn, Sn and Sr were 47, 62, 229, 209, and 3217 µg/L , respectively observed in the Rio Grande at the international boundary near the ASARCO smelter site. The stormwater runoff was observed with the greatest mean concentrations of Al, Cu, V, and Zn at 48.8, 40.2, 5.9, 48.7 µg/L, respectively. The concentrations of Be, Hg, Sb and Se were mostly less than detection limits.

The mass balance approach was applied in order to estimate the mass loads of metals in the Paso del Norte region during the non-irrigation season. The mean daily mass loads in the American Canal downstream of the Robert Bustamante wastewater treatment plant were estimated to be Al (3.54), As (2.4), Ba (10.3), Cd (0.05), Cr (0.2), Cu (2.21), Fe (6.7), Li (35), Mn (4.9), Ni (1.0), Pb (0.43), Sn (20.4), Sr (311), U (7.2), V (1.2), W (1.3), and Zn (10.8), all in kg/day. Through this study, the water quality analysis and the mass balance analysis revealed elevated concentrations of Cd, Ni, Pb, V and W in the stream segment between the Sunland Park and the Montoya Drain, which may be a result of underground discharge or buried waste.

With respect to the hypotheses of this research (during the non-irrigation season), the Montoya Drain provides a significant load of salinity to the river, but the wastewater treatment plant effluents and stormwater runoff dilute the salinity. However, stormwater runoff was observed to contain relatively high concentrations of metals. High metals concentrations were also observed at the international boundary near ASARCO, but the flow though this segment during non-irrigation is negligible. It is recommended that point-source control measures be evaluated, such as engineered wetlands, for mitigating metals discharge to the river.
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Chapter One

Introduction and Literature Review

1. Background

Water shortages and the scarcity of freshwater are some of the major environmental crises that pose some of the greatest concerns for the world decision makers (UNEP, 2007). In the coming decades, it is expected that the increase in water stress will be the main problem in many regions around the world. This is the result of many factors such as population growth, climate change, and pollution of surface water and groundwater (Water Resources e-Atlas, 2007).

According to the World Health Organization (WHO), the greatest challenges for the world’s water supply are the different issues that affect water quality (WHO, 2008). These factors include natural-use factors such as wildlife, climate, topography, geology, and vegetation. Human-use factors, including point sources (e.g., municipal and industrial wastewater discharges) and non-point sources (e.g., urban and agricultural runoff, including livestock or recreational use) also have an effect on water quality. Urbanization and the changing patterns of land use correspond to rapid degradation and worsening of water quality (Ran et al., 2003). Urban stormwater runoff adds more contents of nutrients, suspended solids, heavy metals, fecal coliforms, and salinity to the receiving water in the urban catchment (Al Bakri et al., 2008; Kose et al., 2008).

Industrial activities near streams and rivers can be major sources of physicochemical environmental pollution, such as heavy metals (Pb, Cd, Cu, Zn and Cr) (Yayintas et al., 2007). Improper wastewater disposal practices for an extended period of time can lead to the accumulation of undesirable loads of organic and inorganic chemicals (pollutants) to the streams and sediments. For example, in irrigated soils, in particular, water quality can be impacted in
metal concentrations like Cd, Cr, Cu, Ni, Pb, and Zn (Yayintaş et al., 2007) (Wang et al, 2009). Figure 1.1 illustrates the water cycle within urban areas and the returns to the river. As presented in this figure, urban development adds additional amounts of water to runoff, wastewater treatment discharge, and agricultural irrigation. And it gives an indication of further decrease in the water quality and sustainable availability of both local and regional levels. Typically, pollutants are not completely removed from municipal sewages, effluents of industrial activities, and urban surfaces runoff such as streets and building roofs. Moreover, it is difficult to remove pollutants from livestock and irrigation drainage of agricultural fields due to their high content of pesticides.

![Water Cycle Diagram]

Source: (SEQ Healthy Waterways Partnership, 2008)

Figure 1.1: Water cycle with agricultural and urban impacts
Streams polluted with heavy metals have become a great concern of the public and scientific communities due to their toxicity and harmful effects on the human health and biological systems (Anazawa et al., 2004). Humans can be exposed to high concentrations of heavy metals from stream water and accumulated metals in irrigated soils through various exposure pathways (routes) causing adverse effects on human health (Weber et al., 2006). Human consumption of crops grown in soils polluted by heavy metals is one of the major exposure pathways of heavy metals to humans. The risk of exposure to heavy metals is high because they are extremely persistent in the environment and this causes them to accumulate, reaching toxic levels (Bohn, 2001).

1.1 Description of Study area

The Rio Grande serves as the international boundary between United States and Mexico from the Paso del Norte region (El Paso, Texas and Ciudad Juarez, Chihuahua) to the gulf coast, and it serves as a major source of irrigation water for New Mexico, Texas, and Mexico. The goal of this research to determine the metal contents and fluxes into the Rio Grande from anthropogenic activities through studying the load contributions of effluent discharges of wastewater treatment plants (WWTPs), the agricultural return drains, and stormwater runoff.

The Rio Grande is the fifth longest river in North America; it originates in the southern Rocky Mountains of Colorado and New Mexico and lies within an arid and semi-arid basin of the Chihuahuan Desert. The Rio Grande extends for 600 miles from its headwaters to the border cities of El Paso, Texas, USA, and Ciudad Juarez, Chihuahua, Mexico, and for over 1200 miles it forms the longest international river border between Mexico and the United States downstream of El Paso (Creel, 2010). Three U.S. and five Mexican states are depending on the Rio Grande water for agricultural irrigation, and these are rapidly growing states. The population of the
border communities in the last four decades has doubled every 20 years, and there are population studies indicating another doubling by 2030 (Jurgen, 2002). Figure 1.2 indicates the El Paso county population in the period 1960 to 2010 and the projections to 2030.

El Paso is located in western Texas near latitude 31°48' and longitude 106°24' (USGS, 1998) and occupies an area of 1,014 square miles (Richardson, 1909). El Paso has an arid climate with an average annual precipitation of about 5.9 inches (Parcher et al, 2010). The average annual high and low temperatures are 95°F and 33°F, respectively (TWRI, 2010). Most of El Paso’s rainfall occurs in the summer with short duration storms or showers which are occasional and heavy and sometimes give rise to running and torrential floods. Accordingly, with the high evaporation rates, the runoff is brief and minimal (Parcher et al, 2010; USIBWC, 2011).

High salinity levels, the presence of heavy metals as a result of anthropogenic activities, high sediment load, inconsistent water flows, and the runoff of mineral mines and metal smelting wastes are some of the environmental problems of the Rio Grande. The combined effects of
these environmental issues contribute to the degradation of the water quality and have negative impact on the habitat and aquatic ecosystem of the Rio Grande (Assadian et al., 1998; Jurgen, 2002; Shmueli, 1999). The Rio Grande basin has variable flows and has experienced periods of drought. Since 1969, the total annual Rio Grande inflow into the border portion has averaged 4.51 billion cubic meters with about 60% of the inflow estimated to originate from Mexico (Miyamoto et al, 1995).

1.2 Problem Statement

According to literature, rivers are the main system pathways for the transport of pollutants between regions (Ramani et al, 2012). The population growth causes the water quality issues to remain significant public importance. The farmers and the downstream communities of the Paso del Norte region use the river’s water for irrigation as well as for industrial and municipal purposes (Miyamoto et al., 1995). The Rio Grande has several contamination and environmental problems, including salinity, metals, bacteria, and sediment.

ASARCO is an industrial smelter which has been a major source of pollution in El Paso. The environment of the Juarez - El Paso region is affected by the metals pollution in the soil, air, groundwater, and surface water (Edmonson et al, 2008). Also, the irrigation with Rio Grande water adds more heavy metals to the soils thus to the plant issue (Rios-Arana et al, 2004; Assadian et al., 1998).

1.3 Hypotheses

The fundamental hypothesis of this research is that the inorganic contaminants (major ions and metals) in the Paso del Norte segment of the Rio Grande are significantly influenced by urbanization and anthropogenic activities, especially during the non-irrigation season. More specifically, the following water quality hypotheses are proposed for the non-irrigation season:
a) Stormwater from urban runoff decreases the total dissolved solids (TDS) and metals concentrations in the river and agricultural canals;
b) groundwater flowing through the ASARCO site increases the metals concentrations locally, but it represents a small contribution to the mass loads;
c) The agricultural drain water contributes significant salinity and metals content to the Rio Grande water.
d) Treated wastewater effluent does not significantly increase the metals concentrations in the river.

1.4 Objectives

In order to audit the water quality of the Paso del Norte segment of the Rio Grande with respect to metals during the non-irrigation season, this study carried out the following objectives:

(1) Quantify the metal concentrations in the Rio Grande from anthropogenic activities within the region of Sunland Park, NM, El Paso, TX, and Ciudad Juarez, CH. Practically, this was conducted by collecting weekly samples of the wastewater treatment plants, urban stormwater, Montoya drain water, and ASARCO groundwater discharge.

(2) Estimate the heavy metals loads in the Rio Grande from the measured anthropogenic sources and construct a qualitative network mass-balance within the river system by using the upstream and downstream water quality data during the research period. Identify significant differences between the upstream and downstream concentrations and determine the trends of these constituents in the river to provide a better understanding of physical processes that affect inflow of pollutants to the Rio Grande.
2. Literature Review

2.1 Stream Water Quality

In order to have minimal negative effects on rivers and streams, managing and monitoring the industrial and human activities is a major step in controlling the streams pollution (Schipper et al., 2008; Karlsson et al., 2010). Intensive industries such as textile, metal, and leather add high concentrations of heavy metals to the urban wastewater. The Al, Cr, Fe, and Zn exhibited the highest concentrations for 23 monitoring months in 2002 and 2007; with the exception of Cr all of them met the limits of guidelines for agricultural applications (Ekrem G., 2009).

The disposal of the treated wastewater affects the environmental quality of the disposal area and reduces the rivers water quality and causes crop contamination (Singh et al., 2004; Assadian et al., 1998). All environmental media, water, soil, crops, vegetation, and food grains are affected by the high levels of toxic pollutants present in the treated wastewater such as metals and pesticides. Consequently, they will create adverse impact on the environmental quality of the disposal area (Singh et al., 2004).

A variety of pollutants such as heavy metals (Cd, Cr, Ni, Pb, and Zn) can be found in the stormwater from different surfaces such as streets and roofs in the urban areas. These concentrations mostly exceeded the threshold values of the standard guidelines (Schipper et al., 2008), (Karlsson et al., 2010). The agriculture activities increase the loads of nitrate and pesticide in surface and ground waters, and drainage from agricultural operations in some soil types cause the leaching of toxic metals from the subsurface to surface and ground waters (Creel, 2010). Agricultural practices are the main source of Cd in the stream sediments, whereas the automobile traffic and industry is the major source of Pb (Nguessan et al., 2009). Until now many WWTP are
not significantly reducing heavy metals in wastewater, which may pollute receiving streams and render it unsafe for human use and unsupportive for aquatic organisms (Sajidu et al, 2007).

