

Preliminary environmental monitoring of water quality in the Rio Grande in the Laredo-Nuevo Laredo Region

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The international border region of the Rio Grande faces severe environmental and economic challenges. Contamination and degradation of its fragile lotic environments are mainly due to stresses from rapid population growth and unchecked industrial development. This study evaluates the water quality of the Rio Grande in the area of Nuevo Laredo, Mexico and Laredo, Texas, USA, in terms of physical, chemical and bacteriological parameters, as well as total metals, organochlorine pesticides, volatile organic compounds (VOC), semi-volatile organic compounds (SVOC) and radioactivity. Surface water samples were collected at 3 sites along the river. Two additional non-river sites (potable water and residual water) were studied for a better assessment of water quality in the region. Three series of samples were taken every other day during one week (November 3 to November 8, 2005) from the five sampling sites. Levels of oil and grease in all the river samples exceeded the limits established by Mexican regulations. Concentrations of aluminum above the permissible limits for source of drinking water and for quality for protection of freshwater biota were also found in all of the river sites. A number of unregulated elements (Cd, Sr, Mg, Na, Fe, Si, Li and K) appeared in the river samples. The average concentrations of Ba and Na in the potable water samples were below the permissible limits. Ca, Sr, Mg and Si were also found but are not regulated. The majority of the organic compounds studied in both the river and in residual water samples was below detection limits. In all the potable water samples, bromodichloromethane and dibromochloromethane were found above their limit of quantitation (LOQ), but these compounds are not regulated. This preliminary study suggests the need for consistent periodic monitoring to track the environmental status of the Rio Grande.

Keywords: Lotic system; maquiladora; metals; pesticides; Rio Bravo; Rio Grande; VOC; water quality.

Introduction

Along its 3,000 km-long course, the Rio Grande is a source of life for the animals and plants supported by its ecosystem and a source of resources for the large numbers of people that live nearby. The Rio Grande begins in the United States, from water that descends from the snow-covered mountains of Colorado and New Mexico, and heads south to El Paso, Texas, where it bends sharply to the southeast to its terminus in the Gulf of Mexico. The portion from El Paso to the Gulf of Mexico forms a 2,000 km stretch of the border between the United States of America (USA) and Mexico, as shown in Figure 1. During this long journey, the Rio Grande, in Mexico known as the Rio Bravo, is sustained by its main downstream trib-

utaries that maintain a permanent flow in the low dam of the Rio Grande, in spite of numerous demands that communities place on its water. These tributaries include the Pecos River in the United States and Rio San Juan and Rio Conchos in Mexico. These tributaries cross the states of Durango, Chihuahua, Coahuila, Nuevo Leon and Tamaulipas in Mexico and Colorado, New Mexico and Texas in the United States.

The Rio Grande represents the lifeblood for the border communities along its basin, serving as the most important supply of water for both municipal and agricultural purposes. However, the river basin ranges from dry to semiarid and has a delicate ecology that is affected by the rapid population growth and industrial development in the area. The maquiladora industry—the manufacturing plants (maquilas) concentrated along the Mexican side of the border whose primary business is assembling foreign components for re-export—represents both the economic and environmental challenges of the border region. Several authors have linked the maquilas to problems of air and water contamination as well as generation of toxic waste.^[1–5]

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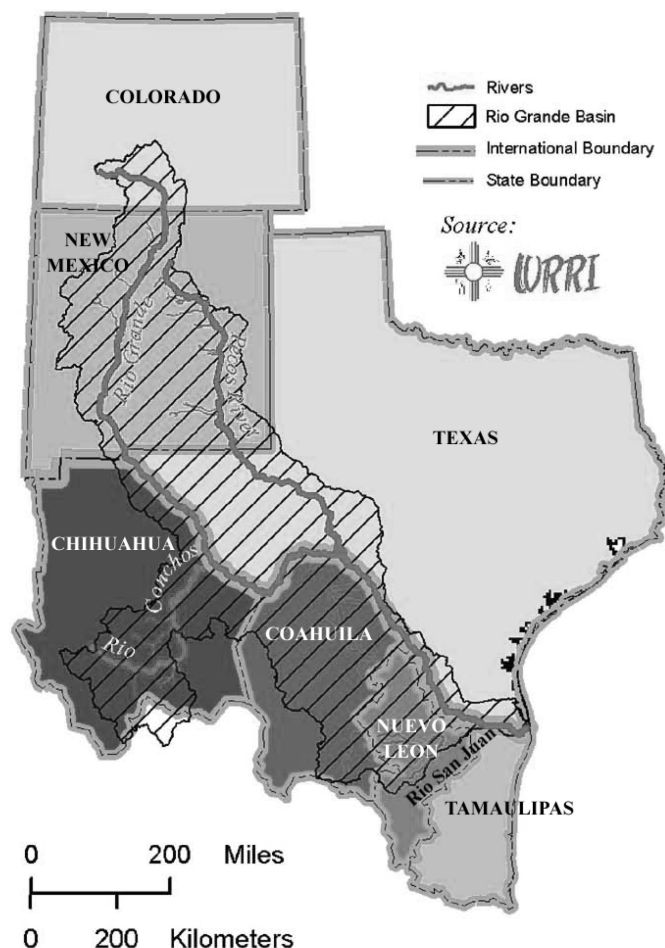


Fig. 1. Location of the Rio Grande Basin (adapted from New Mexico State University's web site).

