

Water-Quality Assessment of South-Central Texas— Comparison of Water Quality in Surface-Water Samples Collected Manually and by Automated Samplers

Surface-water sampling protocols of the U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program specify samples for most properties and constituents to be collected manually in equal-width increments across a stream channel and composited for analysis. Single-point sampling with an automated sampler (autosampler) during storms was proposed in the upper part of the South-Central Texas NAWQA study unit, raising the question of whether property and constituent concentrations from automatically collected samples differ significantly from those in samples collected manually. Statistical (Wilcoxon signed-rank test) analyses of 3 to 16 paired concentrations for each of 26 properties and constituents from water samples collected using both methods at eight sites in the upper part of the study unit indicated that there were no significant differences in concentrations for dissolved constituents, other than calcium and organic carbon.

In 1991, the U.S. Geological Survey (USGS) implemented the National Water-Quality Assessment (NAWQA) Program to describe the status and trends in water quality of a large, representative part of the Nation's surface- and ground-water resources. The program is based on a multidisciplinary approach using standardized protocols to collect data in more than 50 study units on a rotational schedule (Hirsch and others, 1988; Leahy and others, 1990). The South-Central Texas (SCTX) study began in 1994.

The NAWQA design (Gilliom and others, 1995) and the surface-water sampling protocols (Shelton, 1994) specify that surface-water samples for most properties and constituents should be collected manually in equal-width increments (EWI method) across a stream channel to ensure collection of a representative sample. The surface-water component of the NAWQA program requires collection of water-quality samples during extreme flow conditions as well as during more normal flow conditions. Because streams in the upper part of the SCTX study unit are "flashy" (water levels rise and fall in a short period of time) during storms, sampling the streams during storms with an autosampler was proposed. Autosamplers allow collection of water-quality samples without endangering field personnel during hazardous conditions, and autosamplers can collect samples

throughout the duration of a storm. The use of autosamplers raises the question of whether property and constituent concentrations in automatically collected samples differ significantly from those in samples collected using the EWI or other standard manual methods.

Cross-sectional variations in stream water quality can occur because of incomplete mixing of upstream tributary inflows, ground-water seepage, and point-source discharges. Previous water-quality studies have reported cross-sectional variations in concentrations of suspended sediment and constituents associated with sediment such as phosphorus, trace metals, and hydrophobic pesticides (Martin and others, 1992). Unlike EWI and other manually collected samples that comprise composite subsamples, automatically collected samples are obtained from a single point in the stream. Therefore, differences in property and constituent concentrations between samples collected manually and those collected automatically could occur.

The purpose of this report is to compare property and constituent concentrations in water-quality samples collected manually using the EWI method (or other standard manual method) with concentrations of samples collected by autosamplers. Statistical comparisons are used to analyze 3 to 16 paired concentrations for each of 26 properties and constituents from water samples collected at eight sites in the upper part of the SCTX study unit.

Environmental Setting

The upper part of the SCTX study unit comprises the Edwards aquifer in the San Antonio region and its catchment area. The upper part of the study unit is divided into two distinct landforms by the Balcones escarpment (fig. 1). North and west of the escarpment is a rugged, steep terrain of upland plateaus and rolling hills that are dissected by many small streams that flow into the deeply incised valleys of several major streams. This area of rocky soils is known locally as the Texas Hill Country. South and east of the escarpment, the terrain smooths to rolling prairies and broad stream valleys with clayey soils. Primarily steep terrain coupled with intense rainfall account for the rapid rise and fall of streams during storms.

Sample Collection and Analysis

Two sets of paired water samples were collected at each of eight sites in the upper part of the study unit. One of each pair of samples was collected manually using the EWI or other standard manual method following NAWQA protocols; the other sample was pumped from a single point in the stream into glass bottles by an autosampler. Identical sample processing and procedures following NAWQA protocols were used for both samples. Each set of paired samples was collected simultaneously to reduce potential temporal variation. Paired samples were not collected during storms because of potential physical danger to field personnel. Although samples were not collected during storms, most samples were collected when discharge at the sites was greater than the 50th percentile of discharge for the month of collection (for the respective periods of record) (table 1). Discharge at each of the eight sites when the first set of paired samples was collected was larger (1.07 to 10.6 times) than when the second set of paired samples was collected. All paired samples were analyzed for major ions, nutrients, dissolved and suspended organic carbon (DOC and SOC), and suspended sediment. Paired samples for pesticide analysis were collected only at the three sites where pesticide samples were collected routinely (08178800, 08180640, 08181800). All samples were analyzed by the USGS National Water Quality Laboratory.

