

Appendix 3. Sampling and analytical methods and summary of field quality control data for chemical contaminants measured in domestic wells sampled for the NAWQA Program, 1991–2004

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Sampling and Analytical Methods

The sampling methods used in the NAWQA assessment studies are described in Koterba and others (1995), U.S. Geological Survey (variously dated), Kolpin and others (1998), Embrey and Runkle (2006), and Moran and others (2006). Wells were pumped until a minimum volume of water was removed (at least three well-casing volumes in most cases) and the field measurements of pH, water temperature, specific conductance, and dissolved oxygen had stabilized. After diversion from the well, the water contacted only Teflon, stainless steel, glass, or aluminum materials and was processed in an environmental chamber to minimize contamination. A low flow rate (about 0.1 gallon or 500 milliliters per minute) was used for sampling. Equipment was cleaned after sampling following procedures described in Koterba and others (1995). Samples were analyzed for alkalinity, major ions, nutrients, dissolved organic carbon, trace elements, pesticides, VOCs, and radon; for some wells, the samples were analyzed for fecal indicator bacteria, gross alpha- and beta-particle radioactivities, and radium.

Samples collected for analysis of alkalinity, major ions, dissolved nutrients, trace elements, gross alpha- and beta-particle radioactivities, and radium were filtered on site through 0.45-micron capsule or plate filters. Samples for analysis of major cations and trace elements were preserved with nitric acid to pH less than 2; samples for analysis of major anions were not preserved. Samples for analysis of nutrients were collected in brown polyethylene bottles and were immediately chilled on ice for shipment to the laboratory. Before 1995, nutrient samples were preserved using mercuric chloride for all analytes; thereafter, samples were not preserved except for those for analysis of total concentrations, which, after 1998, were preserved with sulfuric acid to pH less than 2. Samples collected for analysis of pesticides were filtered through 0.7-micron baked glass-fiber filters into amber-colored glass bottles and were immediately chilled. Samples for analysis of VOCs, radon, and fecal indicator bacteria were not filtered. VOC samples were collected into 40-milliliter septum vials with no headspace, preserved with hydrochloric acid to pH less than 2, and immediately chilled. Radon samples were collected using a pressurized in-line sampling assembly and a gas-tight syringe and were injected into glass scintillation vials below mineral oil. Samples for analysis of dissolved organic carbon were filtered through 0.45-micron silver membrane filters, and silver from the filters served as a preservative; samples were immediately chilled on ice. Samples for analysis of fecal indicator bacteria were collected in sterile, amber-colored bottles and immediately chilled.

The physical properties pH, water temperature, specific conductance, and dissolved oxygen were measured at the time of sampling in a flow-through chamber using methods described in the U.S. Geological Survey National Field Manual (U.S. Geological Survey, variously dated). Alkalinity (carbonate alkalinity) was determined on site with incremental

titration with sulfuric acid (Koterba and others, 1995; U.S. Geological Survey, variously dated). For about 25 percent of samples in this study, alkalinity [in mg/L as calcium carbonate (CaCO_3)] was calculated from reported bicarbonate concentrations. Samples collected for analysis of the fecal indicator bacteria, total coliform bacteria and *Escherichia coli* (*E. coli*), were processed on site within 6 hours of collection (U.S. Geological Survey, variously dated; Embrey and Runkle, 2006). Total coliform bacteria were enumerated using mENDO medium (method 9222B, American Public Health Association and others, 1992) or MI medium (method 1604, U.S. Environmental Protection Agency, 2002c); *E. coli* were enumerated using NA-MUG medium (method 9222G, American Public Health Association and others, 1992), mTEC medium (method 1103.1, U.S. Environmental Protection Agency, 2002b), or MI medium.

