

# VOLATILE ORGANIC COMPOUNDS IN STREAMS NEAR WASTEWATER OUTFALLS, ROCKDALE COUNTY, GEORGIA, 2002–2004

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**Abstract.** The U.S. Geological Survey operates a water-quality and water-quantity monitoring network in Rockdale County, Georgia. The program was established to provide data to monitor water-quality changes brought about by increasing urbanization in the county. Water-quality samples have been collected since November 2002 from 13 sampling sites distributed among the five major watersheds of the county. Samples are collected and analyzed for a variety of inorganic and organic constituents, including many U.S. Environmental Protection Agency (USEPA) priority pollutants.

One goal of the program is to monitor point-source pollution from wastewater treatment plant outfalls in Rockdale County. To accomplish this goal, one background site is sampled upstream from an outfall and four sites are sampled downstream from wastewater outfalls. One hundred and eleven samples were collected from these five sites and were analyzed for a full suite of USEPA priority pollutants including a combination of inorganic and organic constituents, volatile organic compounds (VOCs), semivolatile compounds, and pesticides. The scope of this paper is limited to the 66 VOCs analyzed. Of the eight VOCs detected, six likely result from the chlorination of wastewater. Trihalomethanes (THMs) are disinfection by-products resulting from chlorination of drinking water as well as wastewater. At elevated concentrations in drinking water, these compounds can be deleterious to human health. The two remaining compounds are methyl tert-butyl ether, a gasoline additive, and toluene, an organic solvent. The VOCs concentrations ranged from 0.1 to 1.6 micrograms per liter and were all below drinking-water standards.

## INTRODUCTION

Rockdale County, like most of the Atlanta metropolitan area, has experienced rapid growth and development. Because Rockdale County is approximately 25 miles from Atlanta, development has occurred only recently and within a short period of time. The population of the

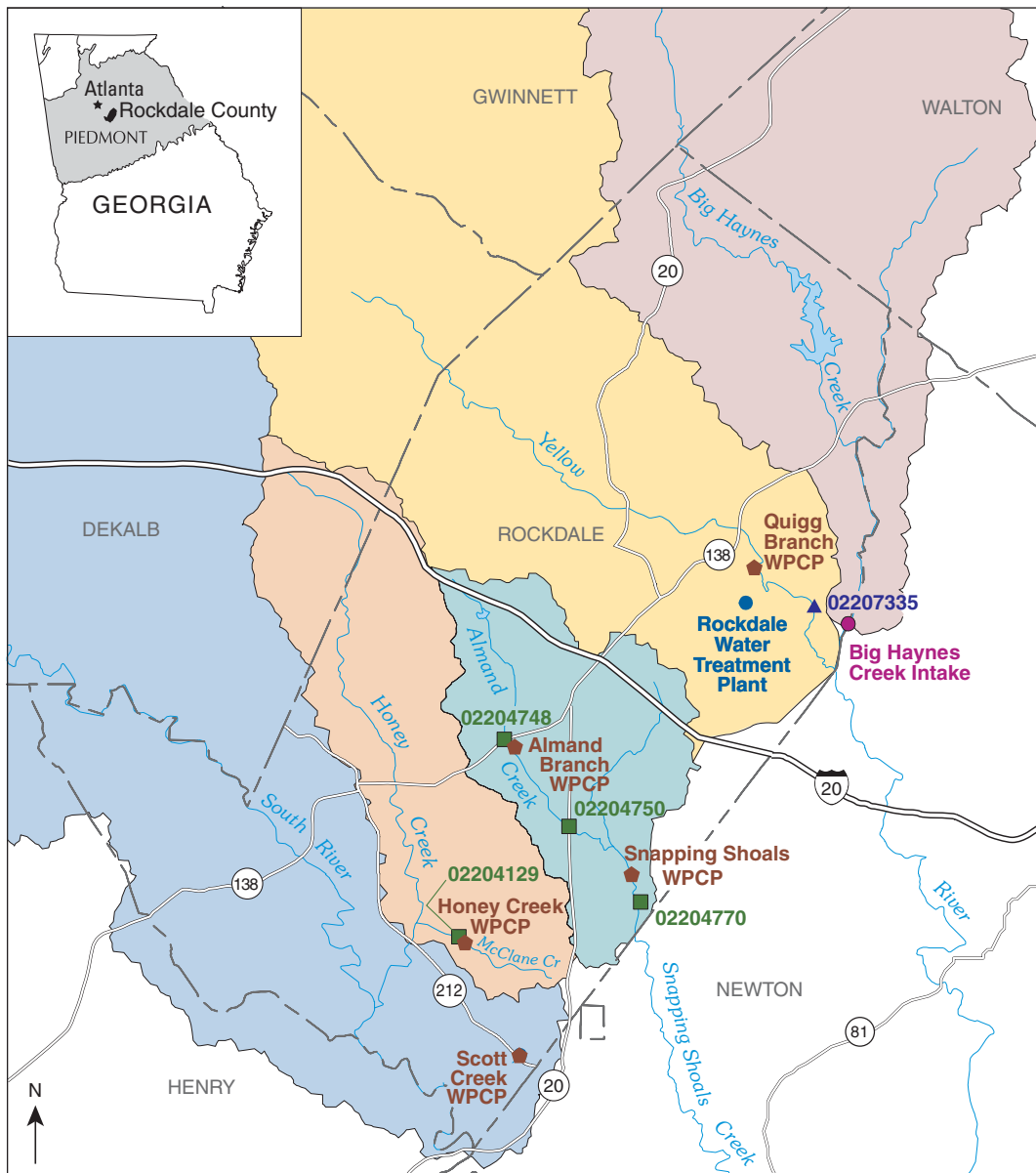
county was 70,000 during 2000 and is expected to nearly double by the year 2020 (U.S. Census Bureau, 2004). Because of concerns regarding the effects of development on water quality and aquatic biota, during 2001 Rockdale County requested that the U.S. Geological Survey (USGS) develop and operate a long-term water-quality and aquatic-biology monitoring program throughout the county.

