Appendix 3—Quality-Assurance/Quality-Control Data

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Quality control (QC) for this study included servicing and calibration of the continuous water-quality monitor used to record the physicochemical properties, collection of field QC samples (blanks, replicates, and spikes), and laboratory QC analyses (surrogate additions and low-level pesticide calibration standards). About 16 percent of samples analyzed were field QC samples. At least one type of QC sample was collected for each type of analysis: dissolved ions and alkalinity titrations, nutrients, dissolved elements, soluble pesticides, and volatile organic compounds (VOCs).

Physicochemical Properties

The continuous multiparameter water-quality monitor installed in Main Spring was serviced 36 times from July 2003 through July 2005. For servicing, the monitor was removed from the spring orifice, sensors were cleaned, and sensor measurements were verified against standard solutions and adjusted if necessary. The median time between servicing was 21 days. The longest time between servicing (39 days in November 2004) was caused by flooding in Barton Creek, and the shortest time between servicing (3 days in January 2005) was caused by poor sensor performance shortly after deployment.

Continuous data were rated mostly good to excellent, with some rated fair to poor, as defined by Wagner and others (2000). All water temperature data were rated excellent, as values were always within 0.1 degree Celsius of standard values. pH data showed systematic drifting during each deployment, but still were rated good (within 0.5 unit of standard values). Specific conductance data were within 2 percent of standard values (rated good) except for servicing before October 2003; during this time, faulty standard solutions caused a bias of between 10 and 15 percent (rated fair). Turbidity data were rated mostly fair to poor (greater than 10 percent outside standard values), and dissolved oxygen data were rated fair to poor (greater than 0.8 milligram per liter [mg/L] outside standard values).

Specific conductance and temperature data were available for 95 percent of the study period, turbidity for 75 percent, pH for 71 percent, and dissolved oxygen for 68 percent. Data rated as poor were omitted from the reported dataset, and other small gaps in the dataset were caused by either sensor servicing or data transmission errors. As in many continuous water-quality monitoring studies, turbidity and dissolved oxygen sensors were prone to frequent fouling and reliability problems. For example, dissolved oxygen sensors were faulty for 17 percent of all servicing events.

Chemical Data

QC of environmental samples consisted of analysis of field blanks, replicates, and spiked samples; surrogate additions; and low-level pesticide calibration standards. Field blanks were collected by filling the sample container with laboratory certified blank water at the field site, after which the field blanks were treated identically to environmental samples. Replicate samples were collected identically and immediately subsequent to environmental samples. Spiked samples were collected identically to environmental samples, and the spike solution was added either at the U.S. Geological Survey (USGS) Texas Water Science Center laboratory in Austin (for soluble pesticide analysis) or at the USGS National Water Quality Laboratory (NWQL) (for VOC and pharmaceutical analysis). Surrogate additions were performed at the NWQL and were added to all samples. Low-level pesticide calibration standards, prepared by the NWQL at concentrations very close to the laboratory reporting level for each compound, were analyzed at the beginning and end of each analytical run of 10 samples.

Major Ions

Six blank samples were analyzed for major ions. No ions were detected above the reporting level in five of six blank samples. In the blank sample in which major ions were detected, the concentrations were less than 1 percent of the minimum concentration detected in any environmental sample.

Twelve sets of replicate samples were analyzed for major ions (fig. 3.1). Of 105 major ion replicate sample measurements, 103, or 98 percent, were within 5 percent of the corresponding environmental sample measurement. The two replicate measurements that differed by more than 5 percent were for dissolved potassium and differed from the corresponding environmental sample by 7.2 and 9.9 percent, respectively.

Twenty-four replicate samples were analyzed for alkalinity, expressed as bicarbonate (fig. 3.1). Twenty-one (88 percent) replicate sample results for alkalinity were within 5 percent of the corresponding environmental sample result. The three replicate measurements that differed by more than 5 percent from the corresponding environmental measurement had respective differences of 8.4, 12.7, and 15.3 percent.