Water samples were analyzed at the USGS National Water Quality Laboratory (NWQL) in Lakewood, Colorado, for inorganic and organic analytes. The inorganic analytes and methods used were: major ions, by atomic absorption spectrometry (AA), colorimetry, or inductively-coupled plasma (ICP) (Fishman and Friedman, 1989; Fishman, 1993); nutrients, by various methods (Fishman, 1993; Patton and Truitt, 2000); trace elements, by ICP-atomic emission spectroscopy (ICP-AES), ICP-mass spectrometry (ICP-MS), graphite-furnace AA, or hydride generation AA (Fishman and Friedman, 1989; Faires, 1993; McClain, 1993; Garbarino, 1999); and radon, by liquid scintillation (American Society for Testing and Materials, 1996). Dissolved organic carbon was analyzed by ultraviolet-light-promoted persulfate oxidation and infrared spectrometry (Brenton and Arnett, 1993). Iron and manganese were analyzed using methods for major ions and trace elements; data used in this study were the results of the trace-element methods because these had lower reporting limits than the methods for major ions. Nitrate was analyzed as nitrite plus nitrate; however, nitrite concentrations were very low, averaging less than 0.1 percent of nitrite plus nitrate concentrations. Consequently, nitrite plus nitrate is referred to as nitrate in this report.

Pesticides were analyzed by two methods at the NWQL: 47 pesticides were analyzed by solid-phase extraction using a C-18 cartridge and gas chromatography/mass spectrometry (GCMS) (Zaugg and others, 1995), and 36 pesticides and pesticide degradates were analyzed by graphitized carbon-based solid-phase extraction and high-performance liquid chromatography/mass spectrometry (HPLC) (Werner and others, 1996; Furlong and others, 2001). Data in this study for carbaryl, carbofuran, and linuron, which were analyzed by both methods, were the results of analysis by GCMS. Results from HPLC analyses during March 1999 to March 2000, in which sample holding times were exceeded (E.T. Furlong and others, U.S. Geological Survey, written commun., 2003), were excluded from the study. Nearly all VOCs were analyzed using purge and trap capillary column GCMS (Rose and Schroeder, 1995; Connor and others, 1998). Another method (USGS 0-3120-90; Fishman, 1993) was sometimes used

for ethylene dibromide (EDB) and dibromochloropropane (DBCP) to achieve lower detection limits for these compounds (Moran and others, 2005). Gross alpha- and beta-particle radioactivity were analyzed at the NWQL by low background Planchet counting post-evaporation (USEPA method 900.0, U.S. Environmental Protection Agency, 1980). Radium isotopes (radium-226 and radium-228) were analyzed by coprecipitation and alpha planchet counting, radon de-emanation, or beta counting after progeny ingrowth (U.S. Environmental Protection Agency methods 903.0, 903.1, and 904.0, respectively; U.S. Environmental Protection Agency, 1980) or by alpha and gamma spectral methods (Focazio and others, 2001; Szabo and others, 2005; Zoltan Szabo, U.S. Geological Survey, written commun., 2007).

Analytical results from the NWQL for the analytes measured during the study period were given using several reporting conventions. Major ions, nutrients, trace elements, and radon were reported primarily in terms of minimum reporting levels (MRLs). MRLs were defined for the NWQL as the minimum concentration of a constituent that can be reliably measured with an analytical method (Childress and others, 1999). MRLs for individual analytes were established using various methods that may have included statistical analysis of quality-control samples. Pesticides and VOCs were reported relative to MRLs that were statistically determined and, towards the end of the study period, relative to long-term method-detection levels (LT-MDLs). The LT-MDL is similar to the method detection level (MDL) defined by the U.S. Environmental Protection Agency in that it is statistically determined as the minimum concentration of an analyte that can be measured and reported with 99-percent confidence that the concentration is greater than zero (Childress and others, 1999). In other words, for analytical results at or above the MDL or LT-MDL, there is at most a 1-percent chance that an analyte is reported as detected when it is not there (false positive). The LT-MDL differs from the USEPA-defined MDL in that it accounts for more potential sources of variability, for example, from multiple analytical instruments and operators; the LT-MDL is recalculated each year. For methods that incorporated the use of LT-MDLs, analytical results were reported in terms of LT-MDLs and laboratory reporting levels (LRLs). The LRL is the concentration at which there is no more than a 1-percent chance that an analyte will not be detected when it is actually present (false negative; the chance of false negatives occurring at the LT-MDL is 50 percent). The LRL is about two times higher than the LT-MDL. For methods that use LT-MDLs, non-detections were reported relative to the LRL by the NWQL and were stored in this way in the NAWQA Data Warehouse; positive detections at concentrations less than the LRL were not censored but were reported as estimated values (Childress and others, 1999). Analytical results less than the lowest calibration standard or greater than the highest calibration standard also were reported as estimated. The uncertainty associated with estimated values is expected to be higher than that of other, unqualified concentrations (Childress and others, 1999). In this study, estimated values were used without

