

SELECTED LABORATORY EVALUATIONS OF THE WHOLE-WATER SAMPLE-SPLITTING CAPABILITIES OF A PROTOTYPE FOURTEEN-LITER TEFLON[®] CHURN SPLITTER

by Arthur J. Horowitz, James J. Smith, and Kent A. Elrick

ABSTRACT

A prototype 14-L Teflon[®] churn splitter was evaluated for whole-water sample-splitting capabilities over a range of sediment concentrations and grain sizes as well as for potential chemical contamination from both organic and inorganic constituents. These evaluations represent a “best-case” scenario because they were performed in the controlled environment of a laboratory, and used monomineralic silica sand slurries of known concentration made up in deionized water. Further, all splitting was performed by a single operator, and all the requisite concentration analyses were performed by a single laboratory.

The prototype Teflon[®] churn splitter did not appear to supply significant concentrations of either organic or inorganic contaminants at current U.S. Geological Survey (USGS) National Water Quality Laboratory detection and reporting limits when test samples were prepared using current USGS protocols. As with the polyethylene equivalent of the prototype Teflon[®] churn, the maximum usable whole-water suspended sediment concentration for the prototype churn appears to lie between 1,000 and 10,000 milligrams per liter (mg/L). Further, the maximum grain-size limit appears to lie between 125- and 250-microns (μ m). Tests to determine the efficacy of the valve baffle indicate that it must be retained to facilitate representative whole-water subsampling.

INTRODUCTION

The U.S. Geological Survey (USGS) expends substantial resources collecting representative whole-water (water plus suspended sediment) samples for a variety of physical and chemical tests. Typically, this requires the collection of an isokinetic depth- and width-integrated composite sample using either equal discharge-increment (EDI) or equal width-increment (EWI) sampling procedures (Edwards and Glysson, 1999). These representative composite samples may range in volume from as little as 3 to well over 30 liters. Current USGS water-quality studies entail a myriad of physical and chemical tests performed in multiple laboratories. Variations in the volumetric requirements for these tests, chemical constraints (for example, various preservation techniques for different chemical parameters, potential sample contamination), and the geographical spread of several facilities performing these tests, requires the separation of numerous representative subsamples (aliquots) from each single composite sample. USGS sample collection and processing protocols require that these representative subsamples be obtained using one of two different sample splitting devices—either a churn splitter or a cone splitter (Webb, and others, 1999).

The current plastic churn splitter comes in three sizes; 4-, 8-, and 14-liter versions, and the plastic is a combination of polyethylene and polypropylene. The churn splitter has

been in use since 1976 (Capel and Larson, 1996). Because of their plastic composition, churn splitters are not used to obtain subsamples for analyses of either organic carbon or a variety of trace organic chemical compounds (for example, herbicides and insecticides). The original cone splitter was manufactured from Lucite[®] and metal (the device sat in an aluminum frame, on aluminum legs, which did not contact the sample) and came into widespread use in 1980 (Capel and Larson, 1996). In the mid-1980's, Teflon[®] cone splitters came into use, and although originally designed for use with precipitation samples, could be employed to obtain representative subsamples from any source for the subsequent determination of all water quality chemical constituents except volatile organic compounds (VOCs) (Capel and Larson, 1996).

Since the introduction of the first churn splitter, followed by the subsequent introduction of the cone splitter, there has been substantial controversy over the splitting capabilities of each device. In 1996, Capel and Larson summarized the history, documentation, and existing published and unpublished data on the splitting capabilities, and the contamination potential of churn (8- and 14-liter versions) and cone splitters (plastic and Teflon[®]). The Capel and Larson (1996) review left a number of unanswered questions:

- Could the cone splitter be used interchangeably with the churn splitter in the USGS protocol for collecting and processing water samples for inorganic analyses at the part-per-billion level (Horowitz and others, 1994), without contaminating the subsamples?
- Could the churn splitter be used to accurately split samples that contain sand-sized particles (>63- μ m), and if so, were there any concentration or particle-size limits?
- What, if any, was the effect on the precision and accuracy of cone splitter-generated subsamples for certain chemical analyses when multiple passes were needed to meet current USGS National Water Quality Laboratory (NWQL) volumetric requirements (for example, 250 mL subsamples for trace elements, major cations, and anions, and a 125 mL subsample for nutrients)?