The Rio Grande receives a good deal of attention as a result of the contamination and degradation of its lotic environment. Issues such as high evaporation, high sediment content, heavy metal runoff from mining, and industrial and agriculture discharges, are known to affect the river.^[6–10]

The water quality in the metroplex of El Paso and its larger Mexican sister city Ciudad Juarez is perhaps the most compromised. The presence of metals such as arsenic, silver, cadmium, copper, lead, nickel and zinc in the river that exceed state or federal standards, identified by a number of studies, threaten the wellbeing of aquatic and human health^[6,11–13] As recently as 2003, Rios-Arana et al.^[14] assessed the river in the El Paso-Juarez area and found zinc and lead levels above the freshwater criteria. They attributed this condition to poor water management, runoff and wind deposition. Similarly, Assadian et al.^[10] studied metal concentration in canal sediments and drains in the El Paso-Juarez area, and reported multiple sources of metals, rather than single inflow sources, with the highest metal concentrations coinciding with growing town-

ships. But more than metals have been found in the Rio Grande. A number of organic contaminants with broad concentrations were identified by Garcia et al.^[8] They sampled water and sediments, as well as adjacent soil, from several points along the Rio Grande Valley and found aliphatic hydrocarbons and plasticizers in all the samples. Moreover, industrial estrogens were found in almost all the samples and pesticides were detected in all of the soil samples collected. They identified discharges from industrial and agricultural activities as potential sources of the contaminants.

The progression of organic contaminants and heavy metals into birds and fish in the Rio Grande Valley was studied by Maruya et al.^[15] and by Mora et al.^[16,17] They found significant concentrations of DDE and toxafeno organochlorines, as well as arsenic, that could pose potential health problems for the species. They also reported a strong effect of location on concentrations of contaminants.

In 2000, an intensive, binational water quality monitoring study in the lower region of the river at the sister cities of Laredo, Texas and Nuevo Laredo, Mexico by the International Boundary Water Commission, United States and Mexico,^[18] identified aluminum as well as organic compounds such as hexachloro-1-3-butadiene, hexachloroethane and 1-4 dichlorobenzene at concentrations higher than those allowed in water quality regulations. The purpose of this study was (i) to evaluate the water quality of the Rio Grande in the Laredo/Nuevo Laredo area and (ii) to increase the existing data over a wide range of environmental compounds. This study examined metals and organic compounds, as well as physical, chemical and bacteriological parameters. Surface water samples were collected at three sites of the Rio Bravo. Two additional sites connected to water quality, but out of the river, were studied for a better assessment of water quality in the region.

Materials and methods

Sampling sites

Water samples were collected from five sites: three from the principal stream of the Rio Grande as it passes through Laredo/Nuevo Laredo and two more from selected locations in Nuevo Laredo. These sites (Table 1) were selected not only to assess water quality, but also to provide a strategy to pinpoint the source of any pollution found. The three river sampling sites (1, 3 and 5) were chosen geographically along the path of the Rio Grande with respect to Laredo and Nuevo Laredo. Site 1 lies before the river enters the cities, just north of the World Trade Bridge, 18 km upstream of both towns. Site 3 is located in the center of both cities, after the last untreated discharge from the Nuevo Laredo storm drains and 1.6 km upstream of the river water intake of the Nuevo Laredo potable water plant southeast.

Table 1. Location of sampling sites

Site	Name of site	Sample type	Latitude	Longitude
1	Rio Grande upstream	Surface water	N 27°36'6.3"	W 99°34'42.5"
2	Potable water plant southeast (PPS)	Potable water	N 27°25'27.6"	W 99°29'45.8"
3	Rio Grande, 1.6 km upstream of PPS intake	Surface water	N 27°25'47.4"	W 99°29'33.9"
4	Infuent/Inflow of the PITARNL	Residual water	N 27°25'10.9"	W 99°29'47.6"
5	Rio Grande, 1.6 km downstream of PPS intake	Surface water	N 27°24'8.2"	W 99°29'19.5"

Site 5 is located after the river leaves the twin cities, 1.6 km downstream of the river water intake of the Nuevo Laredo potable water plant.

To analyze water quality in Nuevo Laredo, including any effects of the maquiladora industry, samples were also collected from two additional sites. Nuevo Laredo drinking water was sampled at site 2 at the distribution pump of the potable water plant southeast (Planta Potabilizadora Sur-Oriente, PPS) before its delivery to residents of the city of Nuevo Laredo. Finally, to have an idea of the contaminants generated within the city, residual water was sampled at site 5 at the inlet of the water treatment plant (Planta Internacional de Tratamiento de Aguas Residuales de Nuevo Laredo, PITARNL), which receives the municipal and industrial discharges from Nuevo Laredo.

Sample collection

Three series of samples were taken every other day from November 3 to November 8, 2005. The protocol for collecting both grab and composite samples followed standard NMX-AA-003-1980 of the Mexican National Water Commission. The sites on the Rio Grande (Sites 1, 3 and 5) were accessed from the Mexican shore, using a johnboat. At the sampling point, the boat stopped at midstream width of the river, where grab water samples were collected. Surface water samples were collected using a home-made grab sampler consisting of a 1 m long pole attached to the outside of a 1 L glass jar. Another 1 m long pole was attached to the top of a Teflon coated closing lid. The glass jar with the lid superimposed was submerged about 30 cm below the water surface of the river with the jar opening facing upstream, at which time the lid was removed and the sample collected. The sampling device was thoroughly rinsed with river water immediately before collection of the sample. Samples from site 2 were taken at the sampling port of the main distribution pump of the potable water plant (PPS). After the valve had been left open for approximately one minute, a water sample was taken by hand using a 1 L glass jar. Samples from site 4 were taken from the reservoir head where residual water arrives, before receiving any treatment in the plant. Simple samples were taken by submerging a 1 L glass jar attached to a plastic cord approximately 30 cm below the water surface. The sampling jar was repeatedly rinsed with residual water immediately before the samples were taken.

After collection, all samples were stored on ice during the sampling trip and transport to the lab. At the lab samples were kept at 4°C in a cold room until analysis. Each set of samples was accompanied by the chain of custody form and by data sheets that recorded the field parameters.