qualification, and non-detections that were reported relative to LRLs were redefined relative to their associated LT-MDLs using information on historical LT-MDLs for analytical methods from the NWQL. The LT-MDL and LRL reporting conventions were phased into use at the NWQL beginning in October 1998. Radon, near the end of the study period, and radium isotopes, throughout the study period, were reported relative to sample-specific minimum detectable concentrations (SSMDC; Zoltan Szabo, U.S. Geological Survey, written commun., 2006).

Summary of Field Quality Control Data

Field Quality Control Data Overview

The collection of field quality-control (QC) samples was an integral part of NAWQA assessment studies. For each assessment study of about 25 to 30 wells, the study design included routine collection of at least 2 to 3 field blanks for all analytes except radionuclides; 2 to 3 replicates for major ions, nutrients, trace elements, and radon; 2 to 3 field-spiked samples and field-spike replicates for pesticides and VOCs; 1 source-solution blank for DOC, and trip blanks and (or) source-solution blanks for VOCs (Koterba and others, 1995). Field blanks were collected by passing water that did not contain the analyte(s) of interest (except for some VOCs) through sampling equipment in the field; these can be used to assess the introduction of contamination into environmental samples during sampling and analysis. Trip blanks can be used to assess contamination from sample shipping and handling. Replicate samples are sequentially collected ground-water samples, which can be used to assess the effects of sampling and analysis procedures on measurement variability. Field-spiked samples are environmental samples to which a known amount of the analyte(s) of interest was added in the field; these can be used to assess bias from matrix interferences or analyte loss during sample holding and processing. Spiked samples also were routinely prepared in the laboratory using environmental samples or other solutions. The USGS Branch of Quality Systems also routinely submitted and analyzed the results from blind samples for inorganic and organic analytes to the USGS NWQL during the study period (<http://bqs.usgs.gov>). Field QC sample data have been evaluated in reports by individual study units (<http://water.usgs.gov/nawqa>) and also have been evaluated at the national scale for nutrients, trace elements, pesticides, VOCs, fecal-indicator bacteria, and radionuclides. QC results for various contaminants in ground water sampled in the NAWQA Program are described in this section; the discussion is based on summaries at the national scale, where available.

Environmental data determined to be affected by contamination are specifically identified in the NAWQA Data Warehouse ("V-coded" data); these data were not used in the

present study of domestic-well water quality. Criteria for identifying these data were as follows: there was direct evidence of contamination, concentrations were significant compared to environmental concentrations, and the contamination was well understood, for example in terms of source and magnitude (U.S. Geological Survey, 1997). Analyses of field blanks, of other QC samples, and of sampling processes were used by study unit and national synthesis personnel to identify data that were affected by contamination. Environmental data were rarely V-coded; about 0.1 percent of analytical results (excluding radionuclides or fecal indicator bacteria) for the domestic wells in the present study received the V-code designation. Analytes with the most V-coded analyses included (in descending order) aluminum, chloroform, 1,2,4-trimethylbenzene, zinc, ammonia, tetrachloroethene, copper, orthophosphate, 1,2-dichloropropane, toluene, chromium, nitrite plus nitrate, and several other VOCs.

Major Ions

Concentrations of major ions in water samples from domestic wells appeared unaffected by contamination and were reproducible based on a review of field QC data described in reports from 20 NAWQA study units. Most major ions were either not detected in blank samples or were detected at concentrations much lower than those in environmental samples (for example, see Menheer and Brigham, 1997; Hamlin and others, 2002; Bruce and McMahon, 1998; Reutter and Dunn, 2000; Fong and others, 1998; Apodaca and Bails, 2000). Silica was detected in blanks in a few study units at concentrations near those in environmental samples (Savoca and others, 1999; Inkpen and others, 2000), but these findings were not widespread. The variability of measured concentrations of major ions was low, with relative percent differences (RPDs) of replicate pairs nearly always less than 10 percent; larger RPDs sometimes occurred when concentrations were near MRLs (for example, see Coes and others, 2000; Glass, 2001; Pope and others, 2001; Robinson, 2003; Bexfield and Anderholm, 1997; Milby-Dawson, 2001). In many cases, RPDs of replicate pairs were less than 5 percent.