To resolve these questions, the USGS Office of Water Quality (OWQ) authorized, and the USGS Instrumentation Committee (ICOM), funded a series of laboratory trials to evaluate both the churn and the cone splitting devices. The trials demonstrated that both devices could be used interchangeably at suspended-sediment concentrations

1,000 mg/L and where grain sizes did not exceed 250- μ m (Office of Water Quality Technical Memorandum 97.06). Because of material incompatibilities, however, the churn splitter could not be used to obtain representative subsamples for the determination of organic compounds.

In late 1999, the USGS Louisiana District Office funded the Federal Interagency Sedimentation Project (FISP) to design and then construct a 14-liter Teflon[®] churn splitter. FISP designed the device and had a prototype fabricated. Although the prototype was machined from solid Teflon[®], rather than molded as is typical for the polyethylene churn splitter, every attempt was made to retain the same dimensions in the prototype. However, some dimensional/construction differences were inevitable.

In 2001, the USGS OWQ and the National Water Quality Assessment program requested an evaluation of the prototype 14-liter Teflon[®] churn splitter to determine if it could be used routinely for USGS water-quality sample collection and processing. The evaluations mirrored those performed in 1995 (Office of Water Quality Technical Memorandum 96.07) during the original churn and cone splitter trials. Results of that evaluation are presented herein.

CONSTRUCTION AND DESIGN ISSUES

Several construction and design issues with the current prototype should be taken into consideration should the device prove acceptable, and additional Teflon[®] churns be constructed. Some of these issues result from the fact that the prototype was machined from a solid piece of Teflon[®], whereas production versions are more likely to be molded. These issues include the following:

- The paddle handle is too long, or the churn handle is too short. In the current configuration, if a user grabs the churn handle in the middle, his/her hand could be crushed between the churn and paddle handles.
- The walls of the 'funnel', intended to permit sample entry into the churn through the top, are too short. Currently, it is too easy to miss the funnel opening when pouring a 'large-volume' sample into the churn, especially if it is at the bottom of a 40-gallon churn carrier.
- The tab that prevents the paddle from unwanted rotation during use currently is set in the churn lid, and fits into a groove on the paddle handle; the groove could trap sediment. This design change, relative to the current polyethylene version of the churn splitter, was necessitated because the

prototype was machined rather than molded, and the Teflon[®] material that was used could not be glued or welded, hence, the tab could not be attached to the wall of the churn after machining. This design change would not be required if subsequent units are molded.

- The valve currently used to drain the churn, and through which representative aliquots are collected, is not quite flush with the interior wall of the churn. This could lead to sediment trapping.
- The new prototype valve design is a major improvement because it does not contain a metallic spring (a source of potential contamination); on the other hand, the ‘pull-tab’ probably is too small to grip easily if the user is wearing gloves. The tab size should be increased.
- The use of a threaded paddle handle so that the paddle can be disassembled is an improvement as it will make cleaning and transport simpler and easier. However, this creates the possibility that the user may not properly align the valve baffle with the drain valve. This potential problem would be eliminated if the tab for the paddle is moved from the lid to the wall of the churn. On the other hand, if the current design is retained, then users must be reminded to check that the valve baffle is correctly aligned before using the Teflon[®] churn.

