# RIO GRANDE AND MANADAS CREEK WATER AND SEDIMENT CHRONIC TOXICITY STUDIES

# Dr. Sushma Krishnamurthy College of Science and Technology Department of Natural Sciences

# Introduction

The Rio Grande is the sole source of drinking water for most cities along the Texas -Mexico border. Increases in populations in both Mexico and the United States along the river are expected to continue. The Laredo/Nuevo Laredo portion of the river alone is experiencing rapid growth and has at present, a combined total population of about 500,000 people. Growing vehicular and pedestrian traffic across the river, maquiladoras and ranches are an integral part of the local landscape.

The ephemeral Manadas Creek drains into the Rio Grande only during a rainfall event. During dry periods, water collects in standing pools in the creek. Manadas Creek is lined with warehouses that store a variety of goods ranging from chemicals to clothing. The creek and its banks have also become a popular dumpsite for used tires, cement, scrap metal and occasionally appearing unlabeled drums of chemicals. This is of particular concern as a variety of pollutants could be loaded into the Rio Grande. While the volume of the waters of Rio Grande may dilute the incoming pollutants, lesser quantities of the toxins may gradually accumulate in the river sediments. These toxins could slowly enter aquatic organisms, accumulate in their tissues over a period of time and cause chronic toxicity.

A binational study conduced in 1994 shows that the Rio Grande at Laredo, TX, contains seventeen priority pollutants (International Boundary and Water Commission (IBWC), 1995). Further, the study also shows the presence of six chemicals that exceed screening levels in Manadas waters, sediment and carp tissue, by factors ranging from 1.2X - 5.6X (IBWC, 1995). The very existence of the pollutants in Manadas Creek and the Rio Grande pose a risk to human health and aquatic life. Combinations of these toxins might pose an entirely different level of risk to aquatic life in the river as well to the people dwelling in close proximity to the river. Toxicities of individual pollutants have been evaluated and interpreted by various researchers over the years, however 'mixed toxicity', which is unique to each polluted site is far from being understood let alone quantified.

## Objective

This study attempts to evaluate the sediments and water of the Rio Grande and Manadas Creek for chronic toxicity. Chronic tests are important in that they predict adverse effects on an organism when exposed to a toxin aver the course of its lifetime. The Microtox Chronic Toxicity test was used in this study, which yields results in 22 hours.

## **Methods and Materials**

*Sampling Sites*: Four sampling; sites were chosen for the study. The three sites along the Rio Grande were International Bridge I, El Cenizo and San Ygnacio municipal water intake facility covering a stretch of approximately 35 river miles. Of these three sites, the International Bridge I site had the most activity with heavy vehicular and pedestrian traffic. El Cenizo, a colonia, 11.4 mi south of International Bridge I, does rat have a bridge but seems to be an area of illegal border crossings as evidenced by clothing frequently found discarded in the water. San Ygnacio lies 30.97 mi downstream of El Cenizo. Our sampling site at San Ygnacio was 100 ft from the municipal water intake pump for the town. Manadas Creek, a tributary of the Rio Grande was the fourth site where sampling took place at the municipal culvert on Mines Road.

Water and sediment samples from each site were collected monthly (April - August 2001). Flowing water was collected from the Rio Grande from a foot below the water surface. Basic water quality parameters (temperature, pH, dissolved oxygen (DO), turbidity and conductivity) were then recorded on site. Temperature and pH were measured with a *Oakton pH 10 series portable meter, DO* with an *Oakton Portable DO100 35640*, turbidity with an *Orbeco - Hellige Model 966 Turbidimeter* and conductivity with an *Oakton 35630-00 portable pH/ Con 10 meter*. Chemical Oxygen Demand (COD) levels were determined in the laboratory using the Bioscience Accu-test COD system. Underwater sediment samples were collected with a corer to a depth of 6 inches. The samples were then transported to the laboratory for further analyses. Chronic toxicity tests were conducted in the laboratory an both water and sediment samples within 2 hours of sampling. TNRCC (1999) guidelines were followed for sample collection and handling.

*Microtox Chronic Toxicity Test: This* test makes use of the *Microtox Model 5000*, a photomultiplier with sample incubation chambers for *Vibrio fischeri* (NRRL # B-11177), a luminescent bacteria, which rapidly detects the presence of chronic toxicity agents. After incubating *V. fischeri* in serial dilutions of sampled water and sediment extracts for 22h, luminescence or cell growth in the bacteria are inhibited if a toxin is present in the sample (Azure, 1998). The Microtox chronic toxicity test correlates well with the traditional standard 7d static renewal chronic toxicity tests using the Cladoceran *Ceriodaphnia dubia*, as well as the minnow, *Pimephales promelas* (Sweet et al. 1997).