Trace Elements

QC data for 23 trace elements were evaluated at the national scale to estimate bias and variability in all water samples collected by the NAWQA Program from 1991 to 2002 (Apodaca and others, 2006). The number of field blanks and replicates varied by trace element, but there were about 350 blanks and about 275 to 350 replicate-sample pairs for most trace elements. Potential contamination in ground-water samples was estimated from field blanks with 95-percent confidence to be less or near 1 mg/L in 95 percent of samples for many trace elements; this value (1 mg/L) was the MRL for many trace elements. Potential contamination for antimony, arsenic, beryllium, cadmium, cobalt, lead, molybdenum,

nickel, selenium, silver, thallium, and uranium was estimated to be less than 1 mg/L in 95 percent of samples; for barium, chromium, and manganese, potential contamination was estimated to be at or near 1 mg/L in 95 percent of samples. The potential for contamination was relatively large for aluminum, boron, and zinc. Potential contamination for these three trace elements was estimated with 95-percent confidence to be at or greater than 1 mg/L in at least 50 percent of samples, and concentrations greater than 9 mg/L for aluminum, 15 mg/L for boron, and 18 mg/L for zinc were estimated to occur in at least 5 percent of samples. Potential contamination for copper, iron, and strontium was estimated to be at or greater than 1 mg/L in 75 to 85 percent of samples. Too few field blanks were collected for lithium or vanadium to estimate potential contamination for these trace elements. Except for aluminum, the concentration levels for potential contamination in samples analyzed for trace elements were less than one-tenth of any drinking-water standards at the 95- or 99-percent confidence levels (Apodaca and others, 2006). Variability, represented by the mean relative standard deviation (RSD) for all concentration ranges, was estimated to be less than 10 percent for antimony, arsenic, barium, boron, cobalt, iron, lithium, manganese, molybdenum, strontium, and uranium; variability was less than or equal to 15 percent for the remaining trace elements aluminum, cadmium, chromium, copper, lead, nickel, selenium, vanadium, and zinc. Variability could not be estimated for beryllium, silver, or thallium because there were too few replicate pairs. This analysis indicates that potential contamination and variability are unlikely to affect interpretations in this report for most trace elements at the national scale.

Nutrients

A national-scale evaluation of field QC data indicated that little significant contamination had occurred from field or laboratory procedures and low variability for nutrients in all ground-water samples collected for the NAWQA Program (Mueller and Titus, 2005). The analysis was based on 541 field blanks and 520 replicate sample pairs collected along with environmental samples from 1991 through 2001. For nitrite plus nitrate, ammonia plus organic nitrogen, orthophosphate, and total phosphorus, potential contamination was estimated to be near the associated MRLs in at least 80 percent of environmental samples, and near the MRLs in at least 75 percent of samples for ammonia. Potential contamination in 95 percent of samples was estimated with 99-percent confidence to be less than 0.09 mg/L as N for nitrite plus nitrate, less than 0.044 mg/L as N for ammonia, less than the MRL of 0.2 mg/L as N for ammonia plus organic nitrogen, and less than 0.02 mg/L as P for orthophosphate. Variability was estimated separately for low and high concentration ranges using the standard deviation (SD; low concentrations) or RSD (high concentrations) of replicate-sample pairs. For high concentrations, average variability was estimated to be 2.9 percent for

nitrite plus nitrate (concentrations greater than 1 mg/L as N), 1.3 percent for ammonia (concentrations greater than 0.3 mg/L as N), 7.8 percent for ammonia plus organic nitrogen (concentrations greater than 0.5 mg/L as N), and 10 percent for orthophosphate (concentrations greater than 0.1 mg/L as P). For low concentrations, variability was estimated to be 0.043 mg/L as N for nitrite plus nitrate, 0.0047 mg/L as N for ammonia, 0.022 mg/L as N for ammonia plus organic nitrogen, and 0.0039 mg/L as P for orthophosphate.