MATERIALS AND METHODS

All the splitting tests were performed on laboratory-created sediment suspensions made up in deionized water. The suspensions were made using a monomineralic, commercially available silica “sand” from Ordovician St. Peter Sandstone quarried in north-central Illinois. This material has been described as

99.7% pure, natural, well-rounded quartz. Use of this quartz sand was intended to eliminate all variability due to density variations, while still employing a natural material that typically composes the majority of suspended sediment. Prior to use, the silica sand was thoroughly washed, dried, and subsequently dry-sieved into standard grain-size ranges (<63- m, 63 to 125- m, 125 to 250- m, 250 to 500- m, and 500 to 1,000- m).

The various concentration and grain-size ranges selected for testing span the full range of conditions

under which a sample splitter might be used (Table 1). It should be noted, however, that the higher and coarser concentrations tested are not typical of most water-quality studies. This conclusion is predicated on USGS National Stream Quality Accounting Network (NASQAN) data for 1974–81 which indicated that the median suspended-sediment concentration was 67 mg/L, whereas the 25th and 75th percentile concentrations were 18 and 193 mg/L, respectively (Smith and others, 1987). All the suspensions were 14 liters in volume. All laboratory tests were performed in the Sediment Partitioning Research Laboratory in the USGS Georgia District Office, in Atlanta, by a single operator. All sediment concentration determinations were performed in the USGS Kentucky District Sediment Laboratory.

Table 1. Concentration and grain-size ranges of sediment in samples used to evaluate the 14-liter Teflon[®] churn

Suspended Sediment Concentrations, in milligrams per liter				
Grain-size range, in microns	50	100	300	1,000
silt and clay, < 63	X	X	X	X
very fine sand, 63 to 125	X	X	X	X
fine sand, 125 to 250				X
medium sand, 250 to 500				X

Churn suspensions were prepared by adding appropriate sediment masses (weighed on an analytical balance to the nearest 0.01 g) to 200 mL of deionized water (DIW) in a 600-mL glass beaker. This suspension was thoroughly agitated, and the sediment thoroughly wetted, by inserting an ultrasonic probe into the beaker for 5 to 10 minutes. The contents of the beaker were then added to 12.5 liters of DIW already in the churn while the churn paddle was in motion. Agitation of the suspension continued until all appropriate withdrawals were made.

At the request of the FISP, the utility of the valve baffle, located on the agitating paddle, was evaluated during these tests to see if the baffle could be eliminated. This test entailed rotating the paddle so that the baffle did not cover the churn valve during one of the five sets of either single or multiple withdrawals (see the experimental results section of this report).

QUALITY ASSURANCE

The balances in the Sediment Partitioning Research Laboratory are calibrated once a year using National Institute of Science and Technology (NIST) traceable weights. As an additional quality-assurance check, separate individual samples, encompassing each of the concentration and grain-size range combinations used in the evaluations (Table 1), were generated in Atlanta during these splitting tests. These “reference” samples were intermixed with the actual churn test samples and submitted contemporaneously to the USGS Kentucky Sediment Laboratory. In essence, they served as “blind” samples. The concentration results for the “blind” samples are provided in Table 2 and indicate that the USGS Kentucky Sediment Laboratory was capable of determining reproducible and relatively unbiased suspended-sediment concentrations.

Table 2. Results for “blind” reference slurries by the U.S. Geological Survey, Kentucky Sediment Laboratory

Sediment Laboratory		
Prepared concentration, in milligrams per liter	Determined concentration, in milligrams per liter	Grain-size range, in microns
1,096	1,110	250 to 500
1,001	1,000	125 to 250
1,051	941	63 to 125
1,050	1,040	<63
320	322	63 to 125
283	280	<63
97	106	63 to 125
98	95	<63
52	52	63 to 125
48	44	<63