Samples collected from sites 1, 2, 3 and 5 were all grab samples, and thus instantaneous. On the other hand, with one exception, the residual water samples from site 4 were determined from a 24-hour composite sample containing 6 grab samples, 1 taken every 4 hours in an amount proportional to the plant's inlet flow. The single exception was the measure of oil and grease composition. As required by Mexican regulations, to obtain this figure, a second sample was collected immediately after each individual sample that formed the composite sample was taken. An average value, proportional to the oil and grease concentration and the plant's inlet flow, was then calculated to determine the oil and grease measure. It should also be noted that in each 24-hour sampling period, the samples from site 4 were completely collected first, and then the samples at the remaining sites were collected. Table 2 lists the parameters analyzed and number of times each was analyzed per site.

Sample analysis

Parameters such as temperature, conductivity and pH were measured on site. The remaining parameters were measured upon laboratory arrival. The laboratory methods used to determine metals by AA (mercury, iron and silicon), as well as the physical, chemical and bacteriological parameters, were the Mexican protocols for water analysis issued by the Mexican National Water Commission, identified by NMX-AA-NNN(method number)—YYYY(year). All the other parameters—metals by ICP/MS, organics (VOC, SVOC, pesticides, herbicides) and radioactivity—were analyzed following USEPA protocols. Table 3 shows the laboratory methods used and the parameters' units.

The sample collection and analysis were performed at a private Mexican laboratory accredited by the official Mexican accreditation agency (Entidad Mexicana de Acreditación) and approved by the Mexican National Water Commission to conduct this type of analysis. The only exception involved the analyses of gross alpha and beta radioactivity, which were performed by an accredited U.S. laboratory. Quality control comprised method blanks and initial

Table 2. Parameters analyzed and number of times analyzed per site

<i>Parameter</i>	<i>SITE 1 River water</i>	<i>SITE 2 Potable Water</i>	<i>SITE 3 River water</i>	<i>SITE 4 Residual water</i>	<i>SITE 5 River water</i>
Temperature	3	3	3	3	3
pH	3	3	3	3	3
Conductivity	3	3	3	3	3
Total suspended solids	3		3	3	3
Total dissolved solids	3	3	3		3
Fecal coliforms	3	3	3		3
BOD ₅				3	
COD				3	
Alkalinity	3		3		3
Total hardness		3			
Total phosphorous	3		3		3
Nitrogen (Nitrate) (NO ₃)	3	3	3		3
Nitrogen (Nitrite) (NO ₂)	3	3	3		3
Dissolved Oxygen	3		3		3
Sulfate	3	3	3		3
Total Metals	3	3	3	3	3
VOC (EPA 8260)	3	3		3	3
SVOC (EPA 8270)	3	3		3	3
Pesticides (EPA 608 2000)	3	3			
Oil and grease	3		3	18	3
Radioactivity α , β		1			

Table 3. Units of parameters studied and methodology

<i>Parameter</i>	<i>Units</i>	<i>Methodology</i>
Temperature	°C	NMX-AA-007-SCFI-2000
pH	UpH	NMX-AA-008-SCFI-2000
Conductivity	mS/m (Ω)	NMX-AA-093-SCFI-2000
Total suspended solids	mg/L	NMX-AA-034-SCFI-2001
Total dissolved solids	mg/L	NMX-AA-034-SCFI-2001
BOD ₅	mg/L	NMX-AA-028-SCFI-2001
COD	mg/L	NMX-AA-030-SCFI-2001
Partial alkalinity	mg/L CaCO ₃	NMX-AA-036-SCFI-2001
Total alkalinity	mg/L CaCO ₃	NMX-AA-036-SCFI-2001
Total hardness	mg/L	NMX-AA-072-SCFI-1981
Total phosphorous	mg/L	NMX-AA-029-SCFI-2001
Nitrogen (Nitrate) (NO ₃)	mg/L	NMX-AA-079-SCFI-2001
Nitrogen (Nitrite) (NO ₂)	mg/L	NMX-AA-099-1987
Dissolved Oxygen	mg/L	NMX-AA-012-SCFI-2001
Sulfate	mg/L	NMX-AA-074-SCFI-1981
Oil and grease	mg/L	NMX-AA-005-SCFI-2000
Fecal coliforms	NMP/100 mL	NMX-AA-042-1987
Total Metals (AA)	mg/L	NMX-AA-051-SCFI-2001
Total Metals (ICP/MS)	mg/L	USEPA 6020 A-1998
VOC	μ g/L	USEPA 624-2000
SVOC	μ g/L	USEPA 625-2000
Pesticides	μ g/L	USEPA 608-2000
Phenoxy herbicide	μ g/L	USEPA 8321B-2000
Radioactivity alpha	Bq/L	USEPA 00-02
Radioactivity beta	Bq/L	USEPA 900.0

calibration verification after initial calibration. To assure continuous quality control, continuous calibration verification, control samples, and use of control charts were utilized.

In this study, metal concentration in the samples was measured as total, which includes dissolved and suspended metals. The concentrations of mercury, iron and silicon metals were measured on a Varian AA-10 atomic absorption (AA) spectrometer. An Agilent 7500A inductively coupled plasma mass spectrometer (ICP-MS) was used for determination of the following metals: aluminum, antimony, arsenic, barium, beryllium, bismuth, cadmium, calcium, cobalt, copper, chromium, tin, strontium, lithium, magnesium, manganese, molybdenum, nickel, silver, lead, potassium, selenium, sodium, thallium, titanium, uranium, vanadium, zinc and zirconium.

The limit of detection (LOD) for any given analytical procedure is the lowest amount of analyte in a sample that can be quantitatively determined with reasonable accuracy, whereas the limit of quantitation (LOQ) is the lowest amount of analyte that can be quantitated with suitable precision and confidence. In this work, the LOQ supplied by the lab is used, which is defined as three times the LOD.