The current USGS monitoring network was designed to provide the data for Rockdale County to manage water resources more effectively and to identify current and future water-quality problems resulting from urban development. The water-quality network consists of five major components:

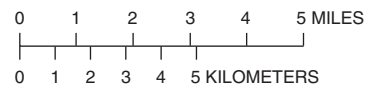
- Biological monitoring
- Baseflow and stormflow chemical sampling
- Drinking-water supply monitoring
- Point-source pollution monitoring
- Streamflow monitoring, including measuring several continuous water-quality parameters.

This paper focuses on the point-source monitoring component of the program, which was established to identify water-quality conditions associated with point-source pollution from wastewater treatment plant outfalls in Rockdale County. Four of the five sites selected for point-source monitoring are downstream from the four major water-pollution control plants (WPCPs) in the county, and one is slightly upstream from the Almand Branch WPCP (Fig. 1, Table 1).

During 1999, Rockdale County developed a watershed assessment and management plan that identified as major goals the elimination of small WPCPs and the expansion of the two largest WPCPs (Tetra Tech, Inc., 1999). Rockdale County WPCPs use an activated sludge process, and wastewater is chlorinated and dechlorinated several times prior to release into streams (Kenneth Moore, Rockdale County Operations Management International Incorporated, verbal commun., 2004). Chlorination with chlorine gas is a common practice in the wastewater industry to disinfect wastewater by killing microbial contaminants.