EXPERIMENTAL RESULTS

Evaluating potential for sample contamination

Before testing the prototype 14-L Teflon® churn’s splitting capabilities, the churn was evaluated for potential chemical contamination. To that end, 16 liters of both organic-free and inorganic-free water were obtained from the USGS Ocala Water Quality and Research Laboratory in Florida. First, the churn was cleaned following standard USGS protocols for organic parameter sampling (Wilde and others, 1998), flushed with one liter of organic-free water, and then filled to capacity with the remaining water. With the paddle agitating the water, the valve was opened and three aliquots were collected from the churn (first liter,

seventh liter, tenth liter), retained, and adequately preserved for subsequent chemical analysis. An aliquot of the source water also was retained and adequately preserved for subsequent chemical analysis, should any ‘hits’ have to be evaluated. The organic blanks and source water subsample were analyzed by the NWQL for dissolved organic carbon (DOC), as well as for those constituents included in NWQL schedules 2001 (pesticides) and 9060 (pesticides). No concentrations above the detection limit were reported (see Appendix A for a list of constituents and the analytical data).

After the organic contaminant evaluation, the churn was re-cleaned using standard USGS protocols for inorganic sampling (Wilde and others, 1998), flushed with one liter of inorganic-free water, and then filled to capacity with the remaining water. With the paddle agitating the water, the valve was opened and three aliquots were collected from the churn (first liter, seventh liter, tenth liter), retained, and adequately preserved for subsequent chemical analysis. An aliquot of the source water also was retained and adequately preserved for subsequent chemical analysis, should any ‘hits’ have to be evaluated. The inorganic blanks were analyzed by the NWQL for DOC, as well as for those constituents included in NWQL schedules 1069 (nutrients), 2710 (trace elements), and 2701 (major ions). Very low, but detectable concentrations of:

- nitrite plus nitrate (NO₂ + NO₃),
- manganese (Mn),
- nickel (Ni), and
- solids residue at 180 °C

were found in all or some of the blank aliquots (see Appendix B for a list of constituents and the analytical data). The detected concentrations were either at the method detection limits (MDLs), and/or less than half the current reporting limit. As such, all the “hits” were deemed to be insignificant.

Particle-size and concentration-range evaluations for the prototype 14-L Teflon® churn for a single withdrawal

This experiment called for creating a series of slurries of known concentration, ranging from 50 to 1,000 mg/L, for specific grain-size ranges (see Table 1). Five separate slurries for each concentration and grain-size range were made, and a 1-liter aliquot was withdrawn while each slurry was agitated with the paddle (Table 3). Each withdrawal was made after seven liters of slurry had been drained from the churn. The churn was cleaned between each run.

Table 3. Replicate results from the prototype 14-liter Teflon® and polyethylene churn splitters for single withdrawals for a variety of concentrations and grain-size ranges

Original Results from the 1995 Churn (Cone) Tests										
Concentrations, in milligrams per liter	1,000	1,000	1,000	300	100	50	1000	300	100	50
Grain size, in microns	250 to 500	125 to 250	62 to 125			38 to 62				
Single Split 1	1,166	1,218	1,078	327	106	53	1,068	315	105	56
Single Split 2	1,050	1,248	1,128	312	110	59	1,086	323	102	55
Single Split 3	1,097	1,238	1,064	325	106	55	1,051	301	104	53
Single Split 4	895	1,198	1,072	329	108	55	1,070	313	105	57
Single Split 5	1,108	1,182	1,057	318	108	55	1,042	314	104	54
Mean	1,063	1,217	1,080	322	108	55	1,063	313	104	55
Standard deviation	103	27	28	7	2	2	17	8	1	2
Percent relative standard deviation	10	2	3	2	2	4	2	3	1	3
Percent bias	6	22	8	7	8	11	6	4	4	10

Results from the 2001 Teflon® Churn Tests										
Single Split 1	978	1,065	970	302	106	54	927	293	100	49
Single Split 2	888	1,046	974	308	99	49	986	302	101	51
Single Split 3	1,098	1,027	1,050	317	104	49	937	296	98	50
Single Split 4	973	1,026	1,040	322	105	55	982	301	99	49
Single Split 5	^{1/} 589	^{1/} 947	964	^{1/} 268	103	51	998	287	96	50
Mean	987	1,033	1,000	310	103	52	966	296	99	50
Standard deviation	86	19	42	9	3	3	32	6	2	1
Percent relative standard deviation	9	2	4	3	3	5	3	2	2	2
Percent bias	-1	3	<1	3	3	3	-3	-1	-1	<1

^{1/}These data points were significantly different from other data points as a result of the repositioning of the baffle (see text); and therefore, were excluded.