## **RESULTS AND DISCUSSION**

## Manadas Creek

The water quality of Manadas Creek is generally poor. Table 1 shows large variations in Dissolved oxygen (DO) levels, which are critical to aquatic life in the Creek. The DO levels in a water body are directly proportional to temperature and must hence exhibit a strong positive correlation. We found a weak Pearson's correlation of r = 0.30. During our study period. the dissolved oxygen levels fell below the Texas Natural Resource Conservation Commission (TNRCC) limit of 5.0 mg/L. High Chemical Oxygen Demand (COD) values confirm oxygen-consuming substances present in water. The highest COD

levels recorded (319.77 mg/L) were on July 2, 2001, strongly indicating the presence of industrial wastes/chemicals and or domestic wastes.

Any changes in water temperature can be generally attributed to seasonality, as at this time we do not have reason to believe otherwise. The pH levels at the creek have been consistent through the period of study (SD = 0.27). Total dissolved solids in water were found to be extremely high and very variable (SD = 2159) with an average of 5098 mg/L. Once again this could be due to varying amounts of chemicals reaching the creek.

The conductivity of rivers in the United States generally ranges from 50 to 1 500  $\mu$ mhos/cm. (EPA 2001). Fresh waters that have ranges above or below 50 - 500  $\mu$ hos/cm might :not be suitable for many fish and invertebrates. The Manadas conductivity levels exceeded those limits at all times.

Of grave concern is the consistent presence of agents that cause chronic toxicity in Manadas Creek, through our sampling period. We have found chronic toxicity in the waters as well as the sediments of the Manadas. An 80% inhibition of light was commonly seen in *V. Fisheri* at sample concentrations of 6.25%. As Manadas Creek empties into the Rio Grande, it could carry with it chronic agents that could impair aquatic life in the latter. On two occasions (April 4 and June 18, 2001), we found all fish and crayfish dead at Manadas. The waters also had a reddish brown hue, more intense than usual. The June 18 fish kills could be attributed to rainfall that occurred 3 days prior to sampling as well as very low levels of dissolved oxygen in the waters. It is possible that oxygen consuming toxins dumped on the banks of Manadas and soil were transported into its waters by the rainfall. One could also speculate the dumping of chemicals into the creek during a rainfall event so that the toxins are carried beyond their point of origin.

#### The Rio Grande

The results of the basic water quality tests conduced at International Bridge I, El Cenizo and San Ygnacio can be seen in Tables 2A, 2B, & 2C. The pH levels in water remained constant (SD= 0.2)and were higher than the minimum limits of 5mg/L (TNRCC acceptable range). An increase in water temperature was seen from April -August as summer set in The largest temperature changes were observed between the months of April and May, after which water temperatures were constant. The DO levels at all three sites were found acceptable. The DO values ranged between 6.56 and 8.71 mg/L. The oxygen content of the river water did not fall below 5 mg/L at any point in time.

The levels of dissolved solids and turbidity in water widely varied with each sampling site and day. This was expected as flow rates (which depend on water releases into the Rio Grande) varied. The conductivity of the waters at all three sites increased with temperature increases in the water. All conductivity levels were higher than 500  $\mu$ mhos/cm.

The COD values at all the sites remained low and were well below maximum acceptable levels.

Chronic tests however reveal a different scenario. All three sites atom the Rio Grande were found to have agents that cause chronic toxicity. Light levels in *V. Fisheri* dropped 80% with sample concentrations of 25%. Sediment samples taken from the sites showed increasingly clayey soil downstream from the International Bridge (46% clay) to San Ygnacio (90% clay). Clay has the tendency to keep chronic contaminants bound to it. The organic: content of the soils in all three sampling sites was below 2%. Low soil organic contenta such as these are typical of soils in the Southern United States. The organic material may play a minor role by keeping toxicants bound to them.

The flooding of the Rio Grande this past week might have caused turbation and resulted in the flushing of the sediments by removing some organic material and toxins but also depositing debris from points upstream.

#### TABLE 1

#### MANADAS CREEK

1

2

Parameters (2001)	Apr 4	May 22	May 29	Jun 18	Jun 27	Jul 2	Aug 6	Avg.	SD
Turbidity(NTU)	10		20	57	95.2	89.8	14.7	40.95	39.47
pH° cc	7.58	8.35	7.8	7.77	7.99	8.08	7.79	7.908	0.25
Temp. (°C)	24.9	19.4	25.1	27.2	24.7	27.7	27.5	25.21	2.87
DO (mg/L)	5.6	8.28	8.14	4.26	7.86	8.7	7.07	7.13	1.63
Conductivity µs/cm	2.82	7.96		4.27	6.31	7.44		4.8	3.05
TDS (mg/L)	1,702.42	6,103.6	7,486.22	3,362.7	5,443.9	6,493.33	6,089.33	5,240.1	2,006.8
COD (mg/L)	19.42		337.47	122.97	148.82	319.77	55.28	143.3	137.19
Soil Organic Content (%)	1.63	1.12	1.72	1.31	0.92	1.36	0.24	1.19	0.50
Chr. Tox In Water	+	+	+	+	+	+	+	+	+
Chr. Tox in Sediment	+	+	+	+	+	+	+	+	+
DO Dissolv	D Dissolved Oxygen						Standard Deviation		
COD Chemic	Chemical Oxygen Demand					Avg.	Average		
TDS Total D	Total Dissolved Solids					+	Indicates presence		
Chr. Tox. Chronic	Chronic Toxicity -					-	Indicates absence		

l = Rainfall on June 14 & 15 totaling 03 inches (from TAMIU - CEES)

Temperature

2 = Rainfall on July 1, 2, 3 & 4 totaling 1.47 inches (from TAMIU - CEES)

\* TNRCC Standard

Temp.