Discharged pollutants, especially heavy metals such as Pb, Cd, Cu, Zn and Cr, may accumulate in fauna (e.g., fish organs such as gill, liver, and muscle) and then transfer to humans through the food web (Yayintaş et al., 2007; Vicente -Martorell, 2009). In flora, growth substrate contaminated with heavy metals concentrations can affect plant growth by reducing the root growth more than shoot growth and lead to an inability of the plants to respond to the conditions of improved soil moisture (Santala and Ryser, 2009). Lottermoser (2011) observed changes in metal chemistry of soils in Germany with long-term (> 100 years) irrigation with municipal wastewater; soil (especially farm topsoil) was enriched with precious metals (Ag, Au) and heavy metals (Cd, Cu, Ni, Pb, Sn, and Zn) compared to local and regional background soils. Consequently, the quality of drinking water supplies into underlying aquifers may be affected by leaching of these metals (Lottermoser, 2011).

2.2 Water Quality of the Rio Grande

Historically, the ASARCO smelter has been one of the major sources of pollution in El Paso; it led to pollution of soil, air, surface water, groundwater, and drinking water of El Paso (Edmonson et al, 2008). The Rio Grande was affected by the excessive concentrations of arsenic from ASARCO, which is withdrawn downstream for use as drinking water (Edmonson et al, 2008).

The heavy metals, As, Cr, Cu, Ni, Pb, and Zn, were found in Rio Grande with high concentrations in sediments compared to the river water. Elements like Pb and Zn were commonly dissolved and recoverable in both water and sediment samples, and these concentrations of Pb and Zn exceeded the freshwater chronic criteria (Rios-Arana et al. 2004).
Assadian et al. (1998) examined the transport of heavy metal onto fertile soils irrigated by treated wastewater discharged into the Rio Grande. They conducted their study on two alfalfa fields; one of them in San Isidro, Chihuahua, Mexico, and a second field in San Elizario, Texas. Both soil and forage tissues were analyzed for heavy metal concentrations. The concentrations of heavy metals did not exceed 20 mg/kg, and they took the order Zn > Cr > Ni > Pb > Co > Cd. By their investigations, they found that heavy metals accumulated in greatest concentrations in soils close to the irrigation canal, which is the water application point, and decreased with increasing distance from the canal (Assadian et al., 1998).

2.3 Chemical Mass Balance

The concept of chemical mass balance is applied in order to study the change of concentrations and mass loads of pollutants along the water stream. Runkel and Bencala (1995) described the mass balance method based on the transport of mass by advection and dispersion of solutes. The basic form of mass balance is simply a quantification of the mass accumulated during a time period, which is equal to the difference between the transport of mass into and out of a control volume.

Due to numerous outfalls of untreated municipal and industrial wastes of the region at regular intervals, River Kali in Western Uttar Pradesh (India) is subjected to varying degrees of metals, and these outfalls do not allow for any self-purification to occur (Jain, 1996). During the period from October 1993 to December 1993, the estimated increase in Fe, Zn, and Cu were estimated to be 60-80% (Jain, 1996).

Jain et al. (2007) carried out chemical mass balance studies for the Hindon River, Western Uttar Pradesh (India), which receives different pollution loads from municipal and industrial activities and nearby agricultural areas. Depending on the land use pattern, the river system in
that study was divided into three stretches, to measure the changes in the concentrations and loads of nitrate and phosphate to the river from non-point sources of pollution, using upstream and downstream sampling locations. The mass balance calculations indicated that the percentages of nitrate and phosphate contribution from uncharacterized non-point sources of pollution due to agricultural activities, ground water contribution and sediment water interactions have been changed from 15.5% to 13.1% for nitrate and from 6.9% to 16.6% for phosphate in the upper stretch and in the lower stretch, respectively (Jain et al, 2007).
Chapter Two

Urban Impact of Dissolved Metals on the Rio Grande Water Quality in the Paso Del Norte Segment during the Non-Irrigation Season

1. Introduction

The Rio Grande is the fifth longest river in North America; it originates from the southern Rocky Mountains of Colorado and New Mexico (Creel, 2010). The Rio Grande is located within arid and semi-arid basins (Jurgen, 2002). For over 1,255 miles, Rio Grande forms the longest international river border between Mexico and the United States (USIBWC, 2011). It runs for 600 miles from its headwaters to the border region at El Paso, Texas, USA, and Ciudad Juarez, Chihuahua, Mexico (Creel, 2010). Three U.S. states and five Mexican states (which are classified as rapidly growing states) are dependent on the Rio Grande water for agricultural irrigation and municipal water demands. The Rio Grande basin has variable flows and has passed periods of drought. Since 1969, the total annual Rio Grande inflow into the border portion has averaged 4.51 billion with about 60 percent of the inflow is estimated to originate from the Mexican side (Miyamoto, 1995). The population of the border communities in the last four decades has doubled every 20 years and there are population studies indicating another doubling by 2030 (Jurgen, 2002).

El Paso is located in western Texas within latitude 31°48' and longitude 106°24' (USGS, 1998) and occupies an area of 1,014 square miles (Richardson, 1909). The El Paso population in 2010 was 797,699, and it is expected to rise to 902,270 and 978,642 in 2020 and 2030, respectively (Creel, 2010). The average annual high and low temperatures are about 95°F and 33°F, respectively (TWRI, 2010). El Paso has an arid climate with an average annual precipitation of about 5.9 inches (Parcher et al, 2010). Most of El Paso’s rainfall occurs in the
summer with short duration storms or showers which are occasional and sometimes give rise to running and torrential floods (Parcher et al, 2010; USIBWC, 2011).

2. Study Area and Sampling Locations

The Rio Grande is experiencing two seasons along the year; the irrigation season and the non-irrigation season. The “typical” Rio Grande Project irrigation season starts with releases from Elephant Butte and Caballo reservoirs in southern New Mexico in early spring and ends late fall, but recently, due to the multi-year drought, the irrigation season has started late spring and ended early late summer.

The Rio Grande serves as part of the international boundary between the United States and Mexico. It becomes the border just downstream of the American Dam in El Paso. The river’s water within the United States borders is diverted to the American Canal, which is a concrete channel that runs nearly parallel to the Rio Grande through downtown El Paso. The Rio Grande and the American Canal serve as the receiving stream for discharges of agricultural, industrial, and domestic activities within the El Paso region. The study included the discharge points starting upstream from Sunland Park, NM to downstream at Bustamante WWTP for a distance of approximately 50 miles along the river and the American Canal. The sampling points were chosen to examine the effects of point sources of pollution on the surface water quality of the Rio Grande in El Paso region; these locations are shown in Figure 2.1. These points are listed in Table 2.1, which also categorizes each point as one of the following: River/Canal, Agricultural, WW Raw, WW Effluents, Stormwater, and International Boundary.
Figure 2.1: (a) Sampling Locations along the Rio Grande, (b) Stormwater sampling points at UTEP
Table 2.1: Sampling Reference points and the sampling locations.

<table>
<thead>
<tr>
<th>Reference Points</th>
<th>Sampling points</th>
<th>Abbreviation</th>
<th>Category</th>
<th>Number on map</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sunland Park WWTP</td>
<td>Upstream</td>
<td>SPUS</td>
<td>River/Canal</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>SPEF</td>
<td>WW Effluent</td>
<td>SP-WWTP</td>
</tr>
<tr>
<td></td>
<td>Downstream</td>
<td>SPDS</td>
<td>River/Canal</td>
<td>3</td>
</tr>
<tr>
<td>Montoya Drain</td>
<td>Drain Discharge</td>
<td>MDD</td>
<td>Agricultural</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Downstream</td>
<td>MDDS</td>
<td>River/Canal</td>
<td>5</td>
</tr>
<tr>
<td>Northwest WWTP</td>
<td>Influent</td>
<td>NWIN</td>
<td>WW Raw</td>
<td>NW-WWTP</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>NWEF</td>
<td>WW Effluent</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Downstream</td>
<td>NWDS</td>
<td>River/Canal</td>
<td></td>
</tr>
<tr>
<td>ASARCO</td>
<td>Downstream</td>
<td>Rio Grande</td>
<td>USA-Boundary</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>American Canal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Haskell WWTP</td>
<td>Upstream</td>
<td>HSUS</td>
<td>River/Canal</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>Influent</td>
<td>HSIN</td>
<td>WW Effluent</td>
<td>HS-WWTP</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>HSEF</td>
<td>WW Raw</td>
<td></td>
</tr>
<tr>
<td>Bustamante WWTP</td>
<td>Influent</td>
<td>BSIN</td>
<td>WW Effluent</td>
<td>BS-WWTP</td>
</tr>
<tr>
<td></td>
<td>Effluent</td>
<td>BSEF</td>
<td>WW Raw</td>
<td></td>
</tr>
<tr>
<td>University of Texas at El Paso</td>
<td>Campus</td>
<td>UTEP</td>
<td>Stormwater</td>
<td></td>
</tr>
</tbody>
</table>

The sampling included the influents (raw wastewater) of three WWTPs namely, Northwest, Haskell, and Bustamante. It included also the effluents (treated wastewater) of these WWTPs in addition to the effluent of the Sunland Park WWTP. The effluent of the Sunland Park and Northwest directly discharge the treated water to the Rio Grande, but the Haskell and Bustamante plants discharge the effluents to the American Canal. The Montoya Drain provides the river with drainage from agricultural areas in west El Paso and southern New Mexico. Additional points were sampled between the discharge points at different locations along the river and the American Canal. Within a distance of three miles along the river’s study segment there are many industries, including ASARCO, Rio Grande Power Plant and GCC of America (Group Cements Chihuahua). The study segment includes four WWTPs: Sunland Park (SP), EP Northwest (NW), EP Haskell Street (HS), and EP Robert Bustamante (RB).
The University of Texas at El Paso (UTEP) campus was included as the study site to sample the stormwater runoff. The stormwater runoff from UTEP campus is collected in the Arroyo passing the campus, and then it discharges the water into the American Canal. The stormwater runoff drainage of El Paso streets is directly discharged to the Rio Grande without any treatment.

3. Materials and Methods

3.1 Water Sampling

Weekly samples were collected for two annual non-irrigation seasons of the Rio Grande. The first sampling season started in November 2011 and ended in April 2012 and the second sampling season started in October 2012 and ended in April 2013. The sampling of rainstorm runoff began later on in October 2012 and it was conducted according to the storm events.

Water samples were collected in 500 mL polyethylene bottles for subsequent physical and chemical analyses (USEPA, 2012). Before sampling, the bottles were cleaned by detergents, soaked in 2% nitric acid (HNO₃) and rinsed several times with distilled water. In order to diminish any kind of contamination, each bottle was rinsed with the collected water at each sampling location at grabbing time the sample at the site and just prior filling the bottle with the sample. The bottles were filled to the top (no head space) and capped directly to minimize any chemical reactions between the air and the sample contents. Field blanks were obeyed to the same analytical procedures of the samples to examine possibility of the sampling tools contamination. Stormwater runoff samples were collected during storms events using the same procedures and standards used to collect the surface water samples.