The results for the prototype Teflon® churn are similar to those reported by Capel and Larson (1996), as well as those noted by A.J. Horowitz and others (U.S. Geological Survey, unpublished data, 1996) from the original churn and cone tests covered by Office of Water Quality Technical Memorandum 97.06 (Table 3). If anything, the new results are slightly more reproducible, and slightly less biased than those generated during the 1995 tests.

Particle-size and concentration-range evaluations of other prototype 14-L Teflon® churn with multiple withdrawals

This experiment called for making up the same series of slurries as those used in the single withdrawal

study described above (Table 1). The purpose of this set of experiments was to determine the splitting accuracy of the prototype Teflon® churn for given grain-size ranges if multiple withdrawals from the same churn were made, as is typical during normal field operations (for example, were the results reproducible, or did they show a trend). Fourteen-liter slurries of each concentration and grain-size range were placed in the Teflon® churn; then, three 1-liter withdrawals were made while each slurry was agitated with the paddle. Five separate slurries for each concentration and grain-size range were generated. Each withdrawal was made after one (1), seven (7), and ten and a half (10.5) liters of slurry had been drained from the churn. The churn was cleaned between each run (Table 4).

The results for the prototype 14-L Teflon® churn are similar to those reported by A.J. Horowitz and others (U.S. Geological Survey, unpublished data, 1996) from the original churn/cone tests covered by Office of Water Quality Technical Memorandum 97.06 (Table 4). However, the new results are less reproducible (have a greater standard deviation) than the old ones (Table 4). On the other hand, the new results also are less biased than the old ones (Table 4). These differences probably can be ascribed to variations in operator performance, as the same individual did not perform both sets of tests (1995 *versus* 2001).

As indicated in the first part of this report, as well as the older churn/cone results, it appears that particles 125- μ m are not homogeneously distributed in the churn, and tend to concentrate in the lower part of the unit. This is the probable cause of the generally observed decreases in sediment concentration with increasing numbers of withdrawals. More “accurate” subsamples could be obtained by draining between a third and a half of the churn’s contents before actually collecting a whole-water aliquot. Although this procedure could provide a less biased (more accurate) sample in terms of sediment concentration, the grain-size distribution of such a subsample probably would not be representative [it would overestimate the fine fraction (<63- μ m) and underestimate the coarse fraction (> 63- μ m)]. It may be possible to improve the accuracy of a churn splitter (reduce the initial positive bias) by increasing churning speed. However, this must be weighed against the increased chances of accidentally pulling the paddle out of the whole-water sample.

Evaluation of the efficacy of the valve baffle

At the request of the FISP, the utility of the valve baffle, on the agitating paddle was evaluated to see if the baffle could be eliminated without affecting the splitting capabilities of the churn. This evaluation entailed rotating the paddle so that the baffle did not cover the interior churn valve opening during one of the five sets of either single or multiple withdrawal tests. This approach was used due to resource limitations, and provided insufficient data for a rigorous statistical analysis. A review of the data (for example, Table 5), however, indicates that when the valve baffle is not in place, the suspended sediment concentrations determined for that subsample appear to be the lowest, or biased low, relative to the four other subsamples obtained for the same concentration and grain-size range. As such, and on that basis, it appears that the valve baffle contributes to the production of unbiased subsamples and should not be eliminated.