Base modified from U.S. Geological Survey  
1:100,000-scale digital data



**EXPLANATION**

Watershed		Sampling site	
	Big Haynes Creek		Continuous surface water and water quality
	Yellow River		Periodic surface water
	Snapping Shoals Creek		Water Pollution Control Plant (WPCP)
	Honey Creek		Intake site
	South River		Water treatment plant

**Figure 1. Location of U.S. Geological Survey point-source monitoring sites and water pollution control plants, Rockdale County, Georgia.**

**Table 1. U.S. Geological Survey point-source monitoring sites and associated water pollution control plants.**[USGS, U.S. Geological Survey; ID, identification; WPCP, water pollution control plant; Mgal/d, million gallons per day; mi<sup>2</sup>, square mile]

Point-source monitoring site	USGS site ID	Associated WPCP	Approximate location of site relative to WPCP	2004 permitted discharge (Mgal/d)	Drainage area (mi <sup>2</sup> )
Yellow River at Gees Mill Road	02207335	Quigg Branch	1.40 miles downstream	6.00	260.00
Almand Creek upstream	02204748	Almand Branch	0.40 miles upstream	1.25	4.7
Almand Creek downstream	02204750	Almand Branch	1.65 miles downstream	1.25	6.27
Snapping Shoals Creek at Honey Creek Road	02204770	Snapping Shoals	0.30 miles downstream	0.45	15.1
McClane Creek downstream from Troupe Smith Road	02204129	Honey Creek	50 feet downstream	0.50	3.4

## METHODS

The USGS collects monthly samples at the five point-source monitoring sites. Fixed interval sampling (usually monthly) characterizes the spatial and temporal distribution of contaminants in relation to hydrologic conditions and contaminant sources (Shelton, 1997). Water samples are collected following USGS parts-per-billion protocols (Wilde and others, 1998). The samples are analyzed for a full suite of U.S. Environmental Protection Agency (USEPA) priority pollutants including a combination of inorganic and organic constituents, VOCs, semivolatile compounds, and pesticides.

VOC samples are collected using a sampler designed by the USGS and built by Wildco<sup>®</sup>. The sampler is made of noncontaminating materials and is designed to avoid analytic loss. Samples are collected at the centroid of the stream in the same cross-section throughout the project, except at sites that need to be sampled from a bridge at high flow. In shallow streams where the sampler cannot be submerged, a representative sample is obtained by immersing an open vial (dip sample) near the centroid of flow (Shelton, 1997). The sample is collected into four 40 milliliter (mL) VOC vials, which are acidified with 1:1 hydrochloric acid and immediately capped at the streamside to avoid VOC loss and possible sample contamination. Samples are stored on ice, maintained at 4 degrees Celsius, and shipped overnight to the USGS National Water-Quality Laboratory (NWQL) in Denver, Colorado. VOCs are extracted from the water matrix by the purge-and-trap method and the quantitation is done by capillary-column gas chromatography/mass spectrometry. Analytical results are reported in microgram per liter ( $\mu\text{g/L}$ ) (Connor and others, 1998).

USGS personnel routinely measure the streamflow at all five point-source sites so that changes in water quality can be evaluated with respect to streamflow conditions. Yellow River is the only point-source site at which water quality and gage height data are collected on a continual basis. All of the data are gathered and transmitted by satellite telemetry. This site has a continuous streamflow rating developed to correlate with each gage height transmitted. Quality assurance (QA) samples represent 11 per-

cent of the total number of samples collected. For VOCs, QA samples collected to date include equipment, field, and trip blanks, spikes, and replicates. There have been no detections in four trip blank and two equipment/field blank VOC samples collected to date, and no detections in the two spike and four replicate samples. At Almand Creek upstream, toluene was detected in a routine sample but not detected in the correlating replicate sample.

## RESULTS

From October 2002 through September 2004, the USGS collected 111 samples at the five point-source monitoring sites. Of the 66 VOC analyzed, 8 VOCs were detected with concentrations ranging from 0.1 to 1.6  $\mu\text{g/L}$  (Table 2). The most frequently detected constituent was trichloromethane, which was detected 47 times out of 111 samples and most frequently at Yellow River at Gees Mill Road (16 detections out of 21 samples). The next most frequently detected VOC was bromodichloromethane, with 32 detections out of 111 samples. This compound was most frequently detected at Almand Creek downstream (11 detections out of 23 samples). The other six VOCs were detected in 12 percent or less of the total number of samples collected.