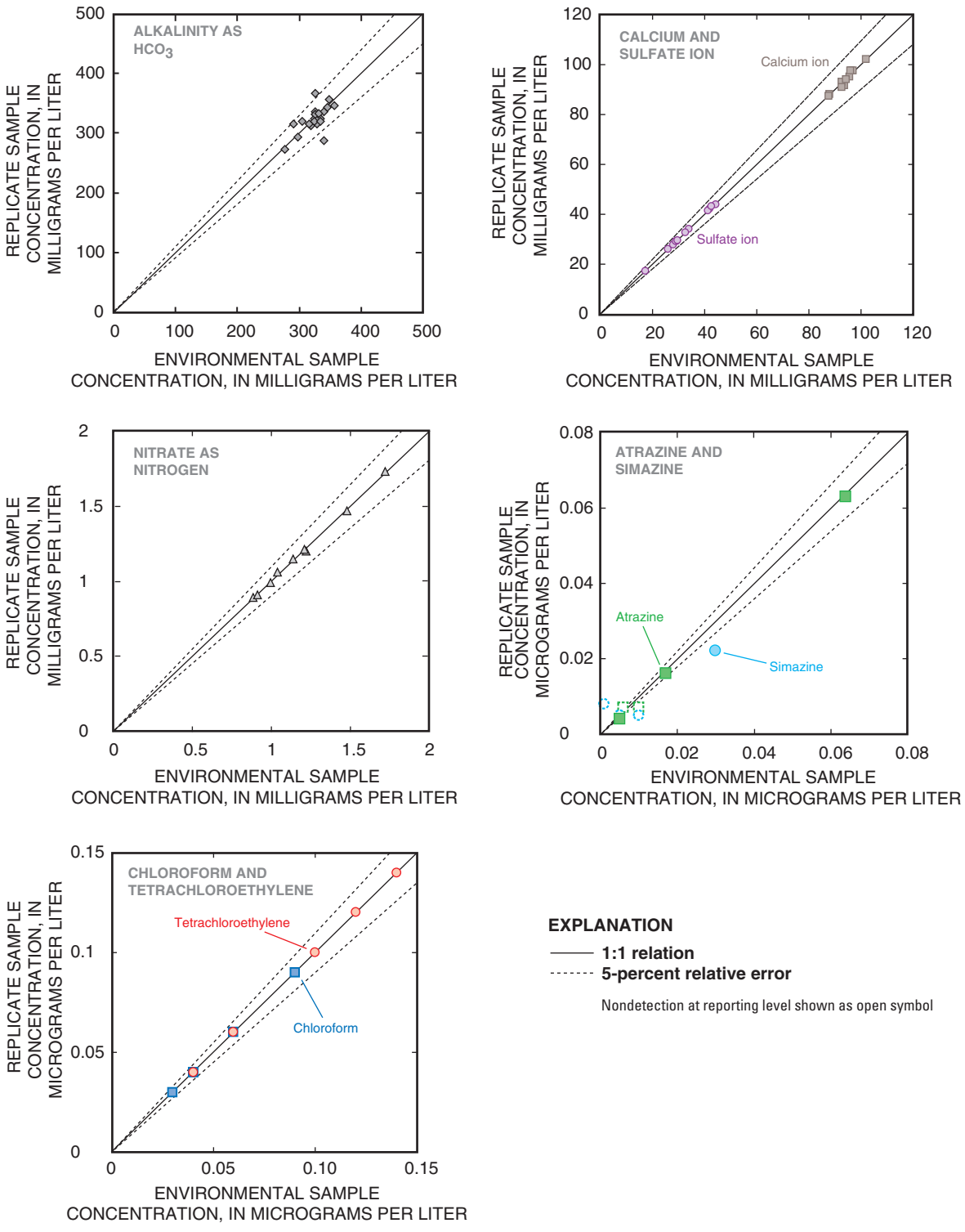

Figure 3.1. Comparison of concentrations of selected major ions, nutrients, pesticides, and volatile organic compounds in environmental and replicate samples from Barton Springs, Austin, Texas.