Radon and Other Radionuclides

The variability of radon was estimated from 343 replicate ground-water sample pairs collected by the NAWQA Program from 1991 to 2002 (Apodaca and others, 2006). The mean SD for low concentrations of radon (about 45 to 700 pCi/L) was 19.9 pCi/L, and the mean RSD for high concentrations (about 700 pCi/L to about 200,000 pCi/L) was 5.9 percent, indicating that radon results were reproducible with low variability at most concentrations. The quality of radium-226 and radium-228 data is described in Zoltan Szabo, U.S. Geological Survey, written commun., 2006.

Organic Compounds

Pesticides

Potential contamination in pesticide samples collected by NAWQA was investigated by Martin (1999a and 1999b) using field blanks collected during 1992–95. Most ground-water field blanks during this time had no detections of any pesticide compound (89 and 98 percent of blanks analyzed by GCMS and HPLC, respectively), and most compounds were not detected in any blank. Overall, pesticides of any kind were detected in 0.3 percent of the analyses of pesticides in blank samples (33 detections in 10,458 analyses). Thirty-two of 47 pesticides analyzed using GCMS were not detected in any field blanks (n equal to 145), and 33 of 37 pesticides analyzed using HPLC were not detected in field blanks (n equal to 98–104). The most frequently detected pesticides in field blanks were p,p'-DDE (4.1 percent), atrazine (2.8 percent), and benfluralin, chlorpyrifos, metolachlor, simazine, and triallate (1.4 percent each); all others were detected in 1 percent or less of field blanks. Greater use in the environment and lower detection limits for pesticides determined using the GCMS method, compared to the HPLC method, likely explained the higher frequency of detections in blanks with the GCMS method (Martin, 1999a). Detected concentrations were very low; maximum concentrations of individual pesticides in ground-water field blanks ranged from 0.001 $\mu\text{g/L}$ (estimated) to 0.02 $\mu\text{g/L}$. The potential contamination indicated by these low detection frequencies and concentrations of pesticides in field blanks could affect interpretations of environmental data, however, for compounds that occur with comparable low

frequency and concentrations, such as bromacil, benfluralin, chlorpyrifos, dacthal, p,p'-DDE, diazoxon, diuron, fenuron, *cis*-permethrin, pronamide, propanil, triallate, and trifluralin (Martin, 1999a). Maximum concentrations of any pesticides detected in field blanks were two to four orders of magnitude less than drinking-water standards or other human-health-based screening levels (except for p,p'-DDE, for which the health standard was 50 times the maximum concentration in blanks), indicating that potential contamination was negligible when evaluating concentrations of potential concern for human health.

The variability of detections and concentrations in pesticide samples collected for the NAWQA Program was investigated using field replicate samples collected during 1992–97 by Martin (2002). The assessment was based on 335 replicate sets of samples for GCMS analysis and 253 replicate sets for HPLC analysis, and included surface- and ground-water samples. The variability of pesticide detections was described by calculating the percentage of replicate sets with inconsistent detections for each pesticide compound (that is, sets in which a pesticide compound is detected in one replicate sample but not in the other), using all detections, including those less than the laboratory MRLs or MDLs. The percentage of inconsistent replicate sets generally decreased with increasing pesticide concentration; it was more likely that compounds would have been detected if they were present in the sample at higher concentrations. For all replicate sets analyzed for all pesticides, the overall rates of inconsistent replicates were 60 percent for pesticide concentrations less than MRLs or MDLs, 14 percent for concentrations at or within an order of magnitude of MRLs or MDLs, and 1 percent for concentrations greater than 10 times the MRLs or MDLs. The variability of measured pesticide concentrations also decreased with increasing concentrations. The typical variability of pesticide concentrations in the data set studied, measured by the median pooled RSD of field replicates with consistent detections, was 11 to 15 percent for concentrations less than 1 $\mu\text{g/L}$ and less than 10 percent for concentrations greater than 1 $\mu\text{g/L}$ (Martin, 2002).

