Chemical Analysis of Industrial Pollution within an Open Canal Located in a Border *Colonia*

Janel E. Owens and Emily D. Niemeyer
Department of Chemistry, Southwestern University, Georgetown, TX 78626

Introduction

A number of treaties between the United States and Mexico have lowered the boundaries for the exchange of goods and workers, leading to a subsequent explosion in industrial development along the U.S.-Mexican border. Along with this development, a surge in population has occurred throughout the border region as workers from the Mexican interior migrate to the border for the promise of jobs in the *maquiladoras,* factories which produce goods in Mexico for export to other countries, primarily the United States. Along with this increase in population and industry, there has been increasing concern about the hazardous environmental conditions that are occurring in communities surrounding the *maquiladoras*. Although the *La Paz Agreement* and its annexes attempted to address a number of transboundary pollution issues between the United States and Mexico, it is widely suspected and has been increasingly documented that a large amount of the chemical waste being generated in the *maquiladoras* is being illegally dumped within the Mexican border.[1]

The effects of such practices on public health within the border region remain unclear, but a report released in 1992 detailing a cluster of neural tube birth defects in infants in Brownsville, TX led to a public outcry.[2] However, to date, there have been only a handful of studies that document the environmental conditions within the border region and/or attempt to understand the impacts of the changing border region on human health.[3] A report published by the National Toxic Campaign Fund in 1991 remains one of the most extensive studies of chemical waste contamination in the waterways of the U.S.-Mexico border region.[4] The report details a number of disturbing findings including the common practice of *maquiladoras* dumping concentrated chemical wastes into rivers and sewers and the resulting widespread chemical contamination within the neighboring communities. Recently, a report was released with initial environmental monitoring data of water, soils, and sediments within the southern Texas border region.[5] Although the goal of this study was to develop sampling methodologies, initial results showed the presence of aliphatic hydrocarbons and plasticizers in every soil, sediment, and water sample collected - over 100 samples in total, some in alarmingly high concentrations.

Clearly, further information is needed regarding the extent of environmental contamination facing the residents of communities in the border region. In order to expand the existing data, we have set out to quantify a host of industrial pollutants in a waterway located within a community in Matamoros, Tamaulipas, Mexico. Communities such as this one, known as *colonias populares*, are often characterized by their cramped and unsanitary conditions, widespread poverty, and rampant infectious disease. This particular *colonia*, *Derechos Humanos* (human rights), contains approximately 350 households, a school, and a medical clinic. Because the city of Matamoros has no municipal wastewater treatment facility, waste is diverted from the city by a number of open wastewater canals, one of which is directly adjacent to *Derechos Humanos*.

In this study, we have concentrated primarily on the wastewater canal as the source of environmental contamination within the *colonia*. We have quantified common industrial chemicals within the waterway including a series of volatile organic compounds, chlorinated organics, heavy metals, and cationic and anionic water quality indicators.

Experimental

Sample Collection and Storage

All samples were collected on July 31, 2001 from four sites along the banks of the wastewater canal running behind the *Colonia Derechos Humanos*. The approximate air temperature was 30 ^{o}C on the day of sampling. Site 1 samples were collected from water flowing from an effluent pipe directly adjacent to the *colonia*; site 2 samples were collected 10 yards upstream from the *colonia*; site 3 was located approximately one-quarter mile upstream from the *colonia* at the base of a wooden pallet foot bridge and across from an effluent pipe that was releasing water from an unknown origin; and site 4 was located at the origin the canal, under the bridge of *Solidaridad* street, under *Findencio Trejo*.

All water samples were collected in duplicate by grab sampling in pre-cleaned *I-Chem* HDPE sample containers. The containers were then labeled, wrapped with Parafilm®, and stored on ice for transport. All water samples were stored in their original containers at 4°C.

Analysis of Water Quality Indicators

The method for the determination of total dissolved solids (TDS) and the membrane filter procedure for the determination of total coliform were from *Standard Methods for the*

Examination of Water and Wastewater, 20th Ed.[6] The pH of each sample was measured using a calibrated pH meter (Accumet, ± 0.01 pH units).