Nutrients

Seven blank samples were analyzed for nitrite plus nitrate nitrogen, and one was analyzed for the full suite of nutrients. None of the nutrients analyzed were detected in any of the blank samples.

Nine replicate samples were analyzed for nitrite plus nitrate (fig. 3.1), and two were analyzed for the full suite of nutrients. Concentrations of nitrate in the replicate samples were within 5 percent of the concentrations in the corresponding environmental measurement. Concentrations of the other nutrients were detected at concentrations within 5 percent of each other, were below the reporting level in both the environmental and replicate sample, or were not detected in either the replicate or environmental sample but were detected at a concentration at or below the reporting level in the corresponding sample.

Dissolved Trace Elements

In the two blank samples analyzed for dissolved trace elements (metals), dissolved elements either were not detected or were detected below the reporting level, except for chromium. Chromium was detected in one of the two blank samples at a concentration of 1.9 micrograms per liter (µg/L) but either was not detected or was detected below the reporting level in all environmental samples.

One replicate sample was analyzed for dissolved trace elements. Two of the seven metals (arsenic and copper) were detected in the replicate sample at a concentration identical to that in the corresponding environmental sample. Chromium was not detected in the environmental sample but was detected at a concentration below the reporting level in the environmental sample. Cadmium, lead, and zinc were not detected in either sample. The replicate measurement for dissolved nickel differed by 7.1 percent from the concentration in the corresponding environmental sample.

Soluble Pesticides

Seven blank samples were analyzed for 52 dissolved pesticides with no corresponding pesticide detections. Five replicate samples (fig. 3.1) were analyzed for 52 dissolved pesticides. Two hundred and fifty of the 260 individual pesticide analyses (96 percent) resulted in a nondetection in both the environmental and replicate samples. Only atrazine (four detections), deethylatrazine (DEA) (four detections), and simazine (two detections) were detected in the replicate sample or corresponding environmental sample, or both. Of these 10 constituent measurements resulting in a detection in the replicate sample or corresponding environmental sample, or both, two were nondetections in one sample and a detection below the reporting level in the corresponding sample. Two sets of samples agreed within 5 percent of each other. Four sets had relative percent differences exceeding 5 percent but were within one unit of precision of each other (for example, 0.011 and 0.012 µg/L); because the differences could result from rounding errors it was assumed not significant. The remaining two sets of measurements were for simazine and DEA. Simazine had a relative percent difference of 30 percent in one set of replicate samples (0.030 compared to 0.022 µg/L in the environmental and replicate sample, respectively). In the same sample, DEA was detected at 0.009 µg/L in the environmental sample but not detected at the reporting level of 0.006 µg/L in the replicate sample. Thus, in both cases, the replicate sample had a lower concentration than the environmental sample. During this sample run, the concentration of simazine and DEA detected in the low-level calibration standard increased from the beginning of the run to the end of the run by 20 and 12 percent, respectively. It is possible that the efficiency of detection of these two compounds decreased during the sample run and affected the concentrations reported.

Three spiked samples were analyzed for dissolved pesticides. Spike recovery is determined by comparing the concentration measured in the spiked sample to that measured in the corresponding environmental sample. Although all spiked compounds resulted in a detection, in most cases the compounds were not detected in the corresponding environmental sample. The possible concentration of a nondetected compound in the environmental sample is thus somewhere between zero and the reporting level; assuming a concentration of zero in the environmental sample results in the highest possible spike recovery, and assuming a concentration at the reporting level

Table 3.1. Pesticide spike recovery ranges for pesticides detected at least once in any environmental sample from the Barton Springs segment of the Edwards aquifer, Texas.