3.2 Analytical Procedures

Analyses of physical and chemical parameters were performed according to USEPA and Standard Methods for drinking water and wastewater. The quality control procedures were
followed through including field blanks analysis to examine the contamination possibilities for the sampling tools. And through spiked samples for the analyzed elements, in order to determine the measurements accuracy of the instrument. The electrical conductivity and pH were measured on site using the multi-probe system (Thermo Scientific Electrode Conductivity Cell, Dura Probe) (USEPA, 2012). The alkalinity measurements were performed directly upon laboratory arrival by titration with H₂SO₄.

Samples were filtered in the laboratory using 0.45 µm CA, 47 mm membranes for analysis using ion chromatography (IC). A Dionex 1100 system was used to determine the major water chemistry Cations (Ca⁺⁺, Na⁺, Mg⁺⁺, and K⁺) with 50 mM methylsulfonic acid (MSA) eluent. Major anions (Cl⁻, SO₄²⁻, F⁻ and NO₃⁻) were analyzed with a Dionex 2100 system with 100 mM KOH eluent. Standards were prepared with concentrations according to the following concentrations:

<table>
<thead>
<tr>
<th>Ion</th>
<th>Std 1</th>
<th>Std 2</th>
<th>Std 3</th>
<th>Std 4</th>
<th>Std 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>18.75</td>
<td>37.5</td>
<td>75</td>
<td>150</td>
<td>300</td>
</tr>
<tr>
<td>Na</td>
<td>18.75</td>
<td>37.5</td>
<td>75</td>
<td>150</td>
<td>300</td>
</tr>
<tr>
<td>Mg</td>
<td>9.375</td>
<td>18.75</td>
<td>37.5</td>
<td>75</td>
<td>150</td>
</tr>
<tr>
<td>K</td>
<td>6.25</td>
<td>12.5</td>
<td>25</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Cl</td>
<td>18.75</td>
<td>37.5</td>
<td>75</td>
<td>150</td>
<td>300</td>
</tr>
<tr>
<td>SO₄</td>
<td>18.75</td>
<td>37.5</td>
<td>75</td>
<td>150</td>
<td>300</td>
</tr>
<tr>
<td>F</td>
<td>0.1875</td>
<td>0.375</td>
<td>0.75</td>
<td>1.5</td>
<td>3</td>
</tr>
<tr>
<td>NO₃</td>
<td>1.25</td>
<td>2.5</td>
<td>5</td>
<td>10</td>
<td>20</td>
</tr>
</tbody>
</table>

The difference in sums of anion and cation concentrations (mEq/L) was calculated for each sample (USEPA, 2012). The mean difference for all samples was +2% of the sum of anions and cations, which indicates a small bias of excess cations. The mean of the absolute value of the difference was 2%.

The samples were filtered then acidified by 2% HNO₃ (Certified ACS) and kept in refrigerator maintained at 4°C to be analyzed using Perkin-Elmer 7300 inductively-coupled
plasma optical emission spectrometry (ICP-OES) operating at a plasma power of 1450 W and sample flow of 1.8 mL/min. Eight standards were prepared using deionized water (< 1 μS/cm) and stock ICP concentration standards (+/- 1%) for concentrations of 0.5, 1.0, 5.0, 10, 50, 100, 500, 1000 μg/L (ppb). Except for Strontium which prepared to have the range of concentration 1-5000 μg/L. Samples were analyzed with five replicates for the wavelengths shown in Table 2.3. The square of the calibration correlation coefficients was > 0.9999 for the analyzed metals. The detection limits for the analyzed metals were determined according to Perkin-Elmer method for ICP-OES and are also shown in Table 2.3.

<table>
<thead>
<tr>
<th>Element</th>
<th>Symbol</th>
<th>Wavelength (nm)</th>
<th>MDL (μg/L)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>Al</td>
<td>308.215</td>
<td>9.3</td>
<td>61.3</td>
</tr>
<tr>
<td>Arsenic</td>
<td>As</td>
<td>193.696</td>
<td>2.4</td>
<td>49.0</td>
</tr>
<tr>
<td>Barium</td>
<td>Ba</td>
<td>493.408</td>
<td>0.18</td>
<td>4.2</td>
</tr>
<tr>
<td>Beryllium</td>
<td>Be</td>
<td>313.042</td>
<td>0.08</td>
<td>1.3</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Cd</td>
<td>226.502</td>
<td>0.09</td>
<td>2.5</td>
</tr>
<tr>
<td>Chromium</td>
<td>Cr</td>
<td>205.56</td>
<td>0.21</td>
<td>5.8</td>
</tr>
<tr>
<td>Copper</td>
<td>Cu</td>
<td>324.752</td>
<td>0.71</td>
<td>30.1</td>
</tr>
<tr>
<td>Iron</td>
<td>Fe</td>
<td>259.939</td>
<td>0.87</td>
<td>25.0</td>
</tr>
<tr>
<td>Mercury</td>
<td>Hg</td>
<td>253.652</td>
<td>5.79</td>
<td>38.3</td>
</tr>
<tr>
<td>Lithium</td>
<td>Li</td>
<td>670.784</td>
<td>0.03</td>
<td>1.2</td>
</tr>
<tr>
<td>Manganese</td>
<td>Mn</td>
<td>257.61</td>
<td>0.18</td>
<td>4.6</td>
</tr>
<tr>
<td>Nickel</td>
<td>Ni</td>
<td>231.604</td>
<td>0.27</td>
<td>10.4</td>
</tr>
<tr>
<td>Lead</td>
<td>Pb</td>
<td>220.353</td>
<td>1.1</td>
<td>33.7</td>
</tr>
<tr>
<td>Antimony</td>
<td>Sb</td>
<td>206.836</td>
<td>1.1</td>
<td>42.7</td>
</tr>
<tr>
<td>Selenium</td>
<td>Se</td>
<td>196.026</td>
<td>2.1</td>
<td>51.9</td>
</tr>
<tr>
<td>Tin</td>
<td>Sn</td>
<td>189.927</td>
<td>0.56</td>
<td>17.0</td>
</tr>
<tr>
<td>Strontium</td>
<td>Sr</td>
<td>421.552</td>
<td>0.11</td>
<td>2.2</td>
</tr>
<tr>
<td>Uranium</td>
<td>U</td>
<td>385.958</td>
<td>2.7</td>
<td>60.9</td>
</tr>
<tr>
<td>Vanadium</td>
<td>V</td>
<td>292.402</td>
<td>1.26</td>
<td>36.6</td>
</tr>
<tr>
<td>Tungsten</td>
<td>W</td>
<td>207.912</td>
<td>4.8</td>
<td>36.8</td>
</tr>
<tr>
<td>Zinc</td>
<td>Zn</td>
<td>213.857</td>
<td>0.14</td>
<td>2.9</td>
</tr>
</tbody>
</table>
4. Results and Discussion

The samples of rainstorm runoff water were collected from building-roof drains, parking lot manholes, streets, and the arroyo of the University of Texas at El Paso (UTEP) campus. The stormwater sampling was performed in the fall of 2012 to investigate the role of urban runoff on adding or diluting inorganic content in the river. El Paso as previously mentioned is a dry region and the rainfalls usually occur in summer with short duration; flash storms or showers. Two storms occurred during the study period in October, 2012. The first storm duration was for one hour, and the second storm lasted approximately 20 minutes.

The analytical results obtained for the collected water samples were used to build a database. The total number of entries in the database were 21,713 (635 sample, 635 category, 635 dates, 32 elements; Sb was analyzed later for only the last 89 samples). The data was analyzed using STATISTICA™8. Field banks were taken to the field; the metals concentrations of all field blanks were below MDL. The mean values of major water quality parameters (pH, electrical conductivity (EC), alkalinity, and major ions) in the sampled waters for both non-irrigation seasons are shown in Table 2.4 by sample location.
4.1 Bulk parameters

A summary of mean pH, EC, and alkalinity values by location is shown in Figure 2.2. The pH values for the river/canal sampling locations were within the range 8.1-8.4, and the pH of the wastewater treatment plant effluents was slightly lower and near-neutral in the range of 7.2-7.7. The mean pH was 7.4 for the collected samples of stormwater runoff from the UTEP campus.

The mean alkalinity was 44.7 mg/L as CaCO$_3$ for the stormwater, and the mean alkalinity of the Montoya Drain samples was 255 mg/L as CaCO$_3$, which was 75% higher than the mean alkalinity of the wastewater treatment plant effluents (145 mg/L as CaCO$_3$). This supports the hypothesis that the Montoya Drain contributes significant concentrations of salinity to the Rio Grande.
Electrical conductivity (EC) is a physical parameter that is well correlated with the total dissolved solids (TDS) or salinity of water. The mean EC was observed to range from stormwater with the minimum at $161 \, \mu S/cm$ to the maximum at $4175 \, \mu S/cm$ for the Montoya Drain water. This confirms the stated hypotheses of the stormwater role in diluting the Rio Grande solids comparing to all other water qualities during the non-irrigation season.

The mean EC of the Montoya Drain was more than double the mean EC of the sampling point in the river upstream of the Montoya Drain at $1900 \, \mu S/cm$. Moreover, the mean EC of the Montoya Drain was more than double the average of the mean EC of the WWTP effluents. Thus, the WWTP discharges were observed to dilute the EC concentrations for the river/ canal water that were elevated due to the Montoya Drain. This supports our hypothesis that the Montoya Drain water contributes significant salinity content to the Rio Grande water during the non-irrigation season.
The seasonal variations of the pH, EC and alkalinity for the two dry seasons of the Rio Grande between the years 2011 and 2013 are presented in Figure 2.2 (d). No significant differences were observed in the measured pH, EC and alkalinity between the first and the second seasons. Most of the data are grouped for both seasons in the same range of values, except the EC and alkalinity values of the stormwater samples.

**4.2 Major Ions**

The mean concentrations of major ions for both non-irrigation seasons are presented in Table 2.4 for all sampling locations, and Figure 2.2 shows the concentrations of Na, Mg, K and Ca by category. The highest mean concentrations for Na and Ca were 758 mg/L and 156 mg/L, respectively, and both were observed from the Montoya Drain.

The international boundary was observed with the highest mean Mg concentration of 77.6 mg/L. The RBEF was providing the canal’s water with the maximum concentration of K.

The concentrations of Na, Mg, and Ca of the river’s water at the international boundary were the highest compared to all waters on the Rio Grande. Consistent with very high electrical conductivity, the Montoya Drain was feeding the river with the maximum concentrations of Na, Mg, and Ca. This supports the hypothesis that the Montoya Drain water contributes high-salinity water to the Rio Grande during the non-irrigation season. In contrast, the Montoya Drain water was observed with the minimum mean concentration of potassium compared to all locations on the river/canal system.