Anionic and cationic water quality indicators were quantified using Zellweger Analytics Lachat IC5000 ion chromatograph (Milwaukee, WI). Zellweger Analytics QuikChem Method 10-510-00-1-A was used to determine the concentrations of fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate in each sample.[7] Briefly, the mobile phase was a 2.8 mM sodium carbonate/2.2 mM sodium bicarbonate solution, delivered at 1.8 mL/min at room temperature. A 200 µL sample loop was used to directly inject the water samples after first filtering them through Whatman No. 1 filter paper and then diluting with Millipore DI water by a factor of ten. The ion chromatograph was operated in background suppression mode with a 0.25 M sulfuric acid/0.05 M sodium sulfate regenerant. A total of six mixed standard solutions were used for instrument calibration.

Cation concentrations (lithium, sodium, ammonium, potassium, magnesium, and calcium) were determined using Zellweger Analytics QuikChem Method 10-520-00-1-B using the non-suppressed conductivity method.[8] The 2.4 mM methanesulfonic acid mobile phase was delivered at a flow rate of 1.8 mL/min, and samples were injected using a 25 µL loop. Throughout the analyses, all standards and samples were prepared in plasticware in order to avoid sodium contamination. A total of six mixed standard solutions were used for instrument calibration. Quality control samples were completed throughout the calibration and sample analysis.

Metals Analysis

Copper, lead, nickel, zinc, cadmium, and chromium were analyzed using a GBC Atomic Absorption Spectrometer (Arlington Heights, IL) using a previously described method.[6] Iron was quantified in each water sample using a spectrophotometric method which has been previously described.[6]

Volatile Organic Compounds

Volatile organic compounds (VOCs) were quantified using solid-phase microextraction (SPME)[9] and EPA method 8260B. In summary, a Varian 3300 gas chromatograph with flame ionization detection (GC/FID) was equipped with a 30 m x 15 _m x 0.5 _m VOCOL column (Supelco, Bellefontaine, PA). A 100 _m polydimethysiloxane SPME fiber (Supelco, Bellefontaine, PA) was used to extract the following VOCs: benzene, toluene, ethylbenzene, _-, *m*-, _- xylenes,

styrene, and 1,2-, 1,3-, and 1,4-dichlorobenzene. All samples and standards were prepared in 6-mL glass crimp top vials sealed with aluminum seal/PTFE/silicon septum tops. One mL of fluorobenzene spike solution, sodium chloride, and a small stir bar to agitate the solution were added to each vial before sealing. Adsorption time for the SPME fiber was 11 minutes in headspace with heating in a 60°C water bath and gentle agitation by the magnetic stir bar during the adsorption time. The fiber was then desorbed in the GC injector for three minutes at 220°C. The GC column was held at 40°C for 1 minute, then ramped to 200°C at 20°C/min. The FID detector temperature was held constant at 220°C throughout the analysis. High purity helium was used as the carrier gas (column head pressure: 7.5 psi; flow rate: 9.3 mL/min; make-up gas: 25 mL/min, H_2 at 20 mL/min, and Air at 300 mL/min).

Results and Discussion

Tables 1 presents the results for the analyses of total coliform, total dissolved solids, and pH as a function of sample site.

Table 1. Total coliform colonies, total dissolved solids (TDS), and pH as a function of sample site.

Sample	total coliform colonies (per 100 mL)	TDS (mg/L)	pH
1	1.10×10^4	2704 ± 311	7.78
2	75.5×10^4	6397 ± 2606	7.48
3	20.5×10^4	1369 ± 181	8.27
4	8.50×10^4	858 ± 105	8.22

Results show exceedingly high concentrations of coliform bacteria detected at each sample location, ranging from a low concentration of 1.10×10^4 colonies per 100 mL at sample site 1 to 75.5×10^4 colonies per 100 mL at sample site 2. Although coliform bacteria are ubiquitous in the environment, they are a good indicator of water quality and their presence is most likely due to the release of raw sewage into the canal from the city of Matamoros. In addition, the high concentration of total dissolved solids within the canal water, ranging from 858 ± 105 mg/L at sample site 4 to 6397± 2606 mg/L at sample site 2, is most likely also due to releases into the canal, either from Matamoros or local industry.

Tables 2 and 3 present the concentrations of anions, cations, metals, and VOCs quantified as a function of sample site.

Table 2. Anion, cation, and metal concentrations as a function of sample site. All concentrations listed are in ppm. ND indicates that the analyte was not detected.