Pesticide	Percentage recovery range assuming zero concentration for nondetections in environmental samples	Percentage recovery range assuming reporting level for nondetections in environmental samples
Atrazine	114–133	108–133
Carbaryl	139–181	101–148
Deethylatrazine	33–43	33–40
Diazinon	96–108	92–103
Metolachlor	105–115	95–110
Prometon	111–120	102–112
Simazine	108–120	104–120

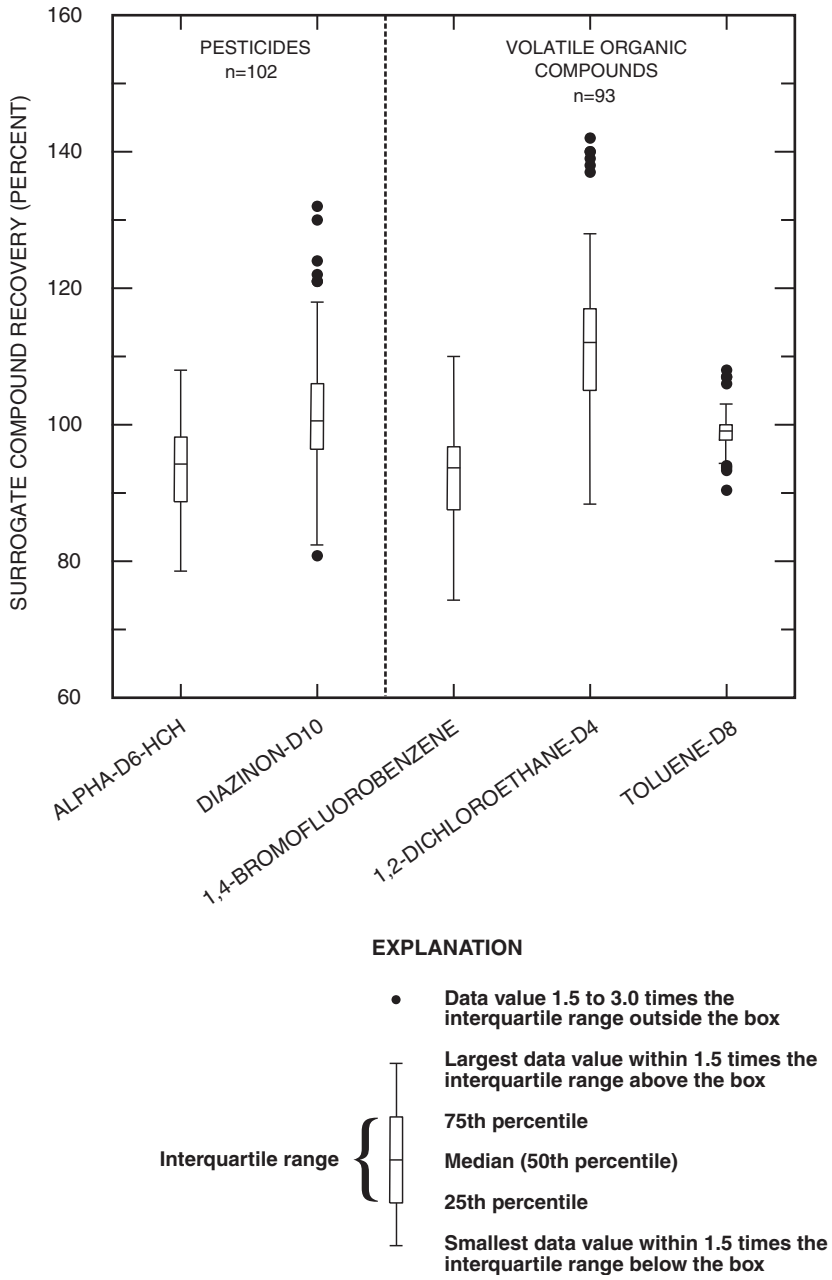

Figure 3.2. Distribution of the percentage of pesticide and volatile organic compound surrogate recovery in environmental samples from Barton Springs, Austin, Texas.

results in the lowest possible recovery (table 3.1). Of the 52 pesticide compounds analyzed, the median recovery for 41 of the compounds was between 80 and 120 percent. Median recoveries for eight compounds were less than 80 percent and for four compounds were more than 120 percent. Of the pesticides detected in the environmental samples, only the median recoveries of DEA and carbaryl were outside the 80- to 120-percent median recovery range. Recovery of carbaryl tended to be high, and recovery of DEA was consistently quite low. These compounds and carbofuran, terbacil, and methyl azinphos have not performed well with this analytical schedule, and results are generally marked by the NWQL as estimated (http://wwwnwql.cr.usgs.gov/USGS/WWW2001/2001FAQ.html#evalu).