Table 4. Replicate results from the prototype 14-liter Teflon® and polyethylene churn splitters for multiple withdrawals for a variety of concentrations and grain-size ranges
 [na, not applicable]

Original results from the 1995 churn (cone) tests																				
Grain size, microns per meter	250-500		125 to 250		62 to 125								38 to 62							
	1,000		1,000		1,000		300		100		50		1,000		300		100		50	
Concentration, milligrams per liter	New	Used	New	Used	New	Used	New	Used	New	Used	New	Used	New	Used	New	Used	New	Used	New	Used
First Liter	1,327	1,136	1,159	1,134	1,120	1,126	348	327	106	101	54	51	1,071	1,023	329	335	101	86	48	40
Second Liter	1,344	1,051	1,130	1,122	1,112	1,082	339	324	111	102	55	47	1,071	1,024	324	319	100	88	51	40
Third Liter	1,208	955	1,101	1,091	1,099	1,065	326	315	112	99	55	50	1,065	1,042	317	297	102	97	47	40
Mean	1,293	1,047	1,130	1,116	1,110	1,091	338	322	110	101	55	49	1,069	1,030	323	317	101	90	49	40
Standard deviation	74	91	29	22	11	31	11	6	3	2	1	2	3	11	6	19	1	6	2	0
Percent relative standard deviation	6	9	3	2	1	3	3	2	3	2	1	4	0	1	2	6	1	6	4	0
Percent bias	29	5	13	12	11	9	13	7	10	1	10	-2	7	3	8	6	1	-10	-2	-20

Results from the 2001 Teflon® churn tests																				
Grain Size, microns per meter	250 to 500		125 to 250		62 to 125								38 to 62							
	1,000		1,000		1,000		300		100		50		1,000		300		100		50	
Concentration, milligrams per liter	New	Used	New	Used	New	Used	New	Used	New	Used	New	Used	New	Used	New	Used	New	Used	New	Used
First Liter	1,452	na	1,251	na	1,296	na	369	na	122	na	62	na	1,080	na	317	na	103	na	52	na
Second Liter	1,066	na	962	na	944	na	298	na	112	na	51	na	975	na	295	na	98	na	48	na
Third Liter	484	na	831	na	868	na	282	na	95	na	48	na	947	na	278	na	94	na	49	na
Mean	1,001	na	1,015	na	915	na	316	na	106	na	54	na	1,001	na	297	na	98	na	50	na
Standard deviation	530	na	186	na	203	na	42	na	13	na	7	na	65	na	20	na	5	na	2	na
Percent relative standard deviation	53	na	18	na	22	na	13	na	12	na	14	na	6	na	7	na	5	na	5	na
Percent bias	<1	na	1	na	-8	na	5	na	6	na	7	na	<1	na	-1	na	-2	na	<1	na

Table 5. Data on the effect of the valve baffle on sediment concentration from the single withdrawal tests

Concentration, in milligrams per liter	1,000	1,000	1,000	300	100	50	1,000	300	100	50
Grain-size range, in microns	250 to 500	125 to 250	62 to 125				38 to 62			
Minimum	888	1,026	970	302	99	49	927	293	98	49
Maximum	1,098	1,065	1,050	322	106	55	986	302	101	51
Mean	984	1,041	1,009	312	104	52	958	298	100	50
Standard deviation	86	19	43	9	3	3	30	4	1	1
Concentration without baffle	589	948	964	268	103	51	998	287	96	50

CONCLUSIONS AND RECOMMENDATIONS

The blank tests on the prototype 14-liter Teflon® churn demonstrate that it is unlikely to contribute significant systematic levels of organic or inorganic contaminants to water samples at current NWQL detection and reporting limits. As such, the new churn is not limited as is its plastic counterpart and can be used to obtain subsamples for the determination of a wide range of water-quality parameters/constituents.