The high concentrations of cations from the Montoya Drain and the international boundary were diluted through mixing process with downstream WWTPs effluents. The Montoya Drain showed the highest median and maximum concentrations for Na and Ca. This supports the hypothesis that the agricultural water contributes significant salinity to the Rio Grande water.
Figure 2.3: (a-d) Box Plot of Na, Mg, K and Ca, respectively according to the Water Quality category and (e) the Seasonal Variation of Na, Mg, K and Ca between the two sequential dry seasons of the Rio Grande in El Paso Segment.
The stormwater runoff was observed with the lowest median and minimum Na, Mg, K and Ca concentrations. This supports the hypothesis that stormwater from urban runoff lowers the total dissolved solids (TDS) and metals concentrations in the river and agricultural canals.

In Figure 2.2 (e), the concentrations of Na, Mg, K and Ca are shown as a function of time for both sequential non-irrigation seasons. No significant difference was observed between the two non-irrigation seasons. Figure 2.2 (e) shows the low range of salinity in the stormwater samples in the second non-irrigation season.

Table 2.4 shows the mean concentrations of Cl, F, NO$_3$ and SO$_4$ by location, and Figure 2.3 shows a summary of the range of concentrations of Cl, F, NO$_3$ and SO$_4$ concentration by category. The maximum mean Cl concentration was 718.5 mg/L, which was found in the Montoya Drain. This concentration was diluted to 663.9 mg/L at Courchesne Bridge, just downstream of the Drain. Concentrations of F were similar among all sampling points. The NO$_3$ concentrations were typically not detectable, except for the wastewater treatment discharge.

The higher mean concentrations of Na, Mg, and K from the Montoya Drain may be due to weathering process of the soil, and the high concentrations of SO$_4$ and Cl may result from inorganic fertilizer, and evapotranspiration process from the agricultural catchments (Collins and Jenkins, 1996).

The stormwater showed the lowest median and minimum Cl, F, NO$_3$ and SO$_4$ concentrations. The stormwater contained very low concentrations of Cl, F, NO$_3$ and SO$_4$, which would dilute the major anions in the river/ canal water body. These results support the hypothesis stated that the stormwater from urban runoff lowers the total dissolved solids (TDS) in the river and agricultural canals during the non-irrigation season.
Figure 2.4: (a-d) Box Plot of Cl, F, NO₃ and SO₄, respectively according to the Water Quality category and (e) the Seasonal Variation of Cl, F, NO₃ and SO₄ between the two sequential dry seasons of the Rio Grande in El Paso Segment.
The highest median Cl and SO₄ concentrations were reported in the Montoya Drain, and the maximum Cl and SO₄ concentrations were reported in the Montoya Drain and international boundary water, respectively. The effluents of the WWTPs experienced the highest median and maximum F concentrations. And by these results confirms also the hypothesis stated that the Montoya Drain water contributes significant salinity content to the Rio Grande water.

Figure 2.3 (e) presents the seasonal variation of Cl, F, NO₃ and SO₄ for collected samples between the two sequential non-irrigation seasons. No significant differences were observed in the trends of Cl, F, NO₃ and SO₄ between the two seasons.

### 4.3 Heavy Metals

The principal objective of this study was to evaluate the water quality of the Rio Grande/American Canal system in the El Paso region with respect to metals concentrations during the non-irrigation season.

Table 2.5 includes the mean concentrations of the dissolved heavy metals (in alphabetical order by symbol) in water samples by category. These metals differ in their fate, transport, and toxicity; each element has different sources, physiochemical behavior and environmental regulations. To interpret the significance of the trends of metals, the data analysis will include two aspects, the spatial and temporal variations.

In the following subsections, a more detailed analysis of the occurrence of metals in Table 2.4 (individually or in groups) will be provided, based on observed trends. The following discussions of the metals behaviors in this thesis is approached individually if the metal trends were highly significant or in groups if they had similar trends and behaviors. The discussion of these trends is also approached with respect to two groups according to the EPA national primary and secondary drinking water regulations (DWR) (USEPA, 2009).
Table 2.5: the Mean Dissolved Heavy Metals Concentrations in Water Quality Categories of Rio Grande.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Agricultural</th>
<th>River/Canal</th>
<th>Boundary</th>
<th>Stormwater</th>
<th>WW Effluent</th>
<th>WW Raw</th>
<th>EPA</th>
<th>Mean</th>
<th>MCL</th>
<th>DWR</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>13</td>
<td>16</td>
<td>17</td>
<td>49</td>
<td>22</td>
<td>29</td>
<td></td>
<td>24.2</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>As</td>
<td>16</td>
<td>156</td>
<td>47</td>
<td>7.3</td>
<td>10</td>
<td>7</td>
<td>17.3</td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>61</td>
<td>48</td>
<td>62.0</td>
<td>27</td>
<td>35</td>
<td>47</td>
<td></td>
<td>46.5</td>
<td>2000</td>
<td></td>
</tr>
<tr>
<td>Cd</td>
<td>0.22</td>
<td>1.10</td>
<td>0.23</td>
<td>0.50</td>
<td>0.21</td>
<td>0.35</td>
<td>0.44</td>
<td>5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>0.29</td>
<td>0.41</td>
<td>0.21</td>
<td>1.6</td>
<td>1</td>
<td>1.73</td>
<td>0.82</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>7.6</td>
<td>8.2</td>
<td>10</td>
<td>40</td>
<td>8.3</td>
<td>8.0</td>
<td>13.8</td>
<td>1300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>3.2</td>
<td>11</td>
<td>12</td>
<td>31</td>
<td>30</td>
<td>76</td>
<td>27.2</td>
<td>300</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Li</td>
<td>508</td>
<td>277</td>
<td>771</td>
<td>18.7</td>
<td>147</td>
<td>133</td>
<td>242</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>20</td>
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<td>227</td>
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<td>50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>1.3</td>
<td>11</td>
<td>1.8</td>
<td>3.2</td>
<td>2.3</td>
<td>7</td>
<td>4.5</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>Pb</td>
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<td>10.9</td>
<td>1.3</td>
<td>3.2</td>
<td>2.0</td>
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<tr>
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<td>209</td>
<td>6</td>
<td>71</td>
<td>80</td>
<td>105</td>
<td>-</td>
<td>-</td>
<td></td>
</tr>
<tr>
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<td>3.8</td>
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<td>26.6</td>
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Table 2.6 shows the metals that were consistently less than the ICP-OES detection limits. The maximum and mean concentrations of Be, Sb and Se were below the MCL (which was greater than the DL). The maximum Hg concentration and the mean of the values greater than the DL exceeded the MCL, but the Hg concentration in 94.5% of all samples was below the DL.

Table 2.6: The metals concentrations of below ICP-OES Detection limits in (µg/L).

<table>
<thead>
<tr>
<th>Metal</th>
<th>DL (µg/L)</th>
<th>Fraction &lt; DL</th>
<th>Maximum Conc. (µg/L)</th>
<th>Mean of Conc. &gt; DL (µg/L)</th>
<th>MCL</th>
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</thead>
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<tr>
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<tr>
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<td>2</td>
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<td>Sb</td>
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<td>0</td>
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<td>6</td>
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<td>2.1</td>
<td>80%</td>
<td>42</td>
<td>7</td>
<td>50</td>
</tr>
</tbody>
</table>
4.3.1 Arsenic

Arsenic originates from both natural and anthropogenic sources. Naturally it is originating from minerals rocks, volcanism, forest fires, geothermal waters, wind-blown dust. Anthropogenic sources of arsenic include agriculture (pesticide use), lumber, livestock, mining, smelting, and glass and cement manufacturing (Smedley and Kinniburgh, 2002).

In Table 2.4, the total mean concentration of arsenic (As) for all collected samples was 17 µg/L. The mean As concentration of international boundary region of the river was 47 µg/L; so by this value it was recorded as the segment of the maximum concentration. In this segment of the river the ASARCO Smelter Company plays a prominent role in adding more metals to the river. Here these results support the hypothesis of that the groundwater flowing through the ASARCO site increases the metals concentrations locally.

The Montoya Drain water was observed with a mean As concentration of 16 µg/L, which is approximately equal to the mean concentration of the points sampled in the river/canal. The stormwater and the WWTPs effluents As concentrations were 7 and 10 µg/L respectively; so they were diluting the higher concentrations in the river/canal water body. The high concentrations of As from Sunland Park WWTP effluent (SPEF) and Montoya Drain discharge (MDD) were diluted by the Northwest WWTP effluent (NWEF).
Figure 2.5: (a) mean concentrations of As by location, (b) box-plot of As by category, and (c) the seasonal variation of As between the two sequential non-irrigation seasons of the Rio Grande in El Paso
As shown in Figure 2.5, the mean As concentration in EPWU WWTPs influents was 7.4 µg/L, which was less than the mean concentration of the WWTP effluent. Note that the SPEF had the highest mean As concentration, and the SPEF concentration was included in the mean concentration of the WWTPs effluents, but the influent concentration was not analyzed. Most likely, the As concentration of Sunland Park raw wastewater is similar to the concentration in SPEF.

In addition to the mean values of As concentrations in Table 2.4, Figure 2.5(b) provides the median, and maximum. Arsenic concentrations in the river/canal, agricultural, and international boundary waters were observed to exceeded the US EPA primary drinking water Maximum Contaminant Level (MCL) of 10 µg/L (USEPA, 2012). Of all samples analyzed, 52% exceeded the drinking water MCL.

Figure 2.5(c) shows the As concentration as a function of time for both non-irrigation seasons. The exceptionally high concentrations (nearly 100 µg/L) observed at the international boundary near the ASARCO site and for stormwater and international boundary, respectively. This supports the hypothesis that groundwater flow through the ASARCO site is contaminated with metals.

4.3.2 Cadmium

The cadmium (Cd) mean concentration in Table 2.4 for each category was below the drinking water MCL of 5 µg/L (USEPA, 2012). However, in Figure 2.6 (a), some samples from the river were observed to have concentrations exceeding the MCL; the range of Cd was 0.05-30.4 µg/L. The sample location with the highest mean concentration was Sunland Park Downstream (SPDS), as shown in Figure 2.6 (b). This anomalous “hotspot” between the Sunland Park effluent and the Montoya Drain will be discussed subsequently.
Figure 2.6: (a) the seasonal variation of As between the two sequential non-irrigation seasons of the Rio Grande in El Paso, (b) mean concentrations of Cd by location.

4.3.3 Barium, Chromium, and Copper

Figure 2.7 (a) shows the minimum, median and maximum concentrations by category for barium (Ba), chromium (Cr), and copper (Cu). With respect to categories, the mean concentrations of Ba were International Boundary > Agricultural > River/Canal > Raw Wastewater > Treated Wastewater > Stormwater. All of the Ba concentrations were below the primary MCL of 2000 µg/L. Sources of Ba are natural processes from deposits erosion, and anthropogenic sources like metal refineries and drilling wastes discharges (ASTDR, 2007).
Figure 2.7(b) shows the Ba concentration change with spatial distribution. The water at SPUS had the higher Ba mean concentration which diluted by the SPEF as reported at SPDS. The MDD and the boundary region added then more Ba, whereas the effluents slightly made little dilution at the downstream section. Remarkably, the Ba removal treatment processes of the influents wastewaters were not sufficiently to remove the concentrations in the effluents on mean concentrations basis. But this happened as appear in Figure 2.8(a) just for few samples, otherwise the seasonal distribution of the samples indicated that the raw wastewater had higher concentrations than the treated wastewater in both seasons. In the first season the higher
concentrations were in the river/canal samples, while in the second season the higher concentrations were changing between all water categories.