In residual water (site 4) the LOQ was 0.05 mg/L for Sb, As, Ba, Be, Bi, B, Cd, Cr, Co, Cu, Pb, Li, Mn, Se, Ag, Sr, Tl, Sn, Ti, U, V, Zn, Zr, Ni, and Mo. For Al and Mg, the LOQ was 0.5 mg/L, whereas for Ca, P, K and Na the LOQ was 5.0 mg/L. On the other hand, for potable and river water (sites 1, 2, 3 and 5) the LOQ was 0.005 mg/L for Sb, As, Ba, Be, Bi, B, Cd, Cr, Co, Cu, Pb, Li, Mn, Se, Ag, Sr, Tl, Sn,

Ti, U, V, Zn, Zr, Ni, and Mo; whereas for Al and Mg, the LOQ was 0.05 mg/L. For Ca, P, K and Na the LOQ was 0.50 mg/L. For the metals detected by atomic absorption in residual water as well as in potable and river water—Hg, Fe and Si—the LOQ were 0.005, 0.15, and 5.0 mg/L, respectively.

Concentrations of organochlorine pesticides aldrin, dieldrin, endrin, DDT, chlordane, lindane, hexachlorobenzene, heptachlor, heptachlor epoxide, and methoxychlor were measured using a Hewlett Packard 6890 gas chromatograph with electron capture detector (GC-ECD) equipped with a HP-5MS column (30 m length, 0.25 mm i.d., 0.25 μ m film thickness). The LOQ in residual water of these compounds was 0.046 μ g/L, whereas their LOQ in potable and river water was 0.091 μ g/L.

The phenoxy herbicide 2,4-Dichlorophenoxyacetic acid (2,4-D) was measured on a Kontron 332 Liquid Chromatograph with UV-Vis detector equipped with a SPHERI-5 column (100 m length, 4.6 mm i.d., 5 μ m film thickness). The LOQ in residual water of this compound was 0.121 mg/L, whereas its LOQ in potable and river water was 12.12 μ g/L.

Volatile organic compounds were quantified using a Hewlett Packard 5890 gas chromatography/mass spectrometry system, connected to a HP-VOC column (30 m length, 0.2 mm i.d., 1.2 μ m film thickness). The following VOC were determined: vinyl chloride, 1,1-dichloroethylene, carbon bisulfide, acrylonitrile, methylene chloride, methyl ethyl ketone, chloroform, isobutanol, 1,1,1-trichloroethane, 1,2-dichloroethane, benzene, carbon tetra-chloride, trichloroethylene, toluene, 1,1,2-trichloroethane, tetrachloroethylene, chlorobenzene, 1,1,1,2-Tetrachloroethane, 1,1,2,2-Tetrachloroethane, 1,4-dichlorobenzene, 1,2-dichlorobenzene, hexachloroethane, bromodichloromethane, dibromochloromethane, ethylbenzene, xylene, and bromoform. Table 4 shows the LOQ of these volatile organic compounds.

Semi-volatile organic compounds were analyzed on an Agilent 6890 gas chromatography/mass spectrometry system, connected to a HP-5MS column (30 m length, 0.25 mm i.d., 0.25 μ m film thickness). The following SVOC were measured: pyridine, fenol, bis(2-Chloroethyl) ether, o-cresol, m-cresol and p-cresol, nitrobenzene, hexachloro-1,3-butadiene, 2,4,6-trichlorophenol, 2,4,5-trichlorophenol, 2,4-dinitrotoluene, 2,3,4,6 tetrachlorophenol, hexachlorobenzene, and pentachlorophenol. Table 5 shows the LOQ of these SVOC compounds. The LOQ of alpha and beta radioactivity was 0.0495 Bq/L and 0.0850 Bq/L, respectively.

Mexican regulations

The results of the river water samples from sites 1, 3 and 5 were compared with the Ecological Criteria of Water Quality (CE-CCA-001/89) promulgated by the Mexican National Water Commission.^[19] The Commission monitors and regulates bodies of water being utilized as a

Table 4. LOQ of volatile organic compounds

Compound	Limit of quantitation	
	Residual water, mg/L	Potable and river water, μ g/L
Vinyl Chloride	0.028	28.00
1,1-Dichloroethylene	0.240	47.98
Carbon Bisulfide	0.209	41.80
Acrylonitrile	0.984	196.82
Methylene Chloride	0.121	24.15
Methyl Ethyl Ketone	1.197	239.50
Chloroform	0.108	21.53
Isobutanol	3.697	739.40
1,1,1-Trichloroethane	0.109	21.83
1,2-Dichloroethane	0.113	22.53
Benzene	0.050	10.01
Carbon Tetra-Chloride	0.107	21.49
Trichloroethylene	0.180	36.00
Toluene	0.156	31.28
1,1,2-Trichloroethane	0.157	31.39
Tetrachloroethylene	0.158	31.58
Chlorobenzene	0.210	40.14
1,1,1,2-Tetrachloroethane	0.217	43.38
1,1,2,2-Tetrachloroethane	0.312	62.32
1,4-Dichlorobenzene	0.112	22.35
1,2-Dichlorobenzene	0.105	20.92
Hexachloroethane	0.118	23.64
Bromodichloromethane	0.279	55.74
Dibromochloromethane	0.267	53.47
Ethylbenzene	0.143	28.57
Xylene	0.161	32.21
Bromoform	0.164	32.75

source of drinking water, for agricultural irrigation, for livestock consumption, for aquatic life, in aquaculture, or in recreational activities that involve direct contact with the water.

On the other hand, results of the samples of potable water from site 2 were assessed according to Mexican official standards for drinking water (NOM-127-SSA1-1994),^[20] and the quality of the residual water samples from site 4 was compared with Mexican official standard NOM-002-ECOL-1996^[21] that establishes the permissible limit of contaminants in industrial discharges of residual water into urban or municipal sewer systems. Tables 6 to 11 list the maximum permissible levels of the compounds at interest under the Mexican water quality regulations.