Trichloromethane was most frequently detected at Yellow River (detected in 76 percent of samples), Almand Creek at downstream (52 percent), and McClane Creek (59 percent) (Fig. 2A). Bromodichloromethane detections at each of the four sites downstream from wastewater outfalls ranged between 27 and 48 percent of the total samples. The only site where bromodichloromethane was not detected was Almand Creek upstream, which is the background site upstream from the Almand Branch WPCP. Dibromochloromethane and tribromomethane were detected only at Almand Creek downstream and Snapping Shoals Creek. As expected, the site upstream of the wastewater discharge sites, Almand Creek upstream had no detections for the THMs. There were two detections of toluene at this background site. Of the eight VOCs detected in the study, all constituent concentrations range below the maximum concentration level (MCL) (Fig. 2B).

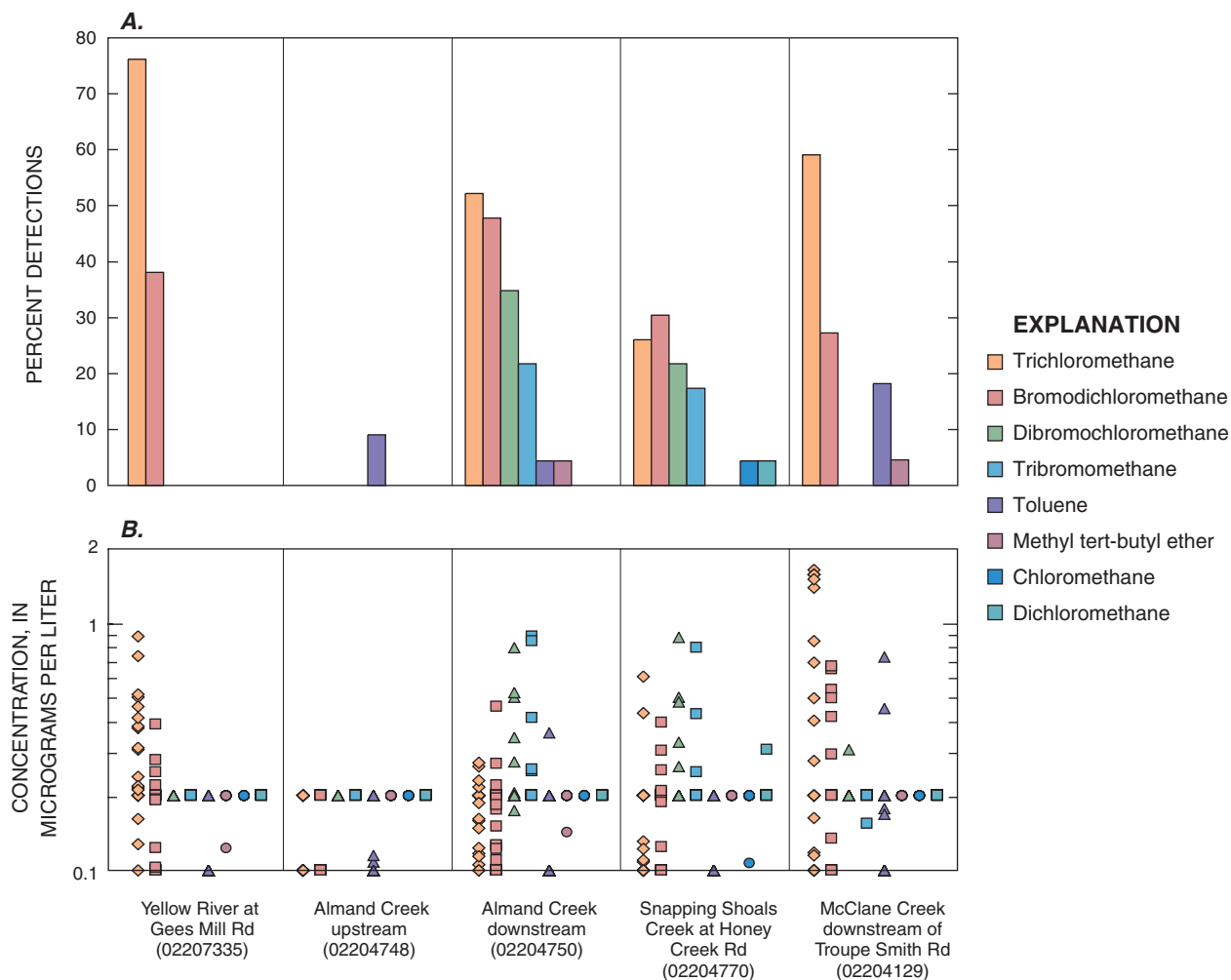
**Table 2. Summary of volatile organic compound results at point-source monitoring sites, Rockdale County, October 2002 through September 2004.**