No significant trend was in Cr mean concentrations, the total mean Cr concentration for all samples was 0.82 µg/L. All the concentrations were below the 100 µg/L; the MCL. The raw wastewater were had the maximum Cr but the treatment processes in the three WWTPs were reduced this concentration in the effluents treated wastewater from 1.7 to 0.7 µg/L. Stormwater added 1.6 µg/L which was the maximum Cr delivered to the river water. Through the two non-irrigation seasons no significant change in the distribution by the seasons.

The total mean Cu concentration for all samples was 14 µg/L. No notable trend was for Cu concentrations between the water categories or sampling locations. The maximum Cu concentrations provided by stormwater the river was 40 µg/L. The sampling locations concentration did not exceed the MCL. By the season change, the Cr categories trends did not significantly changed.
Figure 2.8: (a-c) the Seasonal Variation of Ba, Cr, and Cu between the two sequential dry seasons of the Rio Grande in El Paso Segment
4.3.4 Lead, Uranium, and Vanadium

Lead (Pb) is originating naturally from the deposits erosion and from domestic uses; the household plumbing systems corrosion (USEPA, 2013). The MCL of Pb is Zero and the action level is 15 µg/L, for this reason it is considered a very toxic for infants, children and adults (USEPA, 2013).

Figure 2.9: (a) Box Plot of Pb, U and V per category, (b) Mean concentrations of Pb, U and V at sampling Locations
The total mean Pb concentration for all location samples was 3.7 µg/L with range of mean values from 1.3 µg/L at the international boundary to 11 µg/L in the river/canal water body. The Pb concentrations values were reported within the range from 0.55 to 630 µg/L. This means that all of these concentrations were exceeded the MCL of Pb, therefore they are very significant in terms of Pb contamination and its effects on the El Paso environment.

In Figure 2.9 (a, b) the highest Pb median and maximum concentration values were for stormwater and river/canal water, respectively. The median Pb value for all samples collected from all locations was 1.8 µg/L. The stormwater added significant Pb concentrations to the system. The SPDS was the location which reported the maximum Pb concentration. The variation of Pb with the dry seasons did not show any significant trend; the river/ canal were recording the maximum values in both seasons.

The natural rocks and soils erosion is one of the natural sources of Uranium (U) (ASTDR, 2007). The WWTPs were suffering the raw wastewater with 76 µg/L which was the highest mean concentration. The maximum concentration was tested in the river/ canal samples; mainly at NWDS. The mean concentration added from both the stormwater and the WWTPs effluents was 31 µg/L. Comparing to the other five water qualities, the agricultural water was with no significant U concentrations. The flowing water from SPUS contained less concentration than SPEF which added higher concentration. Downstream of Montoya Drain the concentration became more less with the dilution series by the river and the agricultural water.
Figure 2.10: (a-c) the Seasonal Variation of Pb, U, and V between the two sequential dry seasons of the Rio Grande in El Paso Segment
Both the boundary and the river/canal samples verified mean U concentrations of 16 and 17 µg/L, respectively. Seasonally, no significant variation on U trends between the first and the second seasons. The MCL of U is 30 µg/L, therefore 63 percent of the samples were below the MCL and 36.7 percent exceeded the standards.

The natural sources of Vanadium (V) are the minerals, soil erosion and rocks weathering. The human activities such as municipal sewage, certain fertilizers and the combustion of fossil fuel deposits (coal and petroleum crude oils) are can be sources of V (ASTDR, 2009). The stormwater contribution of V was the highest; the provided mean concentration was 6 µg/L. The wastewater treatment processes added more V to the effluent; the mean influent concentration was 3 µg/L where in the effluents increased to 5 (µg/L). The river/canal sampling locations recorded 4.1 µg/L mean concentration; the maximum concentration of this category was at SPDS. On seasonal basis, no significant trend was noted for V and it was approximately kept the same tendency. No information is provided by EPA about the MCL of V, but it is a very toxic and carcinogenic metal.

### 4.3.5 Aluminum, Iron, Manganese, and Zinc

The stormwater provided the river with the highest Aluminum (Al) mean concentrations. The mean Al concentrations were ranging from 13 and 49 µg/L from agricultural water and stormwater respectively. The wastewater treatment processes reduced the Al from 29 µg/L in the influents to 22 µg/L in the effluents. In this case the treated wastewater provided the river/canal water with Al concentration more than what the agricultural water added.
In Figure 2.11 (a, b) the maximum Al concentration (192 µg/L) was at the NWDS; within the river/canal waters. No significant variation on the seasonal Al concentrations from all location, except that the storms runoff appeared to add more concentration when they occurred.

The Iron (Fe) concentrations were the highest in the WWTPs influents. These concentrations reduced from 76 to 29.7 µg/L in the effluents. No noteworthy behaviors and
trends were noted for the other water qualities. And as appears in Figure 2.12 (b), the seasonal measurements were without any differences between the two dry seasons.

The international boundary sampling points were reporting 228µg/L mean concentration of Manganese (Mn), with maximum concentration reached 675µg/L. This concentration was the highest comparing to other sampling sites and to all water qualities. The WWTPs reduced this concentration in the influents from 53 to 20 µg/L in the effluents of treated water. The stormwater added Mn more than what the agricultural water contributed. The river and canal sampling points were reported a dilution in these concentrations; the mean concentration for the river/canal sampling points was 17.8 and it was the minimum.

Northwest influent was experiencing the highest Mn between other WWTPs influents. No significant percent of treatment were shown in the effluents concentrations. The SPEF reported the minimum concentration comparing to other effluents. The SPUS recorded the minimum concentration of the river sites. With going downstream this concentration became higher with the additions of SPEF and Montoya Drain agricultural water. The soil and crustal rock erosion processes are the natural sources of Mn, and it transfers to the atmospheric air and water by the wind and deposition. The municipal wastewater and landfills sludge, mining, fossil fuels combustion, mineral processing and steel and iron manufacturing are the major anthropogenic sources of manganese released to the Environment (ASTDR, 2007).
Figure 2.12: (a-d) the Seasonal Variation of Al, Fe, Mn, and Zn respectively between the two sequential dry seasons of the Rio Grande in El Paso Segment.
Most of the river/canal samples in the 2011 dry season had concentrations more than those in the second season; the minimum concentration was in 2012 season. The international boundary samples yielded the highest percent of the maximum concentrations. The percent of the samples with concentrations exceeded the MCL 50 µg/L of Mn was 21% of the total samples. Mainly, the total mean concentration of all collected samples was 63 µg/L; which mean it exceeded the MCL.

The highest and lowest mean Zinc (Zn) concentrations were 9 and 49 µg/L, in the international boundary and stormwater samples respectively. The WWTPs effluents were with higher concentration than the influents; the concentration increased from 23.1 to 39 µg/L. The river/canal samples reported this concentration of 27 µg/L. No significant change between the sequent dry seasons; all the concentration kept the same range of values. The SPDS was with the maximum concentration within the river/canal system; but this concentration was diluted by the upstream inflowing water and the agricultural water.

4.3.6 Nickel and Tungsten

The maximum Nickel (Ni) was 750 µg/L at SPDS which led the river/canal water to gain the highest mean concentration which was 11 µg/L, as shown in Figure 2.13 (a, b). The total mean concentration of all water categories was 4.5 µg/L. The Ni was reduced during the treatment of the wastewater from 6.8 to 2.3 µg/L in the influents and effluents of the WWTPs respectively. The Northwest was with highest values in both the raw and treated wastewater. The stormwater mean and median concentration values were higher than other water qualities but the maximum values were in the river/canal and WWTPs samples.

Figure 2.13 (b) specifies the concentration change with the sampling location. The spike concentration of Ni at SPDS sampling point is the main feature of the chart. Then the agricultural
Montoya water which had low concentration was plying a good role in diluting this high concentration comparing to other sampling points. The distribution of the samples concentrations with sampling seasons in Figure 2.14 (a) shows that in the 2011 and 2012 season the river/canal and the WWTPs were with the maximum values. And that the agricultural, stormwater, and the international boundary values all of them lower than 12 µg/L.

The Tungsten (W) trends in both Figure 2.13 and 2.14 are to some extent similar of the Ni trends. The river/canal sampling points recorded 386 and 18 µg/L as the maximum and the highest mean concentrations respectively. The SPDS was the sampling point which verified the most of the highest concentrations and this formed a spike concentration in Figure 2.13 (b).

![Figure 2.13](image.png)

Figure 2.13: (a) Box Plot of Ni and W per category, (b) Mean concentrations Ni and W at sampling Locations.
The raw wastewater water was containing also high W concentration, mainly at Northwest WWTP. The treatment process had No sensible removing of the W between the influents and effluents; the W was 10 and 7.5 µg/L respectively, which means that only 24% of W was removed from the three WWTPs. The median of the stormwater was the highest with mean concentration 10 µg/L. The international and agricultural waters samples reported mean concentrations of 6 and 7µg/L respectively. The agricultural water reduced the spiked concentrations at SPDS; this what indicated by the concentration at Courchesne Bridge.

Figure 2.14: (a,b) the Seasonal Variation of Ni and W respectively between the two sequential dry seasons of the Rio Grande in El Paso Segment.
Figure 2.14: (a) Box Plot of Li, Sn, and Sr per category, (b) Mean concentrations Li, Sn, and Sr at sampling locations.

More detailed explanations can be taken from Figure 2.14 (b), which expresses the distribution of the samples’ concentration through the two dry seasons. The high concentrations in the WWTPs were at the first season. And the river/canal high concentrations were in both seasons within the same range of values.

The maximum and the highest mean Lithium (Li) were 508 and 697 µg/L respectively in the agricultural water. Whereas the minimum mean concentration was 18 µg/L delivered to the
river with the stormwater. The international boundary samples also had high mean concentration; it was 370 µg/L. Figure 2.15 (b) shows the sampling points upstream of the Montoya drain; SPUS, SPDS and SPEF were approximately with the same mean concentrations. This was a reason of low dilution factor of these points on the water of MDD. No significant difference between the influent and effluent concentrations of the WWTPs. The mean concentrations of the raw wastewater lower than the treated wastewater; they were 133 and 146.6 µg/L. The influent of the Sunland Park WWTP was not included; SPEF increased the mean concentration of the influents.

The Li of the collected samples for the two dry seasons in Figure 2.16 (a) distributed in three layers of concentrations. From the top, the agricultural water formed the layer of the maximum values. The river/canal and the international boundary samples came in the second layer then the influents and effluents of the WWTPs. The stormwater was with the minimum values distributed in the lower layer of the other water categories.