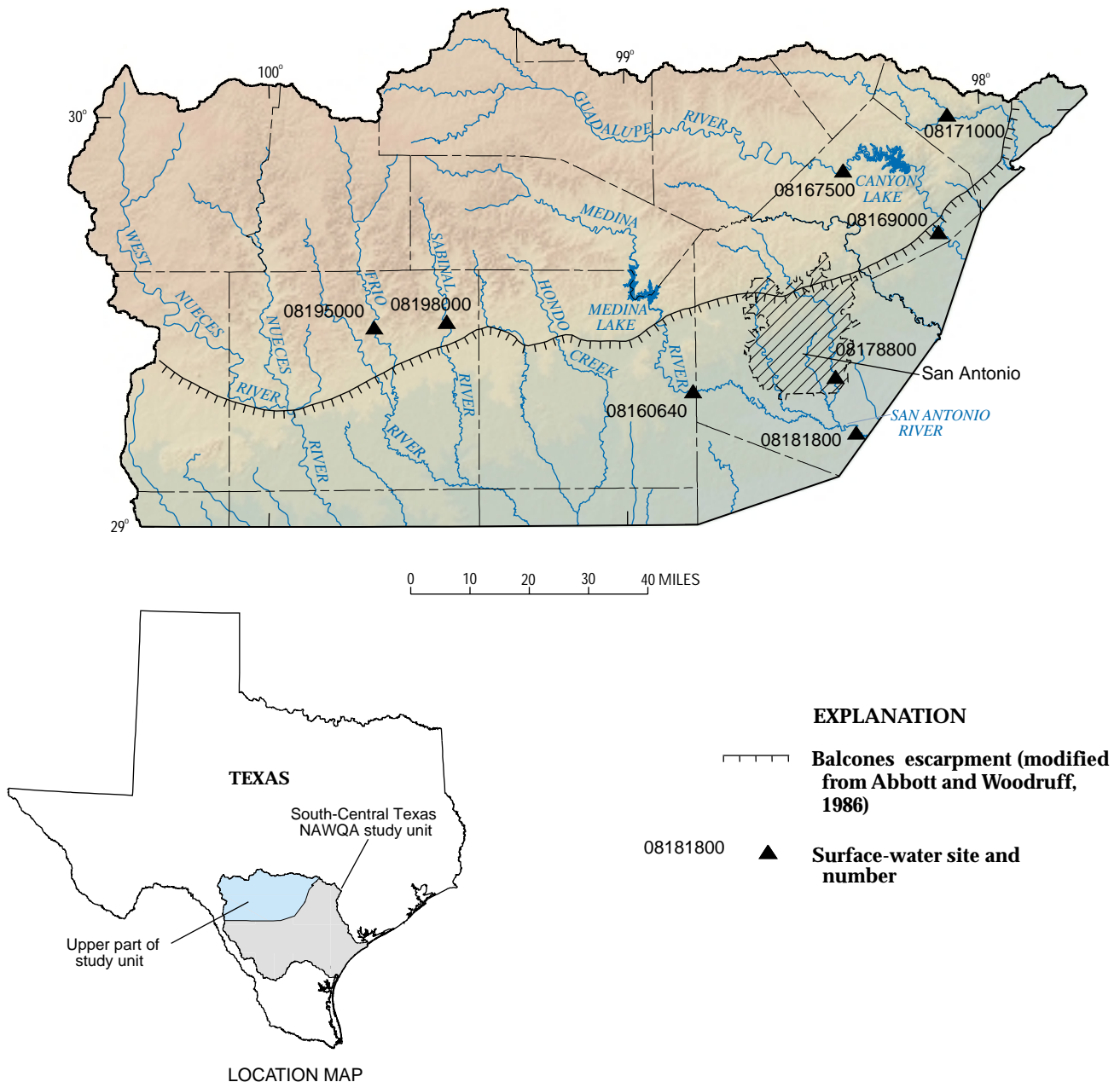


Figure 1. Upper part of study unit and location of sampling sites.



Figure 2. Typically, an autosampler (white object in center of shelter) is installed on relatively high ground with a sampling tube running underground to the stream. Power is supplied by batteries recharged by a solar panel (at left). (Photograph by C.L. Otero, U.S. Geological Survey.)