The surrogate compounds α-d6-HCH and diazinon-d10 were added to all pesticide samples analyzed at the NWQL. A surrogate is a compound that is expected to perform similarly to the compounds being analyzed in a laboratory method. The

surrogate normally is not found in the environment and therefore can be used to monitor the recovery efficiency of the analysis; the NWQL adds surrogate compounds to all environmental and QC samples to monitor compound recovery and potential environmental effects. All recoveries of α-d6-HCH were within acceptable levels as set by the NWQL. All surrogate recoveries for diazinon-d10 except for one were within acceptable levels as set by the NWQL. The exception was a recovery of 124 percent, which exceeded the NWQL maximum acceptable recovery for that run by 1 percent (fig. 3.2).

Table 3.2. Volatile organic compound (VOC) spike recovery ranges for VOCs detected at least once in any environmental sample from the Barton Springs segment of the Edwards aquifer, Texas.

VOC	Percentage recovery range assuming zero concentration for nondetections in environmental samples	Percentage recovery range assuming reporting level for nondetections in environmental samples
Bromodichloromethane	107–129	97–122
Carbon disulfide	78–92	74–87
Chloroform	112	99–119
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113)	90–128	78–119
Isopropyltoluene	78–107	66–99
Tetrachloroethene	110	91–110
Trichloroethane	103–123	101–117
Trichloroethene	99–112	94–103
Toluene	101–109	90–105

Volatile Organic Compounds

Five blank samples were analyzed for VOCs. None of the VOCs analyzed were detected in any blanks, except for one estimated acetone detection at a concentration below the reporting level.

Five replicate samples were analyzed for VOCs (fig. 3.1). Of the 425 total replicate measurements, 412 were nondetections. Of the 13 VOC detections, 12 had identical concentrations in the replicate sample and corresponding environmental sample, and one VOC (carbon disulfide) was not detected in the environmental sample but was detected at a concentration below the reporting level in the replicate sample.

Two spiked samples were analyzed for VOCs. Similar to pesticides, there were numerous nondetections in the environmental sample corresponding to a spiked sample, and two sets of recoveries were computed for nondetections, one assuming a concentration of zero and one assuming a concentration at the reporting level (table 3.2) in the environmental sample. The median recoveries were between 80 and 120 percent for 78 compounds; six compounds had median recoveries below 80 percent, and one compound had a median recovery greater than 120 percent. None of the seven compounds outside the 80- to 120-percent range were detected in any environmental samples.

Three surrogate compounds were added to all VOC samples at the NWQL: 1,4-bromofluorobenzene, 1,2-dichloroethane-d4, and toluene-d8. All surrogate recoveries were within the acceptable levels as set by the NWQL (fig. 3.2).

Pharmaceutical Compounds

Two blank samples were analyzed for 24 pharmaceutical compounds; no pharmaceutical compounds were detected in either sample. One replicate sample was analyzed for 24 pharmaceutical compounds; no compounds were detected.

One spiked sample was analyzed for pharmaceuticals. The spike recovery analysis was performed using the same approach as for pesticide spikes. Twenty-two pharmaceuticals were analyzed for spike recovery, with a median recovery for all compounds of 60 percent. Five compounds had recoveries between 80 and 120 percent, and five compounds had recoveries of less than 40 percent. The analytical method for pharmaceuticals was still in development during this study period, thus the analytical results are interpreted only as detections and nondetections.