The total mean Tin (Sn) concentration was 105 µg/L. The contributions which raised the Sn concentrations were 209, 152, and 113 µg/L at the international boundary, agricultural and river/ canal waters respectively. On the other hand, the stormwater, the influent and effluents of the WWTP with their contributions 5.8, 71 and 79 respectively played the role of reducing this concentration.

The maximum concentration value was in the raw wastewater but it was an extreme value as shown in Figure 2.15(a) and 2.16(b). Approximately the median values for all categories were without any significant trend except the stormwater which was very low comparing to the others. The variation of the concentration with the sampling location indicated that the stormwater was the minimum which was playing the major part of decreasing the high concentrations.
Figure 2.16: (a-c) the Seasonal Variation of Ni and W respectively between the two sequential dry seasons of the Rio Grande in El Paso Segment.
All the WWTPs with their effluents were with the same average concentrations. The SPEF was the water which decreasing the high concentration from upstream segment and the agricultural water. This can be shown at SPDS and MDDS respectively.

In the same trend of Li the Sn distributed seasonally in three value layers. The maximum values at the top; the international and agricultural waters. Then the WWTPs and river/canal waters in the middle, and the third in the bottom it was the stormwater.

The same trend was shown for the Strontium (Sr) tendency and it was very similar to Sn. the international boundary and the agricultural water were with the highest two mean concentrations; 3217 and 2453 µg/L, respectively. These two concentrations led to raise the total mean concentration to 1639 µg/L, because the other four categories were less than this value. They were 1533, 1334, 1152, and 145 µg/L, in the river/canal, treated wastewater, raw wastewater and stormwater respectively.

In Figure 2.15 (b), the high agricultural concentrations of Sr were diluted from the upstream water had slightly less concentrations as reported at SPUS, SPDS and SPEF. This dilution action was also taken place by NWEF as shown at the NWDS. The international boundary concentrations also showed more diluted at HSUS. The most effective dilution factor came from stormwater. The influents of WWTPS had higher concentrations than the influents.

In the first dry season there was no specific trend for each category. The maximum values where came from all water qualities. Whereas, in the second season the agricultural water had the maximum values, in addition to the international boundary which was sampled just in the second season.
4.4 Sunland Park Segment

As shown in the previous section, some metals like Cd, Ni, Pb, U and V had a spike concentration in specific days at SPDS. For this reason an additional sampling week was added in order to monitor the Sunland Park area and to recognize the discharge point of these high concentrations. The sampling grapping was continued for one week on daily samples basis; it was started on April 26, 2013 and ended on May 3, 2013. Figure 2.17 presents the sampling points in the Sunland Park area.

![Map showing sampling points in Sunland Park area](image)

Figure 2.17: the sampling points in the Sunland Park area.

Table 2.7 includes the mean concentrations for the metals at nine sampling points. The sampling included SPUS, SPEF, SPDS, MDD and MDDS in addition to the three more points between these points and the groundwater ditch parallel to the river. And Figure 2.17 shows the distribution of metals concentrations at each point. The Pb and W in were below the detection limits of the ICP-OES, so they not included in this discussion.
Table 2.7: Mean Metals concentrations passing the Sunland Park area during one week

<table>
<thead>
<tr>
<th>Metal</th>
<th>SPUS</th>
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<th>SPEF</th>
<th>SPDS-1</th>
<th>SPDS-2</th>
<th>SPDS-3</th>
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Figure 2.18: Mean Metals concentrations passing the Sunland Park area
The flowing water through SPUS had the highest mean concentrations of As, Mn, Sn and U. The SPEF had the V of highest concentration and the sampling new points between SPUS and MDD with SPDS had the Cd, Cu and Zn of highest concentrations. The concentrations of Se and Sr were the highest at MDD. And the groundwater ditch was containing the highest concentrations of Al, Ba, Be, Fe, Li and Ni. The trends of As, Ba, Fe, Cu, Li, Mn, Ni, Sn, Sr, and U were approximately similar. They were high at upstream and downstream samples and in between less than them. And the Al, Be, Cd, Se, V and Zn were with different trends; they were higher between the upstream and downstream samples. The metals Pb and W were below the detection limit. This may give an indication of the possibility of the present of metals discharging point in the area; Figure 2.18 shows the satellite image of this area in the past and in the present.

Figure 2.19: Sunland Park Area between 2010 and 2013
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Chapter Three


1. Introduction

a. Background

Rivers are the main system pathways for the pollutants transport between regions which receive pollutants from industrial, agricultural, and domestic activities (Ramani et al, 2012). Urbanization and the changing patterns of land use are responsible for adding more pollutant loads to water streams and degrade the quality of water (Ren et al., 2003). Urban stormwater runoff adds more contents of nutrients, suspended solids, heavy metals, fecal coliforms, and salinity to the receiving water in the urban catchment (Al Bakri et al, 2008). A large variety of pollutants such as heavy metals (Cd, Cr, Ni, Pb, and Zn) can be found in the stormwater from different surfaces such as streets, parking lots, and roofs in urban areas. These concentrations can exceed maximum contaminant levels (Karlsson et al., 2010). In highly urbanized areas, the road surfaces comprise about 22% of total catchment area, which can contribute up to 26% of the total runoff volumes with 19-40% of the loads of heavy metals (Cu, Pb, Zn) (Davis and Birch, 2009).

Wastewater treatment plants (WWTPs) receive municipal and industrial wastewaters which typically contain complex mixtures of nutrients and organic and inorganic pollutant loads (EC, 2001). Industrial activities near the stream are typically the major sources of pollutants in water, including heavy metals (Pb, Cd, Cu, Zn and Cr) (Yayintaş et al, 2007). Intensive industries such as textile, metal, and leather add high concentrations of heavy metals to the urban wastewater (Gokhan, 2009). Agricultural practices may provide significant amounts of Pb, Cd, and Zn loads to stream sediments, and automobile traffic and industry may provide significant amounts of Pb.
loads to surface water (Schipper et al., 2008) (Nguessan et al., 2009). Natural geochemical processes also contribute to the metal concentrations and loads in rivers (Klavins et al, 2000).

Jain (2007) carried out chemical mass balance studies for the Hindon River, Western Uttar Pradesh (India), which receives different pollution loads from municipal and industrial activities and nearby agricultural areas. Depending on the land use pattern, the river system in this study has been divided into three stretches, to measure the changes in the concentrations and loads of nitrate and phosphate to the river from non-point sources of pollution, using upstream and downstream sampling locations. The mass balance calculations indicated that the percentages of nitrate and phosphate contribution from uncharacterized non-point sources of pollution due to agricultural activities, ground water contribution and sediment water interactions have been changed from 15.5% to 13.1% for nitrate and from 6.9% to 16.6% for phosphate in the upper stretch and in the lower stretch respectively (Jain et al, 2007).

b. Rio Grande Basin

The Rio Grande runs 1,255 miles along the international boundary between the United States with Mexico, with a total length of 1,901 miles from San Juan in the Colorado Mountains to the Gulf of Mexico (USIBWC, 2011; Creel, 2010). The Rio Grande is the fifth longest river in the United States and one of the top twenty in the world (Parcher, 2010). The total area of the Rio Grande basin covers of approximately 335,000 square miles, with approximately half of the area in the United States and 15% within State of Texas (USIBWC, 2011).

c. Paso del Norte Study Area

El Paso is one of the Texas State cities and a border city between the United States and Mexico. El Paso is located within latitude 31°48' and longitude 106°24' and covers 1,014 square miles of area (USGS, 1998; Richardson, 1909). It subjects to an arid climate with hot summers
(the maximum temperature exceeds 105 °F) and cool winters. The rainfall of El Paso occurs in summer for short duration storms or showers and the average annual precipitation is about 5.9 inches (Parcher et al, 2010; TWRI, 2010).

The Rio Grande has been historically subjected to different loads of pollutants. The ASARCO smelter has been one of the major sources of pollution in El Paso. Rios-Arana et al (2004) performed a study on heavy metals content in the water and sediment of Rio Grande. They resulted that As, Cr, Cu, Ni, Pb, and Zn were had high concentrations in sediments compared to the river water. The freshwater chronic criteria were exceeded for both Pb and Zn concentrations (Rios-Arana et al, 2004).

Irrigation water which contains heavy metals can pollute soil and consequently accumulate in plant tissues irrigated by this water. Assadian et al (1998) studied the heavy metals concentrations on soils and alfalfa crops in two fields on both United States and Mexico sides of the Rio Grande. Their results showed that the soils closer to the irrigation canal were more polluted with heavy metals than those further away (Assadian et al, 1998).

The Rio Grande forms the international boundary between the United States and Mexico. Below the American Dam, it becomes inside the Mexican border and the American water part converts to the American Canal. Different water qualities are discharged to the Rio Grande and the American Canal from agricultural, industrial, and domestic activities within the El Paso region. The study area includes the El Paso segment along the Rio Grande and American Canal from Sunland Park WWTP to the Bustamante WWTP. This segment includes many discharging points of industrial loads like the ASARCO smelter, Rio Grande Power Plant and GCC of America. And the Montoya Drain which discharges agricultural loads in addition to the treated wastewater from Northwest, Haskell, and Bustamante WWTPs.
a. **Goals and Objectives**

The main objectives of the entire study were to evaluate the metals mass loads at each sampling point within the riverine system and the contribution of the discharging points. Accordingly, identify the major sources of the metals mass loading over two terms, the sampling site and the water quality category.

2. **Methodology**

a. **Data Collection**

Weekly samples were collected for two non-irrigation seasons of Rio Grande. The samples were collected and stored in pre-cleaned polyethylene bottles (USEPA, 2012). The samples were analyzed by ion chromatography (IC) and inductively coupled plasma optical emission spectrometry (ICP-OES). The analyses for water quality parameters using the IC and ICP-OES were carried out according to the Standard Methods for the Examination of Water and Wastewater (APHA, 2012).

b. **Mathematical Model**

The mass balance model is the suitable tool to interpret the stream chemical reactions and the physical pollution loads into mathematical approaches. In the regions where featured by wet and dry seasons, the mass balance approach is helpful in study the water bodies receive different contributions and patterns of pollutant loads from the surrounds and tributaries defined by point and non-point sources. The mass balance model is built by including the input/output contribution loads at monitoring stations between the upstream and downstream segments. The mass balance method mainly based on the conversation of mass by advection and dispersion on solute concentration fundamentals; Accumulation = Mass in – Mass out (Runkel and Bencala,
The river/stream systems are either transient or steady state and are identifying by the following equations (Walton, 2008):

The change in storage of mass per unit time = input - output + sources – sinks

\[
\frac{dM}{dt} = \sum_i I_i - \sum_j O_j \pm \sum_k R_k \quad \ldots \ldots (1a)
\]

And in terms of concentration

\[
\frac{dC}{dt} = \frac{\sum_i I_i - \sum_j O_j \pm \sum_k R_k}{V} \quad \ldots \ldots (1b)
\]

where

\( M \) = mass in control volume (kg)

\( t \) = time (s)

\( I \) = input to control volume (kg/s)

\( O \) = output from control volume (kg/s)

\( R \) = rate of creation or destruction by chemical reaction (kg/s)

\( C \) = mass concentration (kg/m\(^3\))

\( V \) = volume of control volume (m\(^3\))

\( i,j,k \) = number of inputs, outputs, and source/sink/reaction terms

Under steady state conditions the mass balance equation is applied to the river segment using the differential pollutant loads between upstream and downstream monitoring stations according to the following equation:

\[
C_D Q_D - Q_u C_u = \sum_{i=1}^{n} L_i \quad \ldots \ldots (2)
\]
where $Q_D$ and $Q_u$ are downstream and upstream flows; $C_D$ and $C_u$ are the downstream and upstream concentrations in the receiving water; and $\sum_{i=1}^{n} L_i$ is the sum of all individual loadings to the receiving water (C.K., 1996).