Figure 3. Equal-width increment sampling is done by wading where stream depths permit. (Photograph by C.A. Hartmann Jr., U.S. Geological Survey.)

Table 1. Discharges for paired water-quality samples collected in the upper part of the South-Central Texas study unit [ft³/s, cubic feet per second]

| Station number | Sample date | Discharge when sample collected (ft ³ /s) | Mean monthly discharge for station (ft ³ /s) | Mean annual discharge for station (ft ³ /s) | Relative magnitude of sampled discharge |
|----------------|-------------|--|---|--|---|
| 08167500 | 03-27-98 | 756 | 362.2 | 353.3 | Greater than 75th percentile for month |
| 08167500 | 04-20-98 | 492 | 391.5 | 353.3 | Greater than 75th percentile for month |
| 08169000 | 03-25-98 | 342 | 301.8 | 293 | At 75th percentile for month |
| 08169000 | 04-23-98 | 321 | 305.3 | 293 | Greater than 50th percentile for month |
| 08171000 | 04-03-98 | 366 | 181.4 | 133.9 | Greater than 75th percentile for month |
| 08171000 | 04-22-98 | 176 | 181.4 | 133.9 | Greater than 50th percentile for month |
| 08178800 | 03-23-98 | 24 | 34.6 | 44.5 | Greater than 25th percentile for month |
| 08178800 | 04-27-98 | 9.8 | 42.5 | 44.5 | Less than 25th percentile for month |
| 08180640 | 03-24-98 | 665 | 261 | 140.1 | Greater than 75th percentile for month |
| 08180640 | 04-24-98 | 63 | 153.8 | 140.1 | Greater than 50th percentile for month |
| 08181800 | 03-26-98 | 794 | 499.1 | 550.7 | Greater than 75th percentile for month |
| 08181800 | 04-28-98 | 201 | 518.7 | 550.7 | Less than 25th percentile for month |
| 08195000 | 04-02-98 | 126 | 107.6 | 123.1 | Greater than 75th percentile for month |
| 08195000 | 04-29-98 | 92 | 107.6 | 123.1 | Greater than 50th percentile for month |
| 08198000 | 04-06-98 | 80 | 58.4 | 63.5 | Greater than 75th percentile for month |
| 08198000 | 04-30-98 | 54 | 58.4 | 63.5 | Greater than 50th percentile for month |

Comparison of Water-Quality Data

The differences between paired concentrations (manual minus autosampler) of properties, major ions, nutrients, organic carbon, suspended sediment, and selected pesticides were computed and mean differences determined (table 2). In general, the mean differences do not show manual concentrations to be consistently larger or smaller than autosampler concentrations. Percentage differences were large for some constituents with small concentrations.

To assess the similarity of the paired concentrations, the Wilcoxon signed-rank test (Helsel and Hirsch, 1992; Hollander and Wolf, 1973) was used to indicate whether the paired concentrations can be considered to be from the same population; in other words, no significant difference exists between them. If the paired concentrations come from the same population, their differences should be symmetrically distributed about zero; accordingly, the test determines whether the median difference between paired concentrations is zero—that is, it tests the hypothesis (null hypothesis) that the median difference between paired concentrations is zero; the alternative hypothesis is that the median difference is either greater than or less than zero (thus, a “two-sided” hypothesis test). Because the ranks of the differences rather than the actual values of the differences are used in the test, the magnitudes of the differences do not influence the outcome of the test. The test result of interest is the p-value, which represents the probability of getting the particular test outcome when the null hypothesis is true—the smaller this probability, the stronger the evidence for rejecting the null hypothesis. P-values of about 0.05 or less offer strong evidence for rejecting the null hypothesis and concluding that paired concentrations are significantly different.

The p-values from signed-rank tests for selected constituents and pesticides (table 2) indicate that for most of the 26 properties and constituents for which p-values could be computed, there are no significant differences between paired concentrations. However, the tests of dissolved calcium and DOC offer strong evidence (p-values 0.028, 0.020) that the two sampling methods yielded significantly different concentrations; and total phosphorus and SOC offer fairly strong evidence (both p-values = 0.062) that the two sampling methods yielded significantly different concentrations. For each of the four constituents that signed-rank tests showed strong or fairly strong evidence of significant difference between manual and autosampler concentrations (dissolved calcium, DOC, SOC, and total phosphorus), at least 80 percent of the manual concentrations were less than or equal to the autosampler concentrations.