Results and discussion

Given the fact different regulations apply to the non-river sites and the river sites, and even between the 2 non-river sites, the contaminants of concern thus differ from site to site. Moreover, given the limited resources available, not all contaminants were analyzed from the samples taken at each site.

Table 5. LOQ of semi-volatile organic compounds

Compound	Limit of quantitation	
	Residual water, mg/L	Potable and river water, µg/L
Pyridine	0.024	24.16
Fenol	0.011	10.57
Bis(2-Chloroethyl) ether	0.010	9.95
o-Cresol	0.010	9.91
m-Cresol	0.010	10.07
p-Cresol	0.010	9.95
Nitrobenzene	0.010	10.02
Hexachloro-1,3-butadiene	0.010	9.93
2,4,6-Trichlorophenol	0.010	9.82
2,4,5-Trichlorophenol	0.010	9.94
2,4-Dinitrotoluene	0.010	9.78
2,3,4,6 Tetrachlorophenol	0.020	20.12
Hexachlorobenzene	0.010	9.97
Pentachlorophenol	0.099	99.04

The average flow of the Rio Grande is monitored by the International Boundary and Water Commission as it passes through the twin cities at the Commission's measuring station located under International Bridge II.^[22] This station is located between sampling Sites 1 and 3, at N 27°30'1.2" and W 99°30'10". The water flow of the river in the area of study is controlled by the Amistad Dam. The reported average daily flows were 72.3, 73.3 and 73.5 m³/s for the first, second and third sampling days, respectively, when grab samples were collected from the river. The instant flow of the Rio Grande at the time of sampling was not measured in this study, but its significance is lessened given the little variation of the flow during the days of sampling and the fact the samples were taken at a similar time each day.

Physical, chemical and bacteriological analyses

The results of the physical, chemical and bacteriological analyses per site and per day, as well as the mean and standard deviations, are shown in Tables 6 and 7. As noted before, the samples for oil and grease in residual water samples were taken once every 4 hours over a 24 hour period, as required by the residual water regulations. As seen in Table 7, there is a different limit value for these individual samples than for the averaged samples. All of the individual determinations of oil and grease in residual samples were below the permissible limit of 100 mg/L, except for the last individual sample taken on the final day of sampling, which gave a concentration of 104 mg/L. In addition, an average value of oil and grease was calculated for each sampling day based on the individual results adjusted to the flow. All of the average concentrations of oil and grease were below the permissible limit, as seen in Table 7. It is interesting to note that the concentrations of oil and grease, as well as fecal coliforms, in each of the river samples showed

great variability, as observed in their standard deviations, which indicate the different conditions from one day to the next.

Almost all the physical, chemical and bacteriological samples analyzed were within the regulatory limits. However, the total dissolved solids of the river samples were slightly above the limits both for bodies of water utilized as a source of drinking water and for water used in agricultural irrigation. Also, oils and grease were observed in the river samples, although regulations do not permit any oils and grease in river water. This is consistent with the results presented in the 2000 IBCW study,^[18] which reported concentrations of total solids and oil and grease above the Ecological Criteria of Water Quality regulations. On the other hand, the 2000 study reported samples with conductivity, phosphates and sulfates above the limit, which was not the case in our study.

Comparing the results of one site to another, it is observed that on average, the pH of the river samples (sites 1, 3 and 5) is higher than those of the drinking water (site 2) and the residual water (site 4) samples. In addition, the temperature, conductivity, and total suspended solids of the residual water were higher than those of the drinking water and river samples. The processes undergone by the residual water before it reaches the treatment plant may cause this increase in temperature and conductivity.

Comparing the parameters from one site to another among the river samples, the values for pH, temperature, conductivity, partial and total alkalinity, total phosphorous, nitrite nitrogen, and dissolved oxygen, remain similar at all three river sites. On the other hand, the concentration of nitrate nitrogen increased as the river passed through the cities, probably as a result of the anthropomorphic activities. In addition, at site 3 concentrations of total suspended and total dissolved solids were slightly lower than at the other two sites. Site 3 was located after the last untreated discharge from the storm drains of Nuevo Laredo. Also site 3 had a concentration of oil and grease below detection limits, as opposed to the high concentrations found at sites 1 and 5. It is important to point out that approximately 25% of Nuevo Laredo's residences are connected to the storm sewers rather than the sanitary sewer system. Thus, not surprisingly, the concentration of fecal coliforms in site 3 was more than twice that of the other sites, although still within the regulations.

It must be noted that measurements of dissolved oxygen from the first day of sampling had to be eliminated, as indicated in Table 6, due to laboratory experimental error. In several instances, concentrations of specific contaminants fell below the detection limit, LOQ. For parameters such as phosphorous and nitrite, where two or all three of the samples gave values below the limit of detection, an average value could not be calculated, and these are reported in the tables as below LOQ. In instances where one of the three samples was below LOQ, this value below LOQ was treated as zero when determining mean and standard deviation.