Sample	F^-	Cl^-	NO_2^-	Br^-	NO_3^-	PO_4^{3-}	SO_4^{2-}
1	0.594 ± 0.080	1053 ± 136	ND	2.61 ± 0.34	1.08 ± 0.21	10.40 ± 0.71	412 ± 83
2	0.889 ± 0.187	444 ± 30.7	ND	0.67 ± 0.06	7.85 ± 11.9	13.4 ± 3.1	229 ± 42.2
3	ND	361 ± 23.5	ND	0.73 ± 0.11	1.54 ± 0.99	7.59 ± 0.95	238 ± 10.2
4	0.588 ± 0.174	165 ± 6.8	ND	1.05 ± 1.60	2.46 ± 2.47	6.03 ± 2.1	178 ± 6.4

	Li^+	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
1	0.18 ± 0.06	713±83	62.0±13.8	18.00 ± 0.92	66.9 ± 6.69	124.0 ± 19.7
2	0.028 ± 0.05	348±32	50.8±4.3	27.8 ± 3.27	35.9 ± 3.1	109 ± 7.3
3	ND	268±22.4	43.3±0.69	12.3 ± 1.5	34.5 ± 5.56	96.0 ± 5.4
4	ND	177±15.0	31.3±1.81	17.2 ± 14.2	21.8 ± 1.51	77.7 ± 2.1

	Cu	Pb	Ni	Zn	Fe	Cd
1	ND	0.052 ± 0.044	0.213 ± 0.189	ND	ND	ND
2	0.087 ± 0.017	0.072 ± 0.145	0.396 ± 0.320	ND	ND	ND
3	0.340 ± 0.054	0.199 ± 0.042	1.07 ± 0.109	ND	ND	ND
4	0.050 ± 0.040	0.400 ± 0.041	1.45 ± 0.462	ND	ND	ND

Table 3. VOC concentrations as a function of sample site. All concentrations listed are in ppm. ND indicates that the analyte was not detected.

Sample	benzene	toluene	ethylbenzene	*m*,*p*-xylene	*o*-xylene	styrene
1A	5.02	ND	ND	0.06	0.15	0.185
1B	9.80	ND	ND	ND	ND	ND
2A	2.19	ND	0.05	0.06	ND	0.185
2B	3.27	ND	0.25	0.06	ND	0.179
3A	4.30	ND	ND	ND	ND	ND
3B	7.08	ND	ND	ND	ND	ND
4A	4.4	ND	ND	ND	ND	ND
4B	5.3	ND	ND	ND	0.07	0.06

	1,3-DCB	1,4-DCB	1,2-DCB
1A	0.278	0.12	0.16
1B	ND	0.25	0.12
2A	0.34	0.40	0.12
2B	0.24	0.34	0.20
3A	0.16	0.09	0.04
3B	0.14	ND	ND
4A	0.13	ND	ND
4B	0.11	ND	ND

Examination of these data show that, in general, the cationic and anionic water quality indicators are present at reasonably low concentrations with small variability as a function of sample site. Sample site 1, located next to the *colonia*, has higher concentrations of several possibly anthropogenic anions and cations of interest (e.g. lithium ion, bromide ion, ammonium ion, and chloride ion) than did the other sites sampled.

Several industrial pollutants of concern were detected within the canal at every sample site. These include lead (ranging in concentration from 0.05 to 0.40 ppm) nickel (ranging in concentration from 0.21 to 1.45 ppm), and benzene (ranging in concentration from 2.19 to 9.80 ppm). In addition, several other pollutants were detected at a majority of the sample sites including 1,3-dichlorobenzene (found in 7 of the 8 samples at concentrations ranging from 0.11 to 0.34 ppm), 1,4-dichlorobenzene (found in 5 of the 8 samples, ranging in concentration from 0.09 to 0.40 ppm), 1,2-dichlorobenzene (found in 5 of the 8 samples, ranging in concentration from 0.04 to 0.20 ppm), styrene (found in 4 of the 8 samples, ranging in concentration from 0.06 to 0.185 ppm), and copper (found in 6 of the 8 samples, ranging in concentration from 0.05 to 0.34 ppm). Several other pollutants were only detected in a small number of samples including ethylbenzene (found at sample site 2) and the xylene isomers (found at sample sites 1, 2, and 4). Toluene, zinc, iron, and cadmium were not detected in any of the samples.