The present study uses the major-ion and heavy metals chemistry data from Phase 1 to construct the mass balance model. This model is calibrated for scenario including the non-irrigation seasons, using the wastewater treatment plant flow data provided by the Water Utility of El Paso (EPWU). And in combination with stream flow and precipitation data are taken from (IBWC) and (USGS).

**a. Flow data**

The stream flow and wastewater treatment plant effluents flow data were used to estimate the metal loads. The required Rio Grande and American canal flow data were taken from the International Boundary and Water Commission (USIBWC) web page (http://www.ibwc.state.gov/Water_Data/histflo1.htm). Two stations were useful for the present study (1) station number: 08-3640.00 at Courchesne Bridge (point number 5 in part (a) of Figure 2.1), and (2) station number: 08-3645.00 at American canal below the American Dam (point number 7 in part (a) of Figure 2.1). The influent and effluent flow rates for the WWTPs of El Paso were taken from the Water Utility of El Paso (EPWU). The Sunland Park WWTP effluent was taken from the EPA web Page (http://www.epa-echo.gov/cgi-bin/get1cReport.cgi?tool=echo&IDNumber=110011027174). The flow rate passing SPUS, SPDS, NWDS, HSDS and RBDS (downstream of the study area), were estimated by addition and subtraction using the available flow rate at other points along the Rio Grande and American canal.
3. Results and Discussion

In this study the mass balance equation for the Rio Grande and American Canal in the El Paso segment described using the differential load contributions between upstream and downstream sampling points. The mass balance model is based on the monitoring data of flow and water quality at each sampling locations for the two dry seasons between the periods from 2011 to 2013. And the mass balance approach was applied on the water flow rate in order to determine the missed values at some points.

The sampling point just upstream of Haskell WWTP which named in this study (HSUS) is the downstream of the river and American canal system sampling points. At the same time it is upstream of both Haskell and Bustamante WWTPs; the downstream loads of the study area were calculated using the formula:

\[ \text{Downstream Loads} = \text{ Loads at HSUS} + \text{ Loads of HSEF effluent} + \text{ Loads of RBEF effluent} \]

4.1 Major Ions

The flow rate was increasing with going downstream of SPUS, as shown in Figure 3.1. Table 3.1 presents the mean flow rate and major ions loads at each sampling point classified according to the loads category; agricultural, river/canal, USA-boundary, WWTPs effluents and Influent (Treated and raw wastewater).
Figure 3.1: The mean flow rate over the sampling points.

Table 3.1: The mean flow rate and major ions loads at each sampling point

<table>
<thead>
<tr>
<th>Sampling Point</th>
<th># Samples (n)</th>
<th>Flow Rate (m³/s)</th>
<th>Major Ions loads (kg/day) (± SE)</th>
<th>Cl</th>
<th>F</th>
<th>NO₃</th>
<th>SO₄</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
</tr>
</thead>
<tbody>
<tr>
<td>River/Canal</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SPUS</td>
<td>45</td>
<td>0.05*</td>
<td>1160 (±238)</td>
<td>2.4 (±0.4)</td>
<td>-</td>
<td>791 (±118)</td>
<td>204 (±32)</td>
<td>45 (±7)</td>
<td>84 (±18)</td>
<td>629 (±95)</td>
<td></td>
</tr>
<tr>
<td>SPDS</td>
<td>45</td>
<td>0.11*</td>
<td>2987 (±190)</td>
<td>9.0 (±0.6)</td>
<td>0.0 (±0.1)</td>
<td>2441 (±186)</td>
<td>508 (±33)</td>
<td>103 (±7)</td>
<td>208 (±16)</td>
<td>3458 (±222)</td>
<td></td>
</tr>
<tr>
<td>MDDS</td>
<td>45</td>
<td>0.26</td>
<td>14731 (±587)</td>
<td>23 (±1.1)</td>
<td>0.6 (±0.2)</td>
<td>14650 (±901)</td>
<td>3010 (±121)</td>
<td>314 (±12)</td>
<td>745 (±40)</td>
<td>14424 (±718)</td>
<td></td>
</tr>
<tr>
<td>NWDS</td>
<td>45</td>
<td>0.58*</td>
<td>21721 (±788)</td>
<td>49 (±1.6)</td>
<td>1.3 (±0.5)</td>
<td>23453 (±2293)</td>
<td>4450 (±265)</td>
<td>768 (±50)</td>
<td>983 (±104)</td>
<td>24587 (±949)</td>
<td></td>
</tr>
<tr>
<td>HSUS</td>
<td>44</td>
<td>0.55</td>
<td>21748 (±1554)</td>
<td>44 (±3)</td>
<td>1.9 (±0.8)</td>
<td>22448 (±2293)</td>
<td>4465 (±265)</td>
<td>743 (±50)</td>
<td>1209 (±104)</td>
<td>24805 (±1702)</td>
<td></td>
</tr>
<tr>
<td>HSDS</td>
<td>-</td>
<td>1.19*</td>
<td>33289</td>
<td>86 (±0.5)</td>
<td>513 (±1.2)</td>
<td>32384 (±490)</td>
<td>7758 (±79)</td>
<td>1658 (±4)</td>
<td>1902 (±27)</td>
<td>36307 (±340)</td>
<td></td>
</tr>
<tr>
<td>Agricultural</td>
<td>45</td>
<td>0.15</td>
<td>9278 (±327)</td>
<td>10 (±0.5)</td>
<td>-</td>
<td>8977 (±490)</td>
<td>2006 (±79)</td>
<td>116 (±4)</td>
<td>483 (±27)</td>
<td>9792 (±340)</td>
<td></td>
</tr>
<tr>
<td>WW Effluent</td>
<td>-</td>
<td>2.28</td>
<td>49033</td>
<td>153 (±0.5)</td>
<td>2668 (±1.2)</td>
<td>46776 (±490)</td>
<td>12841 (±79)</td>
<td>3446 (±4)</td>
<td>2840 (±27)</td>
<td>49255 (±340)</td>
<td></td>
</tr>
<tr>
<td>SPEF</td>
<td>44</td>
<td>0.07</td>
<td>1478 (±58)</td>
<td>4.5 (±0.2)</td>
<td>71 (±5.4)</td>
<td>1376 (±59)</td>
<td>332 (±12)</td>
<td>83 (±3)</td>
<td>72 (±3)</td>
<td>1493 (±58)</td>
<td></td>
</tr>
<tr>
<td>NWEF</td>
<td>44</td>
<td>0.32</td>
<td>7416 (±297)</td>
<td>23 (±1)</td>
<td>274 (±16)</td>
<td>8572 (±344)</td>
<td>1681 (±65)</td>
<td>346 (±13)</td>
<td>347 (±14)</td>
<td>8837 (±335)</td>
<td></td>
</tr>
<tr>
<td>HSEF</td>
<td>44</td>
<td>0.64</td>
<td>11541 (±243)</td>
<td>42 (±1.2)</td>
<td>511 (±12.4)</td>
<td>9936 (±264)</td>
<td>3293 (±100)</td>
<td>915 (±16)</td>
<td>693 (±15)</td>
<td>11501 (±221)</td>
<td></td>
</tr>
<tr>
<td>RBEF</td>
<td>44</td>
<td>1.26</td>
<td>28598 (±523)</td>
<td>83 (±6.2)</td>
<td>1813 (±105)</td>
<td>26892 (±745)</td>
<td>7535 (±253)</td>
<td>2103 (±40)</td>
<td>1728 (±43)</td>
<td>27423 (±396)</td>
<td></td>
</tr>
<tr>
<td>Downstream</td>
<td></td>
<td>2.45</td>
<td>61887</td>
<td>169 (±235)</td>
<td>2325 (±59276)</td>
<td>15922 (±3762)</td>
<td>3631 (±63730)</td>
<td>629 (±95)</td>
<td>24587 (±949)</td>
<td>14424 (±718)</td>
<td></td>
</tr>
</tbody>
</table>

SE = Standard Error = \frac{\sigma}{\sqrt{n}}, \sigma = Standard Deviation

* estimated value
MDD is considered as a collection of the non-point sources of pollution form agricultural activities like fertilizers and pesticides. But in the term of the Rio Grande, the MDD is a point source which over the present study period added more agricultural loads of major ions to the river content. Comparing to SPUS, SPEF, SPDS the upstream points of MDD; it was higher than them for all contributions of the major ions. The maximum treated wastewater outfall was at RBEF and for this reason it reported the maximum loads of major ions. The flow rate in the Rio Grande at the border region (between the United States and Mexico) during the sampling period from this site was zero; so there were no loads of pollutants at this site.

4.2 Heavy Metals

Using the same approach used for the major ions; the metal loads also estimated during the dry seasons of Rio Grande. Figure 3.2 (a-c) presents the mean loads of Al, As, Ba and Cd at each monitoring point from upstream at SPUS to downstream of RBEF outfalls. The loads of these metals were increasing with going downstream toward HSUS and then by more loads from HSEF and RBEF the loads increased more.

The Al, As, Ba and Cd loads increased from 0.73, 0.034, 0.35 and 0.001 kg/day at upstream to 1.6, 2.4, 4.3 and 0.033 kg/day at HSUS and increased to 4.5, 3.6, 12.5 and 0.07 kg/day downstream of the study area, respectively. The loads of Cd at SPDS was coming from the high concentration at this point; and the conclusively explanation for this phenomena is to consider this as a discharge area of this metal. It could be an illegal wasting of this metal waste or it was discharged from natural sources.
Figure 3.2: (a) the mean loads of Al, As, Ba and Cd at each sampling point, (b) the loads classified according to the category, and (c) the seasonal loads of Cd at SPDS.
The second chart is classifying the loads of Al, As, Ba and Cd according to the water category. The domestic wastewaters were loaded with the maximum metals. And it appears that the flowing water through the riverine points in the river/canal body was carrying the maximum loads of these metals. From the beginning of sampling in November 2011 in the first non-irrigation season up to the earlier of February 2012, the Cd loads not changed as shown in Figure 3.2c and it was below 0.0025 kg/day. After that in the middle of this month it increased up to 0.041 kg and then up to 0.18 kg/day in the second season. And also, this confirms the same explanation above of existing of illegal practices in this region. However, the natural processes loads should be constant all the time but not for specific time.