The results from the splitting tests for the new prototype 14-L Teflon® churn should be viewed in the same way as those generated for the plastic churn during the original churn/cone tests, as a “best-case” scenario, because they were performed: (1) in the controlled environment of a laboratory; (2) on carefully prepared monomineralic silica sand slurries made up in DIW; (3) all the tests were carried out by a single operator; and (4) all the sediment concentration determinations were performed in a single laboratory. There is little doubt, based on other studies in which field and laboratory results have been compared, that a similar series of tests, carried out in the field, by multiple operators, with analyses performed by several laboratories, likely would produce substantially poorer results than those reported herein. Even under the “best-case” conditions of this study, the results indicate that the prototype 14-L Teflon® churn splitter, like its polyethylene/polypropylene counterpart, as well as the Teflon® cone splitter, does not provide reproducible and unbiased (accurate) results under all the concentration and grain-size ranges tested. On the other hand, the results are not substantially dissimilar to those generated during the initial cone/churn tests performed in 1995; thus, the prototype Teflon® churn’s splitting capacity is on a par with that of its 14-L polyethylene/polypropylene counterpart. Finally, these tests indicate that the valve baffle improves the splitting performance of the churn and should be retained.

REFERENCES CITED

- Capel, P.D. and Larson, S.J., 1996, Evaluation of selected information on splitting devices for water samples: U.S. Geological Survey Water-Resources Investigations Report 95-4141, 103 p.
- Edwards, T.K. and Glysson, G.D., 1999, Field methods for measurement of fulfill sediment: U.S. Geological Survey Techniques of Water Resources Investigations, Book 3, Chapter C2, 80 p.
- Horowitz, A.J., Dames, C.R., Fitzgerald, K.K., Miller, T.L. and Rickert, D.A., 1994, U.S. Geological Survey protocol for the collection and processing of surface-water samples for the subsequent determination of inorganic constituents in filtered water: U.S. Geological Survey Open-File Report 94-539, 57 p.
- Office of Water Quality Technical Memorandum 97.06, Comparison of the Suspended –Sediment Splitting Capabilities of the Churn and Cone Splitters, May 5, 1997, 3 p.
- Smith, R.A., Alexander, R.A. and Wolman, M.G., 1987, Water-quality trends in the nation's rivers: Science, v. 235, p. 1,607-1,615.
- Webb, W.E., Radtke, D.B., and Iwatsubo, R.T., 1999, National field manual for the collection of water-quality data—collection of water samples: U.S. Geological Survey Techniques of Water Resources Investigations, Book 9, Chapter A4, variously paged.
- Wilde, F.W., Radtke, D.B., Gibs, J., and Iwatsubo, R.T., 1998, National field manual for the collection of water-quality data – cleaning of equipment for water sampling: U.S. Geological Survey Techniques of Water Resources Investigations, Book 9, Chapter A3, variously paged.

Appendix A. Organic parameters determined in the blank samples and source water
[μg/L, micrograms per liter; E, estimated]