Table 6. Physical, chemical and bacteriological analyses per river site and Mexican regulatory standards for maximum limits permitted for river water (CE-CCA)

Parameters	Units	CE-CCA-001/89				SITE 1		SITE 3		SITE 5		
		DW	RC	AI	LC	PB	Mean	SD	Mean	SD	Mean	SD
pH	UpH	5-9		4.5-9.0		$\omega \pm 0.2$	8.313	0.145	8.317	0.169	8.327	0.165
Temperature	°C	+2.5 ϕ				+1.5 ψ	24.100	1.778	22.967	1.893	24.167	0.404
Conductivity	mS/m			100			77.233	1.419	77.533	1.656	78.467	2.259
Partial Alkalinity (Phenolphthalein)	mg/L CaCO ₃						3.313	5.739	0.000	0.000	1.103	1.911
Total Alkalinity	mg/L CaCO ₃	400.0					147.150	10.401	149.643	0.992	153.730	2.412
Total phosphorous	mg/L											
Nitrogen (Nitrate) (NO ₃)	mg/L	5.0			90.0		0.527	0.117	0.640	0.087	0.843	0.067
Nitrogen (Nitrite) (NO ₂)	mg/L	0.05			10.0							
Dissolved Oxygen [ⓧ]	mg/L, minim	4.0				5.0	8.285 [ⓧ]		8.04 [ⓧ]		8.385 [ⓧ]	
Total suspended solids	mg/L	500.0		50.0			15.000	3.606	12.333	0.577		
Total dissolved solids	mg/L	500.0		500.0	1000.0		506.000	28.000	490.000	29.597	528.367	21.452
Sulfate	mg/L	500.0		130.0	0.005		118.637	3.162	122.333	7.136	111.537	30.844
Oil and grease	mg/L	<i>ND</i>					32.667 [Ⓤ]	51.472 [Ⓤ]			39.667 [Ⓤ]	62.74 [Ⓤ]
Fecal coliforms	mg/L	1000.0	200	1000.0			6.000 [Ⓤ]	6.557 [Ⓤ]	15.333 [Ⓤ]	16.042 [Ⓤ]	10.333	10.408

^{*}below LOQ. LOQ of 2 mg/L and 0.08 mg/L for total phosphorous and for nitrogen (nitrite), respectively.

^ωNatural seasonal conditions pH \pm 0.2.

^φNatural conditions \pm 2.5.

^ψNatural conditions \pm 1.5.

DW, quality for use as drinking water provision source.

RC, quality for recreational use with primary contact.

AI, quality for agricultural irrigation.

LC, quality for livestock consumption.

PB, quality for the protection of freshwater biota.

[ⓧ]Calculation based on two values.

[Ⓤ]One of the samples was below LOQ and treated as zero.

ND, Non-detectable or absent.

Table 7. Physical, chemical and bacteriological analyses in potable water site and in residual water Mexican regulatory standards for maximum limits permitted in potable water (NOM-127) and in residual water (NOM-002)

Parameters	Units	NOM-127-	SITE 2		NOM-002-ECOL		SITE 4	
			Mean	SD	DA	INS	Mean	SD
pH	UpH	6.5–8.5	7.813	0.185		5.5–10	7.390	0.184
Temperature	°C		24.100	2.551		40 maxim	26.667	0.306
Conductivity	mS/m		77.667	3.137			142.733	3.707
Total hardness	mg/L CaCO ₃	500.0	234.607	21.420				
Nitrogen (Nitrate) (NO ₃)	mg/L	10.00	0.690	0.096				
Nitrogen (Nitrite) (NO ₂)	mg/L	1.0						
Total suspended solids	mg/L				125		207.200	29.625
Total dissolved solids	mg/L	1000.0	507.667	16.503				
Sulfate	mg/L	400.0	128.937	15.694				
BOD ₅	mg/L				150		201.600	36.952
COD	mg/L						417.483	89.852
Oil and grease	mg/L				75	100	42.680	9.357
Fecal coliforms	mg/L	ND						

*below LOQ.

DA, Daily average.

INS, Instantaneous value.

ND, Non-detectable or absent.

Total metals

The concentration of total metals is presented in Table 8 for river water and in Table 9 for potable water and residual water. During the first day of analyses more elements were detected than during the remainder of the sampling. The elements identified with concentrations above detection limits, LOQ from all the sites, on at least one of the three days of the sampling were: Ba, B, Li, Mn, Sr, Ti, Zn, Al, Mg, Ca, P, K, Na, and Si. Also Fe was found at almost all sites, except for the potable water sample. Ti was found only in the river water in sites 1 and 3 the first day of sampling. Zn was also found above the LOQ only on the first day of sampling in sites 1, 2, 4 and 5. In contrast, concentrations of Sb, As, Be, Bi, Cd, Co, Cu, Cr, Sn, Mo, Ni, Ag, Pb, Se, Tl, U, V, Zr and Hg were below limits of detection in all the samples and thus were not included in Tables 8 and 9. Nevertheless, not all the metals analyzed could be compared with water quality standards, as there are no Mexican regulations for Bi, Ca, Co, Sn, Sr, Li, Mg, Mo, K, Ti, U, Va, Zr and Si.

For sites where two or three samples were below the limit of detection, the results are reported as below LOQ. It must be noted the determination of metals on all of the second day samples for the river samples and for the potable water was done using the LOQ for residual water, due to laboratory error. In those cases where the reading of one of the three samples gave values below the detection limit utilized by the lab, a value of zero was assigned to that value of LOQ for determining mean and standard deviation, as noted in Tables 8 and 9.

For the river samples, Ba, Ca, Sr, Mg, Na, Fe and Si were found above detection limits at all three sites. Al, Li,

Mn, K, Ti and Zn were also detected, although less often. However, only Al, Ba, Mn, Zn and Fe are regulated. Of the elements regulated, the concentrations of Mn, Zn and Fe comply with the standards for all of the uses of river water (supply for drinking water, recreational, agricultural, and feedstock consumption, and biota protection). However, this was not the case for Ba content, which exceeded the amount permitted for protection of the aquatic biota, or Al, which fell above the amounts permitted for both protection of the biota and for drinking water supply. Finally, comparing the average concentrations of river samples, it is noted that the concentrations of Ca, Mg, and Na were higher at site 5, downstream from the cities, than at sites 1 and 3, whereas Fe and Si were higher upstream from the cities at site 1, than at sites 3 and 5.