Figure 3.3: (a) the mean loads of Al, As, Ba and Cd at each sampling point, (b) the loads classified according to the category, and (c) the seasonal loads of Cd at SPDS.
Figure 3.4: (a) the mean loads of Mn, Ni, Pb, and Sn at each sampling point, (b) the loads classified according to category, and (c, d) the seasonal loads of Ni and Pb at SPDS respectively.
Figure 3.5: (a) the mean loads of Sr, U, V, W, and Zn at each sampling point, and (b) the loads classified according to category.

In the same trend the metals Cr, Cu, Fe and Li loads were distributed in Figure 3.3, along the sampling points. They increased with going downstream with increasing the flow rate in the system. These loads increased between the HSUS and the downstream of the segment from 0.03 to 0.21 kg/day for Cr. And increased from 0.69 to 2.6 for Cu, where for Fe it increased from 0.86 to 7.1 kg/day. Also the Li loads increased between these two points from 31.9 to 52.3
kg/day. And the categories loads also this time were the maximum for the river/canal riverine points. No significant distribution was shown for this group of metals.

The metals Mn, Ni, Pb, and Sn showed an increasing with flowing to downstream. Figure 3.4(a-d) shows the distribution of the loads of these metals at each monitoring point. The Mn loads 8.6 kg/day in the American canal downstream of the American dam (border-ASARCO region) was the maximum load. In Figure 3.4 (c and d), Ni and Pb behaved in their trends as in the same of Cd trend and seasonal distribution at SPDS; Ni and Pb recorded the higher loads at SPDS of about 0.34 and 0.35 kg/day respectively. They were in the earlier of the first season with the same level of loading values then from January, 2012 up to the end of the second dry season were higher. The categories loads of Mn, Ni, Pb, and Sn showed the maximum loads in the river/canal category. And that no significant trends noted in their distributions.

Figure 3.5 (a, b) expresses the mean loads of Sr, U, V, W, and Zn at each sampling point. The Sr reported the maximum load of all metals and it was 173 and 397 kg/day between HSUS and downstream of the study segment. Also like all other metal loads, these loads of metals increased with going downstream. The W and Zn loads also became higher at SPDS but not in a significant difference from other points like Cd, Ni, and Pb.

The agricultural loads were the minimum and they were higher in the river/canal and treated wastewater effluents. The point sources of pollution are the main loading contributions in El Paso region; the treated domestic wastewater discharges and some limited industrial contributions. Also, the occasional or no rainfall occurs during the dry season of Rio Grande, makes the point sources of pollution are the significant differential loads between the downstream and upstream monitoring points. Figure 3.6 explains the factor of loading increase between upstream and downstream of the study area as results of the treated wastewater outfalls
from the effluents of Haskell and Bustamante WWTPS. The maximum value of this factor was 8 for Fe and 7 for Cr and Mn.

![Figure 3.6: the factor of load increase between Upstream and Downstream of the study area.](image)

4.3 Stormwater loads

Figure 3.7 shows the study area and the catchment regions of runoff with the contour elevation lines captured from the national map of USGS (NHD), and the total local catchment area above the Bustamante WWTP was 409 km$^2$. Metals loads from urban stormwater runoff were estimated using the equation:

\[
\text{Load} = (\text{catchment area}) \times (\text{average precipitation}) \times (\text{rational coefficient}) \times (\text{concentration})
\]

The annual mean rainfall during the non-irrigation season (October through April) is 82 mm ([http://www.weather.com/weather/wxclimatology/monthly/graph/USTX0413](http://www.weather.com/weather/wxclimatology/monthly/graph/USTX0413)). A rational method runoff coefficient of 0.8 was assumed, which would result in an annual average runoff flow of 1.5 m$^3$/sec for the non-irrigation season.

Table 3.2 shows the major ions and heavy metals loads in kg/day during the non-irrigation season of Rio Grande for the present research study area (based on annual average precipitation). Comparing to the other anthropogenic loads; the treated wastewater and the agricultural water, the stormwater was loading the lowest major ions loads.
Figure 3.7: Catchment area of study region of El Paso
Table 3.2: Estimated loads stormwater metals

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (mg/L and µg/L)</th>
<th>Loads (kg/day)</th>
<th>±SE (kg/day)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Major ions</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>6.9</td>
<td>875</td>
<td>160</td>
</tr>
<tr>
<td>F</td>
<td>0.2</td>
<td>25</td>
<td>2.9</td>
</tr>
<tr>
<td>NO\textsubscript{3}</td>
<td>0.2</td>
<td>25</td>
<td>5.6</td>
</tr>
<tr>
<td>SO\textsubscript{4}</td>
<td>18</td>
<td>2310</td>
<td>265</td>
</tr>
<tr>
<td>Ca</td>
<td>23</td>
<td>2920</td>
<td>284</td>
</tr>
<tr>
<td>K</td>
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<td>37.0</td>
</tr>
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<td>Mg</td>
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<td>82</td>
</tr>
<tr>
<td>Na</td>
<td>8.1</td>
<td>1024</td>
<td>193</td>
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<tr>
<td><strong>Metals</strong></td>
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</tr>
<tr>
<td>Al</td>
<td>49</td>
<td>6.2</td>
<td>0.71</td>
</tr>
<tr>
<td>As</td>
<td>7.3</td>
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<tr>
<td>Ba</td>
<td>27</td>
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<td>0.44</td>
</tr>
<tr>
<td>Cd</td>
<td>0.5</td>
<td>0.1</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr</td>
<td>2</td>
<td>0.2</td>
<td>0.06</td>
</tr>
<tr>
<td>Cu</td>
<td>40</td>
<td>5.1</td>
<td>0.49</td>
</tr>
<tr>
<td>Fe</td>
<td>31</td>
<td>4.0</td>
<td>0.93</td>
</tr>
<tr>
<td>Li</td>
<td>19</td>
<td>2.4</td>
<td>0.61</td>
</tr>
<tr>
<td>Mn</td>
<td>36</td>
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</tr>
<tr>
<td>Ni</td>
<td>3.2</td>
<td>0.4</td>
<td>0.06</td>
</tr>
<tr>
<td>Pb</td>
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<td>0.05</td>
</tr>
<tr>
<td>Sn</td>
<td>6</td>
<td>0.7</td>
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</tr>
<tr>
<td>Sr</td>
<td>146</td>
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<td>U</td>
<td>31</td>
<td>4.0</td>
<td>0.94</td>
</tr>
<tr>
<td>V</td>
<td>6</td>
<td>0.7</td>
<td>0.10</td>
</tr>
<tr>
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<tr>
<td>Zn</td>
<td>49</td>
<td>6.2</td>
<td>0.97</td>
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</table>
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Chapter Four

Conclusions And Recommendations

The occurrence and transport of urban metals were studied through two years (2011-2013) of water sampling the Rio Grande in the El Paso region during the (dry) non-irrigation season. This study analyzed the major agricultural drain and urban loads to the Rio Grande. The contamination of water with heavy metals has garnered attention from environmental scientists and decision makers in recent years. Heavy metals are emitted naturally from geologic weathering, but typically, anthropogenic activities from industries, mining, domestic wastewater and agricultural activities predominate.

4.1 Conclusions

The overarching conclusion from this research is that anthropogenic activities, both point and non-point, are the main sources of metals content in the Rio Grande in the Paso del Norte region during the non-irrigation season. More specifically, this study has developed conclusions in response to each of the four original hypotheses:

a) The results showed that the major ions concentrations were the lowest in stormwater and that the stormwater runoff was observed with the greatest mean concentrations of Al, Cu, V, and Zn at 48.8. These results proved the first part of the hypothesis stated: “stormwater from urban runoff lowers the total dissolved solids (TDS)”. However, this research disproved the second part that “[stormwater] lowers the metals concentrations in the river and agricultural canals”. The stormwater was observed with low salinity and high metals concentration. (True hypothesis).
b) High concentrations of As, Ba, Mn, Sn and Sr were observed in the international boundary section of the Rio Grande near the ASARCO site. The recorded average flow rate in this section was negligible (practically zero). Thus, the hypothesis that the groundwater flowing through the ASARCO site increases the metals concentrations with negligible contribution to mass loads was observed to be true. (True hypothesis).

c) The highest salinity (measured by electrical conductivity) was the Montoya Drain, which contains agricultural water (and possibly contributions from geologic brines). This proved the hypotheses that the agricultural water contributes significant salinity to the Rio Grande water (True hypothesis).

d) Treated wastewater effluent does not significantly increase the metals concentrations in the river; this hypothesis was also observed to be true. The treated wastewater for the four WWTPs did not exhibit any high metal concentrations (True hypothesis).

The Rio Grande and the American canal water body system is receiving and passing high concentrations of metals. Through the present study, the system was experiencing the highest concentrations of Cd, Ni, Pb, and W. The agricultural drain contributed the greatest concentration of Li. The international boundary part of Rio Grande near the ASARCO smelter was observed with the highest concentrations of As, Ba, Mn, Sn and Sr. While diluting the major ions concentrations (salinity) in the river, the stormwater also added high metallic concentrations of Al, Cu, V and Zn.

During the study period, no significant difference was observed in the water quality parameters between the first and the second dry seasons of the Rio Grande except Cd, Ni, Pb, and W at the Sunland Park area. The increase of concentrations observed during the second half
of the first season and throughout the second season suggests a discharge area of metals or effects of previous or current illegal disposal.

The non-irrigation seasons of the period from 2011 to 2013 were suffering from drought and low flow rates in the Rio Grande and American canal water body system in El Paso. The wastewatertreatment plant effluents as point sources delivered significant amounts of treated wastewater to the system with relatively low concentrations.

The mean concentrations of As, Mn, Pb and U for all the collected samples were exceeded the drinking water MCLs values of the EPA, which poses chronic health risk and may also impact the aquatic environment.

### 4.2 Recommendations

Generally, this region would benefit from control of both point and non-point sources of metals. This is a major step in the process of improving and controlling the stream water quality from degradation, and could perhaps be accomplished by bioremediation through engineered wetlands.

Not all of the metal content is dissolved within the stream water; metals typically adsorb to the suspended particles or precipitate with the stream sediment. This research focused on the concentrations of dissolved portion of heavy metals, but it would be beneficial in future research to study the total (dissolved and suspended) metals concentrations.

While the anthropogenic activities add metals to the streams, the natural process of weathering and erosion of geologic deposits also contribute metal content to the streams. El Paso is a dry region and is experiencing many dust storms, which contributes to metals found naturally. It is recommended to quantify the contribution of heavy metals in El Paso from natural processes.
The results of this study showed high concentrations for some metals in the segment between the Sunland Park WWTP effluent and the Montoya drain. It is recommended that a future study locate and remediate the source of these metals.
References


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Vita

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Sumayeh came to the United States in January, 2010 to join the Environmental Science and Engineering PhD program at the University of Texas at El Paso (UTEP). During her study at UTEP she participated in several national and international conferences. While at UTEP, she worked as a teacher assistant in different departments.

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