The bias from matrix interferences or analyte loss during sample shipment or holding was investigated using field and laboratory spiked samples and other laboratory QC data. Median recovery for most pesticides analyzed by GCMS and HPLC ranged from 70 to 106 percent for field matrix spiked samples (61 pesticides) and laboratory reagent spikes (70 pesticides) collected during 1992–96 (Martin, 1999b). For several pesticides, laboratory QC data indicated that analytical results were considered to be negatively biased or unusually variable, and were qualified as “estimated” (Zaugg and others, 1995; Werner and others, 1996; U.S. Geological Survey, 1998; Gilliom and others, 2006). These pesticides were azinphosmethyl, carbaryl, carbofuran, deethylatrazine and terbacil (analyzed by GCMS) and aldicarb, aldicarb sulfone, aldicarb sulfoxide, chlorothalonil, dichlobenil, and 2-methyl-4,6-dinitrophenol (analyzed by HPLC).

Volatile Organic Compounds

Potential contamination of VOC samples collected for the NAWQA Program was investigated using analyses of blank samples collected during three periods during 1997–2005. About 70 percent (64) of all VOCs analyzed were detected infrequently (less than 1 percent) or not at all in field blanks (total n equal to 519; J.S. Zogorski and D.A. Bender, U.S. Geological Survey, written commun., 2008). Of the remaining VOCs, 11 were detected in 1 to 5 percent of field blanks and 11 were detected in more than 5 percent of field blanks. The VOCs detected in more than 5 percent of field blanks were (in decreasing order) toluene, 1,2,4-trimethylbenzene, *m*- and *p*-xylenes, chloroform, ethylbenzene, acetone, dichloromethane, benzene, styrene, carbon disulfide, and *o*-xylene. Because of several factors, including the presence on occasion of some VOCs in the blank water used to process field blanks (Taglioli and others, 2000) and the effectiveness of sampling-equipment rinsing with well water prior to the collection of a ground-water sample in eliminating this and other potential contamination sources, the results for the field blanks overstate the potential for random contamination associated with field protocols in ground-water samples. Analysis of field blank and environmental sample pairs was used to determine whether assessment levels were required to address the potential random contamination associated with field protocols for those VOCs detected in 1 or more percent of field blanks (J.S. Zogorski and D.A. Bender, U.S. Geological Survey, written commun., 2008). Assessment levels of 0.03 $\mu\text{g/L}$ for toluene and 0.05 $\mu\text{g/L}$ for 1,2,4-trimethylbenzene thus were determined to be appropriate. These assessment levels are adequate to limit the estimated probability of false detections of these compounds due to random sample contamination to less than 1 percent, and were used in the present study.

The bias from matrix interferences or analyte loss for VOC compounds during sample shipment or holding was investigated using field and laboratory spiked samples collected during 1997–2001 by Rowe and others (2005). The assessment was based on 428 spiked samples, including field spikes, field spike replicates, laboratory matrix spikes, and laboratory reagent spikes, for 85 VOCs in ground water and surface water. The median recoveries for all 85 VOCs ranged from 64 to 102 percent in field matrix spikes and ranged from 90 to 120 percent in laboratory reagent spikes; these were acceptable levels for all VOCs (Rowe and others, 2005).

Fecal Indicator Bacteria

Data on fecal indicator bacteria in most (95 percent) samples in this study were collected following standard USGS quality-assurance procedures, which at a minimum included the collection of filter-blank QC samples before and after filtration of each water sample (U.S. Geological Survey, variously dated; Embrey and Runkle, 2006). After October 2002, field blanks and positive and negative control samples

also were collected (Embrey and Runkle, 2006). QC data for bacteria samples collected prior to October 2002 were not readily available at the national scale at the time this report was written (2007). However, analysis of available QC data associated with microbiological data after October 2002 indicated that target organisms were infrequently detected in filter blanks (3.4 percent or 13 of 379 blanks; Embrey and Runkle, 2006). Environmental data associated with filter blanks in which target bacteria colonies were greater than 5 percent of the environmental bacteria colony concentrations (“V”-coded data) were not used in this study. Replicate QC samples were collected after October 2002 for microbiological data; RPDs for replicate pairs (n equal to 402) ranged from 0 to 200 percent, with average and median values of 13 and 0, respectively (Embrey and Runkle, 2006).

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