[ $\mu\text{g/L}$ , microgram per liter; MCL, maximum contaminant level; NA, no applicable standard]

Compound	Maximum concentration ( $\mu\text{g/L}$ )	Detection frequency (percent)	MCL ( $\mu\text{g/L}$ ) <sup>1</sup>
Trichloromethane	1.6	42	<sup>2</sup> 80
Bromodichloromethane	29.0	29	<sup>2</sup> 80
Dibromochloromethane	0.9	12	<sup>2</sup> 80
Tribromomethane	0.9	8	<sup>2</sup> 80
Toluene	0.7	6	1,000
Methyl tert-butyl ether	0.1	2	NA
Chloromethane	0.1	1	NA
Dichloromethane	0.3	1	5

<sup>1</sup>U.S. Environmental Protection Agency, 2002.

<sup>2</sup>MCL for total trihalomethanes (sum of trichloromethane, bromodichloromethane, dibromochloromethane, and tribromomethane) is 80  $\mu\text{g/L}$ .



**Figure 2. (A) Percent detections of volatile organic compounds and (B) concentrations of volatile organic compounds at USGS point-source monitoring sites, Rockdale County, Georgia, 2002–2004. Maximum contaminant level (MCL) for total trihalomethanes (sum of trichloromethane, bromodichloromethane, dibromochloromethane, and tribromomethane), 80 micrograms per liter ( $\mu\text{g/L}$ ); toluene, 1,000  $\mu\text{g/L}$ ; methyl tert-butyl ether and chloromethane have no MCL; and dichloromethane, 5  $\mu\text{g/L}$ .**

Along with the other VOCs detected, the total trihalomethanes (TTHMs) (sum of trichloromethane, bromodichloromethane, dibromochloromethane, and tribromomethane) detected are well below the maximum concentration level (MCL). Figures 2A and 2B detail the frequency and actual concentrations of the detected VOCs. Figure 3 displays the concentration of the total trihalomethanes analyzed in each sample at the four point-source sites and the samples below the minimum reporting limit (MRL). Two of the four THMs, trichloromethane and bromodichloromethane, had MRLs lowered by NWQL from 0.2 µg/L to 0.1 µg/L from water year 2002 to water year 2003. Concentration for TTHMs for all five sites range from 0.60 to 2.66 µg/L. Almand Creek upstream is the only site at which all sample concentrations were all less than the MRL. McClane Creek had the highest TTHM concentration at 2.66 µg/L, and Almand Creek downstream had the lowest at 0.60 µg/L. Almand Creek downstream and Snapping Shoals Creek had a total of 23 samples each, McClane Creek and Almand Creek upstream had 22 samples each, and Yellow River had 21 samples, making a total of 111 samples to compare.