In the residual samples Al, Ba, Ca, Sr, Mg, Mn, K, Na, Zn, Fe and Si, were found at least once above the detection limit. Of these elements, Ca, Sr, Mg, Na, Fe and Si were detected in all of the samples. However, only the concentration of Zn is regulated. The concentration of Zn found in the first day of sampling was below the permissible limit. From this, it can be said that the concentrations of contaminants detected in the residual water complied with the regulations during the sampling period.

Al, Ba, Ca, Sr, Li, Mg, Mn, K, Na, Zn and Si, were found at least once above the detection limit in potable water. Only Si was present in all the samples above detection limit. Of the regulated metals found in the potable water, Al, Ba, Mn, Na, Zn, and Fe, complied with the regulatory standards for drinking water. Comparing the average concentrations of different types of water, it is noted that as expected, almost all the metals were below detection limits for the potable

Table 8. Maximum permissible levels of Mexican regulations for contaminants in river water (NOM-002), and mean and standard deviation of total metal analysis per river site

Parameters	Units	CE-CCA-001/89					SITE 1		SITE 3		SITE 5	
		DW	RC	AI	LC	PB	Mean	SD	Mean	SD	Mean	SD
Aluminum	mg/L	0.02		5.0	5.0	0.05	0.061 ^{IO}	0.053 ^{IO}	0.083 ^{IO}	0.074 ^{IO}	0.080 ^{IO}	0.069 ^{IO}
Barium	mg/L	1.0				0.01	0.077	0.003	0.077	0.002	0.076	0.004
Calcium	mg/L						51.500	38.821	49.007	36.781 ^v	77.443	13.858
Strontium	mg/L						0.95	0.08	0.897	0.031	0.950	0.104
Lithium	mg/L						0.012 ^{IO}	0.011 ^{IO}	0.012 ^{IO}	0.011 ^{IO}	0.032	0.023
Magnesium	mg/L						9.577	7.152	9.180	6.897	14.703	1.958
Manganese	mg/L	0.1					0.004 ^{IO}	0.004 ^{IO}	0.005 ^{IO}	0.005 ^{IO}	0.005 ^{IO}	0.004 ^{IO}
Potassium	mg/L						1.837 ^{IO}	1.596 ^{IO}	2.033 ^{IO}	1.762 ^{IO}	2.090 ^{IO}	1.81 ^{IO}
Sodium	mg/L						41.490	31.104	39.890	30.391	64.383	8.977
Titanium	mg/L						*		*		*	
Zinc	mg/L	5.0		2.0	50.0		*		*		*	
Iron	mg/L	0.3		5.0		1.0	0.213	0.042	1.920	1.195	0.213	0.028
Silicon	mg/L						15.707	2.896	32.163	6.080	15.693	2.402

*below LOQ.

^{IO} one of the samples was below LOQ and treated as zero.

DW, quality for use as drinking water provision source.

RC, quality for recreational use with primary contact.

AI, quality for agricultural irrigation.

LC, quality for livestock consumption.

PB, quality for the protection of freshwater biota.

water, except for Si, which stayed in the range of concentration of the river samples. However, it should also be noted that the potable water samples were obtained from the PPS plant, the city's newer and smaller plant that handles only 30–35% of Nuevo Laredo's potable water. Sampling on the main potable water plant was not allowed, as major maintenance, expected to last for up to five months, started on

that plant the same week sampling was to begin. That plant continued to supply 65–70% of the city's potable water during the maintenance period. Thus projections to the overall city water supply could not be obtained.

The 2000 study of the IBWC^[18] analyzed the concentration of Al, As, Cd, Cr, Cu, Pb, Hg, Ni, Ag, Zn, Ca and Mg in the Rio Grande. The Commission reported Al

Table 9. Maximum permissible levels of Mexican regulations for contaminants in potable water (NOM-127) and in residual water (NOM-002), and mean and standard deviation of total metal analyses in potable water site and in residual water

Parameters	Units	NOM-127	SITE 2		NOM-002-ECOL		SITE 4	
			Mean	SD	DA	INS	Mean	SD
Aluminum	mg/L	0.20	*				*	
Barium	mg/L	0.7	0.047 ^W	0.041 ^W				
Calcium	mg/L		49.75 ^W	44.579 ^W			45.010	57.911
Strontium	mg/L		0.623 ^W	0.542 ^W			0.513	0.664
Lithium	mg/L		*				*	
Magnesium	mg/L		9.45 ^W	8.39 ^W			9.227	12.075
Manganese	mg/L	0.15	*				*	
Potassium	mg/L		*				*	
Sodium	mg/L	200.0	38.273 ^W	33.781 ^W			69.290	91.331
Titanium	mg/L		*				*	
Zinc	mg/L	5.0	*		9	12	*	
Iron	mg/L	0.30	*				1.920	1.195
Silicon	mg/L		14.123	1.356			32.163	6.080

*below LOQ.

^W One of the samples was below LOQ and treated as zero.

DA, Daily average.

INS, Instantaneous value.

concentrations above the levels allowed by the Ecological Criteria of Water Quality. In our study, the river sites had average Al concentrations between 0.061 and 0.083 mg/L, again above the permissible limits for a source of drinking water, as well as the maximum limits for the protection of freshwater biota. The presence of aluminum can be attributed to the discharges of industries that use aluminum in their processes and/or as a flocculant agent. As mentioned above, a number of unregulated elements were also found in the river samples.

The average concentrations of 0.047 and 38.27 mg/L for Ba and Na respectively, were within the permissible limits in the potable water samples. Ca, Sr, Mg and Si were also found but these are not regulated. The IBCW study^[18] did not analyze potable water samples. However, the Commission did sample influent from the water treatment plant (PITARNL) and found that aluminum and zinc were the trace compounds with the highest average concentrations of 1.51 and 0.261 mg/L, respectively. Of these, only Zn was regulated for waste water and the Zn concentration was below the permissible limits. In our study, these compounds were largely absent, as only one sample of residual water had Al and Zn concentrations above the detection limits. However, it is interesting to note that the concentrations of 1.73 and 0.26 for Al and Zn, respectively, found in the first day of sampling are very close to the average concentrations reported by the 2000 study. These concentrations of Al and Zn, which are not typical of domestic sewage water, are related to the industrial residual discharges into the sewage system before treatment in the water treatment plant PITARNL.