Two cautions regarding the results of the signed-rank tests are appropriate. Because the number of paired concentrations in the tests is small (15 or fewer nonzero differences

in all but one of the tests), the power of the tests to indicate significant differences is low. In other words, significant differences between concentrations of some constituents might not be detected by the tests. For example, the test of the pesticide simazine that involved only three data pairs did not yield strong enough evidence to reject the hypothesis that there is no significant difference between the manual and autosampler concentrations, although all three of the manual concentrations were less than the corresponding autosampler concentrations. In the case of tebuthiuron also, the small number of data pairs (four) might have contributed to the inability of the signed-rank test to indicate the significant difference; three of four manual concentrations were greater than the corresponding autosampler concentrations. Additionally, in cases where the median difference between paired concentrations is not zero (null hypothesis is false) but is close to zero, the power of the test to indicate rejection of the null hypothesis is low; thus, the probability of failing to reject the null hypothesis (which is false) and concluding that there is no significant difference in concentration is high.

NAWQA sampling protocols for DOC and SOC (unlike for all other properties and constituents sampled for in this study) call for samples to be collected using a single-vertical, midstream method (Shelton, 1994) rather than the EWI method. Whether the lack of similarity between manual and autosampler DOC and SOC concentrations indicated by the signed-rank tests is related to use of the single-vertical, midstream method rather than the EWI method is unknown; but the lack of similarity is enough to indicate caution in the use of autosamplers for DOC and SOC.

Caution in the use of autosamplers for suspended material in addition to SOC also might be prudent, on the basis of the apparent variability in the suspended sediment data (table 2). Additionally, total phosphorus, for which the signed-rank test indicated fairly strong evidence for a significant difference in paired concentrations, typically is associated with suspended material because phosphorus commonly attaches to soil particles. The amount of suspended material in streamflow often is related to discharge. Accordingly, the differences between manual and autosampler concentrations for SOC, suspended sediment, and total phosphorus were divided into two groups on the basis of discharge (larger or smaller) on the dates of sampling (table 1) and statistically tested to determine whether one group of differences was significantly larger than the other. The result of a Wilcoxon rank-sum test (also a two-sided hypothesis test) indicated no significant difference between the concentration differences of paired samples collected when discharges were larger and smaller (p-value = 0.333).

Table 2. Statistics of concentrations from paired water-quality samples collected at eight sites in the upper part of the South-Central Texas study unit

[difference, manual concentration minus autosampler concentration; $\mu\text{S}/\text{cm}$, microsiemens per centimeter at 25 degrees Celsius; mg/L , milligrams per liter; --, Wilcoxon signed-rank test not done because fewer than three data pairs with nonzero differences; $\mu\text{g}/\text{L}$, micrograms per liter]