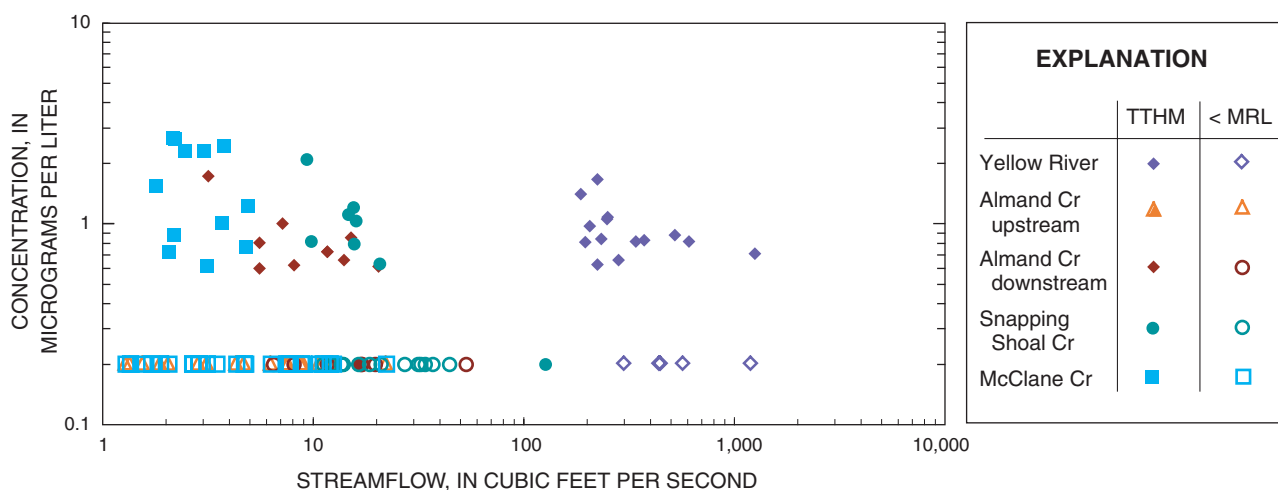
### DISCUSSION

VOCs are organic compounds that are components of many human-made products, such as fuels, solvents, paints, glues, adhesives, deodorizers, refrigerants, and fumigants. Many VOC target analytes have been the focus of national regulations, monitoring, and research since the mid-1980s. Disinfection by-products (DBPs) can be formed when precursors are present in water disinfected at

drinking water or wastewater treatment plants. A class of VOCs called trihalomethanes are formed as a by-product when organic matter in the untreated water reacts with chlorine during the disinfection process in water supply systems (Bender and others, 1999) and are the most common family of DBPs (U.S. Geological Survey, 2004).

The THMs detected thus far in this study include trichloromethane, commonly called chloroform (CHCl<sub>3</sub>); dichlorobromomethane (CHCl<sub>2</sub>Br); chlorodibromomethane (CHClBr<sub>2</sub>); and tribromomethane, commonly called bromoform (CHBr<sub>3</sub>). Currently regulated DBP compounds are THMs, haloacetic acids, chlorite, and bromite because of their carcinogenic and mutagenic nature (U.S. Geological Survey, 2004). The MCL in drinking water for TTHMs—the sum of the concentrations of chloroform, bromodichloromethane, dibromochloromethane, and bromoform—is 80 µg/L (U.S. Environmental Protection Agency, 2002). All the stream samples collected in Rockdale had THM concentrations that were well below the drinking water MCL.

Chloroform is a known animal carcinogen, whereas the other THMs are carcinogenic and mutagenic (Rathbun, 1995). According to the USEPA, bromodichloromethane is a likely human carcinogen, whereas bromoform is a probable human carcinogen and chlorodibromomethane is a possible one. Drinking water standards established by the USEPA are not applicable to the monitoring sites sampled for this study; however, they are provided as a benchmark for comparing the concentrations of these compounds. Although VOCs were frequently detected in the stream samples collected within Rockdale County, the concentrations were significantly lower than drinking water standards. Currently 2005, no aquatic life standards exist for these VOCs.



**Figure 3. Concentrations of volatile organic compounds at U.S. Geological Survey point-source monitoring site against streamflow, Rockdale County, Georgia, 2002–04.** [TTHM, total trihalomethanes (sum of trichloromethane, bromodichloromethane, dibromochloromethane, and tribromomethane); <MRL, less than minimum reporting limit]

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