Closer examination of the data reveals that there is a large degree of inconsistency in the quantitation of several analytes as evidenced by the variation in analyte concentrations for duplicate samples. This variation is most evident for the volatile organic compounds studied, but is also evident in the large standard deviation associated with the concentration of nickel at several sample sites. The variability in the data is likely a direct result of the small number of samples collected for this study, leading to a difficulty in collecting samples that accurately describe the composition of the canal at each location.

Qualitatively, there was a small degree of variability between samples. Several industrial pollutants were found in every sample, including: benzene, a commonly used industrial solvent; lead, which is used in a variety of applications including batteries, automobiles, printing and welding; and nickel, which is commonly found in stainless steel. The presence of these and other industrial chemicals, such as styrene, copper, and the dichlorobenzene and xylene isomers, indicate the need for further testing to determine the extent of chemical contamination occurring within this canal.

Conclusions

The initial results of this environmental monitoring project indicate the presence of a variety of anthropogenic chemical contaminants along the entire bank of the wastewater canal. These include benzene, lead, and nickel which were found at all sampling sites along the canal,

as well as dichlorobenzene and xylene isomers, ethylbenzene, and copper which were found at several of the sites. The variation in duplicate samples indicates the need for a more extensive sampling protocol and further testing. In addition, in order to assess the public health impacts of these industrial pollutants, air and soil sampling and analysis is also imperative.

Acknowledgements

Financial support for this work was generously provided by the Robert A. Welch Foundation and the Camille and Henry Dreyfus Foundation.

References

1. Rich, J.G. *Planning the Border's Future: The Mexican-U.S. Integrated Border Environmental Plan*, Austin, TX : U.S.-Mexican Policy Studies Program, LBJ School of Public Affairs, University of Texas at Austin, **1992**.
2. Texas Department of Health/Centers for Disease Control *An Investigation of a Cluster of Neural Tube Defects in Cameron County, TX*, Austin, TX: **1992**.
3. Several studies include: a) Varady, R.G.; Mack, M.D. *J. Env. Health* **1995**, *57*, 8-14. b) Borderlines 45, 1998, www.us-mex.org/borderlines/1998/b145/b145ch.html. c) Mukerjee, S.; Ellenson, W.D.; Lewis, R.G.; Stevens, R.K.; Somerville, M.C.; Shadwick, D.S.; Willis, R.D. *Environ. Int.* **1997**, *23*, 657-673.
4. Lewis, Sanford J.; Kaltofen, M.; Ormsby, G. *Border Trouble: Rivers in Peril: A Report on Water Pollution due to Industrial Development in Northern Mexico*, Boston, MA: National Toxic Campaign Fund and National Toxics Campaign, **1991**.
5. Garcia, S.S.; Ake, C.; Clement, B.; Huebner, F.J.; Donnelly, K.C.; Shalat, S.L. *Environ. Int.* **2001**, *26*, 465-474.
6. *Standard Methods for the Examination of Water and Wastewater, 20th ed.* Washington, DC: American Public Health Association, **1998** (total dissolved solids 1-21; total coliform 9-56 – 9-57; metals 3-13 – 3-22; iron 3-76 – 3-78).
7. Karmarkar, S.; Bahowick, T. *QuikChem Method 10-510-00-1-A Determination of Inorganic Anions by Ion Chromatography*, Milwaukee, WI: Zellweger Analytics, **1999**.
8. Bahowick, T. *QuikChem Method 10-520-00-1-B Determination of Mono- and Di-valent Cations in Waters and Beverages by Ion Chromatography*, Milwaukee, WI: Zellweger Analytics, **1999**.
9. a) Arthur, C.A.; Killam, L.M.; Motlagh, S.; Lim, M.; Potter, D.W.; Pawliszyn, J. *Environ. Sci. Technol.* **1992**, *26*, 979-983. b) Langenfeld, J.J.; Hawthorne, S.B.; Miller, D.J. *Anal. Chem*. **1996**, *68*, 144-155. c) Eisert, R.; Levsen, K. *J. Chromatogr. A* **1996**, *733*, 143-157.