| Property or constituent | Number of pairs with detections ¹ | Minimum concentration | Maximum concentration | Mean difference | Percent difference | 2-sided p-value ² |
|---|--|-----------------------|-----------------------|-----------------|--------------------|------------------------------|
| Specific conductance ($\mu\text{S}/\text{cm}$) | 16 of 16 | 404 | 878 | 0.50 | 0–4 | 0.648 |
| Alkalinity (as CaCO_3) (field) (mg/L) | 16 of 16 | 160 | 280 | –2.50 | 0–22 | .633 |
| Calcium, dissolved (mg/L) | 16 of 16 | 59 | 91 | –1.25 | 0–7 | .028 |
| Magnesium, dissolved (mg/L) | 16 of 16 | 12 | 20 | .06 | 0–7 | -- |
| Sodium, dissolved (mg/L) | 16 of 16 | 6.1 | 66 | 0 | 0–11 | .844 |
| Potassium, dissolved (mg/L) | 16 of 16 | .77 | 7.3 | .04 | 0–12 | .523 |
| Chloride, dissolved (mg/L) | 16 of 16 | 8.7 | 84 | .35 | 0–21 | .275 |
| Sulfate, dissolved (mg/L) | 16 of 16 | 14 | 71 | –.25 | 0–16 | .524 |
| Fluoride, dissolved (mg/L) | 16 of 16 | .12 | .46 | 0 | 0–13 | .865 |
| Silica, dissolved (mg/L) | 16 of 16 | 8.1 | 14 | –.15 | 0–10 | .124 |
| Manganese, dissolved ($\mu\text{g}/\text{L}$) | 2 of 16 | 13 | 16 | –.50 | 0–7 | -- |
| Ammonia nitrogen, dissolved (mg/L) | 14 of 16 | .0200 | .369 | .01 | 0–61 | .866 |
| Nitrite nitrogen, dissolved (mg/L) | 3 of 16 | .0120 | .108 | 0 | 0–20 | .500 |
| Nitrite plus nitrate nitrogen, dissolved (mg/L) | 15 of 16 | .292 | 11.3 | .03 | 1–63 | .868 |
| Ammonia plus organic nitrogen, dissolved (mg/L) | 7 of 16 | .10 | 1.0 | –.02 | 2–54 | .376 |
| Ammonia plus organic nitrogen, total (mg/L) | 7 of 16 | .11 | 1.1 | –.02 | 0–19 | .188 |
| Phosphorus, dissolved (mg/L) | 6 of 16 | .0100 | 1.73 | 0 | 1–38 | .156 |
| Phosphorus, total (mg/L) | 5 of 16 | .0160 | 1.82 | –.01 | 0–44 | .062 |
| Orthophosphate phosphorus, dissolved (mg/L) | 9 of 16 | .010 | 1.8 | .01 | 0–52 | .875 |
| Organic carbon, dissolved (mg/L) | 16 of 16 | .30 | 3.5 | –.19 | 0–93 | .020 |
| Organic carbon, suspended (mg/L) | 8 of 16 | .20 | 1.1 | –.16 | 0–120 | .062 |
| Suspended sediment (mg/L) | 16 of 16 | 6 | 105 | –3.06 | 11–105 | .195 |
| Atrazine ($\mu\text{g}/\text{L}$) | 6 of 6 | .010 | .56 | –.0080 | 0–90 | .266 |
| Benfluralin ($\mu\text{g}/\text{L}$) | 1 of 6 | .0035 | .0036 | .0001 | 3 | -- |
| Carbaryl ($\mu\text{g}/\text{L}$) | 1 of 6 | .0090 | .010 | –.0011 | 12 | -- |
| Chlorpyrifos ($\mu\text{g}/\text{L}$) | 3 of 6 | .0021 | .0052 | .0002 | 0–22 | -- |
| Desethyl atrazine ($\mu\text{g}/\text{L}$) | 6 of 6 | .0044 | .020 | –.0004 | 3–28 | .688 |
| Diazinon ($\mu\text{g}/\text{L}$) | 5 of 6 | .0010 | .063 | –.0008 | 0–300 | .500 |
| Diuron ($\mu\text{g}/\text{L}$) | 1 of 6 | .030 | .030 | 0 | 0 | -- |
| Lindane ($\mu\text{g}/\text{L}$) | 2 of 6 | .0090 | .013 | .0010 | 11–23 | -- |
| Malathion ($\mu\text{g}/\text{L}$) | 1 of 6 | .019 | .020 | .0010 | 5 | -- |
| Metolachlor ($\mu\text{g}/\text{L}$) | 3 of 6 | .0040 | .0050 | .0003 | 0–20 | -- |
| <i>p,p'</i> -DDE ($\mu\text{g}/\text{L}$) | 1 of 6 | .0030 | .0033 | –.0003 | 10 | -- |
| Prometon ($\mu\text{g}/\text{L}$) | 5 of 6 | .0037 | .040 | 0 | 3–36 | 1.0 |
| Simazine ($\mu\text{g}/\text{L}$) | 3 of 6 | .0051 | .018 | .0009 | 6–15 | .250 |
| Tebuthiuron ($\mu\text{g}/\text{L}$) | 4 of 6 | .0070 | .15 | .0060 | 0–11 | .250 |

¹ Constituent concentrations less than reporting limits omitted from datasets before computation of statistics and Wilcoxon tests.

² p-value from exact Wilcoxon signed-rank test for all properties and constituents except suspended sediment because all property and constituent pairs except suspended sediment had fewer than 16 nonzero differences (Helsel and Hirsch, 1992, p. 144). Suspended sediment p-value from large-sample approximation by statistical software.

The results of the statistical tests indicate that autosamplers probably could be used in place of manual sampling methods for dissolved constituents. This conclusion is qualified because of the signed-rank-test results for dissolved calcium and organic carbon, which indicated significant differences in paired concentrations, and the fact that the dataset analyzed is small—3 to 16 paired concentrations for each of the 26 properties and constituents.

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