In general, most of the metals examined showed considerable variability, as indicated by the standard deviation, which indicates the change in concentration of metals from one day to the next. This underscores the importance of maintaining a regular periodic monitoring of the conditions of the sites studied. Therefore, it is recommended to undertake a consistent (annual or seasonal) monitoring program of the river.

Phenoxy herbicide and organochlorine pesticides

Pesticides were only analyzed in river water before it enters the city and in the potable water (sites 1 and 2). All of the concentrations of the organochlorine pesticides and phenoxy herbicide studied were below the limits of detection.

Volatile organic compounds

Volatile organic compounds were analyzed at all the sites, except for the river samples of site 3. With the exception of toluene, none of the VOC studied in river samples and in residual water was detected above the applicable detection limit, LOQ. Toluene was found in site 4 during the last day of sampling, with a concentration of 147.76 $\mu\text{g/L}$. The concentration of toluene is not regulated in residual water. On

the other hand, of all of the VOC analyzed in the potable water samples (site 2), only bromodichloromethane and dibromochloromethane were reported to be present above the LOQ in all the samples. The average concentration of bromodichloromethane was 132.73 $\mu\text{g/L}$ with a standard deviation of 18.2, while the average concentration for dibromochloromethane was 122.61 $\mu\text{g/L}$, with a deviation of 9.0. In addition, chloroform was found above the LOQ in the final day of testing of the potable water sample with a concentration of 86.7 $\mu\text{g/L}$. None of the three compounds is regulated in potable water. These trihalomethanes are formed as byproducts when chlorine is added to potable water for disinfection.^[23] In water, bromodichloromethane and dibromochloromethane easily evaporate into the air, while some of the chloroform may break down to other chemicals.

The 2000 IBWC study^[18] included the analysis of bromodichloromethane and of dibromochloromethane in river samples and in residual water. These compounds were found below LOQ for all the river samples, and above the LOQ only in one of the days of their analysis in residual water. In contrast to our findings, the IBCW study often detected a number of VOC in the influent of the residual water treatment plant, which included: 1,4-dichlorobenzene, benzene, chloroform, toluene and total trihalomethanes. None of these compounds is regulated by Mexico in the influent of water treatment plants. The 2000 IBWC study reported the presence of hexachloroethane and 1,4-dichlorobenzene in the river samples on only one of the days of testing, although this level turned out to be above the permissible limits for the protection of freshwater biota.

Semi-volatile organic compounds

As with the VOC, semi-volatile organic compounds were analyzed in sites 1, 2, 4 and 5, but all of the samples studied had SVOC concentrations below the limit of detection. The 2000 IBWC study^[18] occasionally detected hexachloro-1,3-butadiene in the river samples, with concentrations above the permissible limit for use as a source for potable water. In the same study, hexachloro-1,3-butadiene, along with cresol and phenol, were found in residual water samples, but their concentrations are not regulated. None of these compounds were detected above the LOQ in our study. However, we can not conclude that the water quality was better during our analysis period than during the analysis of year 2000, given the fact our study included 3 sampling days, whereas the 2000 study included 7 days of sampling. Instead a more intensive monitoring schedule is recommended.

Radioactivity

Radioactivity analyses were performed only on the potable water samples (site 2). Gross alpha radioactivity was below detection level, LOQ, which is well below the amount permitted under the regulations. Although detectable—at

an average concentration of 0.143 Bq/L and standard deviation of 0.016—beta radioactivity was also safely below the allowed amount for drinking water. That means that the levels of alpha and beta particles were below levels of concern at the time of the sampling.

Conclusions

In order to evaluate the water quality of the Rio Grande at the Laredo/Nuevo Laredo area, this study examined physical, chemical and bacteriological parameters, as well as total metals and organic compounds (organochlorine pesticides, VOC and SVOC). Surface water samples were collected at three sites of the Rio Grande in the region of the sister cities of Nuevo Laredo, Mexico and Laredo, Texas, USA. In addition, potable water and residual samples in Nuevo Laredo were obtained.

The vast majority of physical, chemical and bacteriological samples analyzed were within the limits established by Mexican regulation, except for oils and grease and total dissolved solids in surface waters. Oils and grease were observed in the river samples, although regulations do not permit any oils and grease in the river water. Also, total dissolved solids of the river samples were slightly above the limits for use in agricultural irrigation and for bodies of water used as a source of drinking water.

All of the river sites had Al concentrations above the permissible limit for a source of drinking water and above the limits established for the protection of freshwater biota. A number of unregulated elements (Cd, Sr, Mg, Na, Fe, Si, Li and K) were also found in the river samples. The average concentrations of Ba and Na in the potable water samples were below the permissible limits. Ca, Sr, Mg and Si were also found but these are not regulated. Zn is the only metal regulated in residual water, and its concentration stayed below permissible limits.

Almost none of the organic compounds studied in river samples and in residual water were observed above detection limits. For the potable water samples, only bromodichloromethane and dibromochloromethane were found above the LOQ in all the samples. However, the presence of organic compounds can not be ruled out in any of the sampling sites without more intensive monitoring.

Day to day variability in the concentration of some compounds studied emphasizes the importance of sustained monitoring. Therefore, it is recommended to undertake consistent periodic monitoring of the river to obtain more substantial data than that obtained in this preliminary study. Nevertheless, despite its limitations, this work increases the scarce existing data over a wide range of environmental compounds.

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