TABLE 2A LAREDO/NUEVO LA	AREDO INTERNATI	1 ONAL BRIDGE I	2			
	4-Apr-01	22-May-01	18-Jun-01	6-Aug-01	SD	
Turbidity (NTU)	42.7	25.1	24.2	24.433	9.1	
PH	8.15	8.35	8.08	7.85	0.21	
Temp. (°C)	23.5	26.2	27.9	29.2	10.4	
DO (mg/L)	7.33	8.71	6.56	7.56	0.89	
Conductivity ( µmhos/		1848	1044	1654.66	452	
• • •	1.1303	7.3259	6.3259	8.5636	3.3	
COD (mg/L) TDS (m $\pi/L$ )						
TDS (mg/L)	616.3	587.4	655.6	6645.0777	3012.8	
Soil Organic Content (		0.8729	1.1943	0.2641	0.41	
Chronic Toxicity (Sedin		+	+	+	+	
Chronic Toxicity (Wate	r) +	+	+	+	+	
TABLE 2B		I	2			
SAN YGNACIO						
LAREDO/NUEVO LA						
	30-May-01	20-Jun-01	7-Aug-01	SD		
Turbidity (NTU)	47	114.2	78.8	33.6		
PH	8.35	7.88	7.5	0.43		
Temp. (°C)	27.8	28	29.3	0.81		
DO (mg/L)	8.18	7.15	6.85	0.70		
Conductivity ( µmhos/	cm) 1044	1071	9.94 ( µs/cm)	604		
COD (mg/L)	3.3625	1.2279	74.674	41.8		
TDS (mg/L)	635.6	714	6452.22	3335		
Soil Organic Content (		3.4691	0.2672	1.6		
Chronic Toxicity (Sedi		+	+	+		
Chronic Toxicity (Wate		+	+			
emonie Toxienty (wate	1) '	,	,			
TABLE 2C		1	2			
EL CENIZO						
	30-May-01	20-Jun-01	7-Aug-01	SD		
Turbidity (NTU)	84	31.7	20	34		
PH	8.24	7.96	7.69	0.28		
Temp. (°C)	28.5	28.6	29.9	0.78		
DO (mg/L)	7.49	6.97	6.18	0.66		
Conductivity ( µmhos/	cm)	1013	929.333	59.16		
COD (mg/L)	6.3633	0.4251	8.848	4.33		
TDS (mg/L) 650.6671		713	6898.666	3589		
Soil Organic Content (%) 0.9011		1.2144	0.8763	0.19		
Chronic Toxicity (Sediments)		+	+	+		
Chronic Toxicity (Wate		+	+			
DO	Dissolved Oxygen		Sd	Standard Deviation		
COD	Chemical Oxygen De		+ Indicates presence			
TDS	Total Dissolved Solid	s	-	absence		
Chr. Tox.	Chronic Toxicity		Temp.	ure		

## CONCLUSION

The Rio Grande waters appear to be healthy, as basic surface water quality standards were met. However, long-term exposure to the water or sediments could result in the manifestation of chronic toxicity in aquatic organisms. On the other hand, the waters of the Manadas are clearly unhealthy, as evidenced by basic water quality tests and chronic tests, and pose a risk to aquatic life in the creek. The creek could, over a period of time. significantly affect the health of the Rio Grande.

## ACKNOWLEDGEMENTS

1 would like to thank my undergraduate students Maria Conchita Pedraza, Aurora Rosillo, Elsa Hull, Jackie Gallegas and Patrick Delgado without which this project would not have been possible. I would also like to thank Rifatul Mia for his assistance in the statistical analysis of the data.

### REFERENCES

APHA. 1992. *Standard methods for the examination of water and wastewater. 18th* ed. American Public Health Association, Washington, DC.

Bulich A., H. Huynah and S. Ulitzur (1995) Measuring Chronic Toxicity using luminescent bacteria. Azur Environmental, Carlsbad, CA.

EPA Office of Water (2001). http://www.epa.gov/volunteer/stream/vms59.html

International Boundary and Water Commission (IBWC), (1994). *Binational Study Regarding the Presence* of *Toxic Substances in the Rio Grande/Rio Bravo and its Tributaries along the Boundary Portion Between the United States and Mexico.* 

Sweet L.I, Travers, D.F. and Meier, P.G. (1997). Chronic Toxicity Evaluation of Wastewater treatment Plant Effluents with Bioluminescent Bacteria: A Comparison with Invertebrates and Fish. *Env. Tox. Chem.* 16:2187-2189.

Texas A&M International University Center for Earth and Environmental Studies (TAMIU - CEES) Rainfall data.

Texas Natural Resource Conservation Commission (TNRCC) (1999). Surface Water Quality Monitoring Procedures Manual