Parameter	First Liter	Seventh Liter	Tenth Liter	Source Water
Dissolved Organic Carbon, milligrams per liter as carbon	<.33	<.33	<.33	E.307
2,4-D Methyl Est (g/L)	<.0865	<.0865	<.0865	<.0865
2,4-D Dis (g/L)	<.0774	<.0774	<.0774	<.0774
2,4-DB, Filtered (g/L)	<.0538	<.0538	<.0538	<.0538
2,6 Diethylaniline (g/L)	<.0017	<.0017	<.0017	<.0017
3 Hydroxycarbofuran (g/L)	<.0623	<.0623	<.0623	<.0623
3 Ketocarbofuran (g/L)	<.0723	<.0723	<.0723	<.0723
Acetochlor, Filtered (g/L)	<.0041	<.0041	<.0041	<.0041
Acifluorfen, Filtered (g/L)	<.0622	<.0622	<.0622	<.0622
Alachlor, Dissolved (g/L)	<.0024	<.0024	<.0024	<.0024
Aldicarb Sulfone (g/L)	<.1599	<.1599	<.1599	<.1599
Aldicarb Sulfoxide (g/L)	<.0271	<.0271	<.0271	<.0271
Aldicarb, Filtered (g/L)	<.0815	<.0815	<.0815	<.0815
Alpha BHC (g/L)	<.0046	<.0046	<.0046	<.0046
Atrazine, Dissolved (g/L)	<.007	<.007	<.007	<.007
Bendiocarb, Water, Filtered (g/L)	<.0612	<.0612	<.0612	<.0612
Benfluoralin, Filtered (g/L)	<.01	<.01	<.01	<.01
Benomyl, Water, Filtered (g/L)	<.0219	<.0219	<.0219	<.0219
Bensulfuron-Meth (g/L)	<.0482	<.0482	<.0482	<.0482
Bentazon, Filtered (g/L)	<.0193	<.0193	<.0193	<.0193
Bromacil, Dissolved, Recov. (g/L)	<.0807	<.0807	<.0807	<.0807
Bromoxynil, Filtered (g/L)	<.0572	<.0572	<.0572	<.0572
Butylate, Dissolved, Recov. (g/L)	<.002	<.002	<.002	<.002
Caffeine, Water, Filtered (g/L)	<.0805	<.0805	E.0073	<.0805
Caffein, Surrogate, in percent	E143.	E140.	E143.	E137.
Carbaryl, Filtered (g/L)	<.0628	<.0628	<.0628	<.0628
Carbaryl, Filtered @ 0.7- m (g/L)	<.041	<.041	<.041	<.041
Carbofuran, Filtered (g/L)	<.0566	<.0566	<.0566	<.0566
Carbofuran, Filtered (g/L)	<.02	<.02	<.02	<.02
Chloramben, Meth (g/L)	<.1139	<.1139	<.1139	<.1139
Chlorimuron, Water (g/L)	<.0367	<.0367	<.0367	<.0367
Chlorthalonil, Filtered (g/L)	<.0485	<.0485	<.0485	<.0485
Chlorpyrifos, Dissolved (g/L)	<.005	<.005	<.005	<.005
Clpyrralid, Filtered (g/L)	<.0411	<.0411	<.0411	<.0411
Cyanazine, Dis., Recov. (g/L)	<.018	<.018	<.018	<.018
Cycloate, Dissolved, Recov. (g/L)	<.0543	<.0543	<.0543	<.0543
Dacthal Mono-Aci (g/L)	<.0722	<.0722	<.0722	<.0722
DCPA, Filtered @ 0.7- m, Recov. (g/L)	<.003	<.003	<.003	<.003
Deethyl Atrazine (g/L)	<.006	<.006	<.006	<.006
Deethyldeisop At (g/L)	<.0599	<.0599	<.0599	<.0599

Appendix A. Organic parameters determined in the blank samples and source water—Continued
 [µg/L, micrograms per liter; E, estimated]

Parameter	First Liter	Seventh Liter	Tenth Liter	Source Water
Deisopropyl Atrazine (g/L)	<.0737	<.0737	<.0737	<.0737
Diazinon, Dissolved (g/L)	<.005	<.005	<.005	<.005
Dicamba, Filtered (g/L)	<.096	<.096	<.096	<.096
Dichloropro, Filtered (g/L)	<.05	<.05	<.05	<.05
Dieldrin, Dis (g/L)	<.0048	<.0048	<.0048	<.0048
Dionseb, Filtered (g/L)	<.0429	<.0429	<.0429	<.0429
Diphenamid, Dissolved (g/L)	<.0581	<.0581	<.0581	<.0581
Disulfoton, Filtered (g/L)	<.021	<.021	<.021	<.021
Diuron, Filtered (g/L)	<.0793	<.0793	<.0793	<.0793
EPTC, Filtered @ 0.7- m, Recov. (g/L)	<.002	<.002	<.002	<.002
Ethalfuralin, Filtered (g/L)	<.009	<.009	<.009	<.009
Ethoprop, Filtered @ 0,7- m (g/L)	<.005	<.005	<.005	<.005
Fenuron, Filtered (g/L)	<.0735	<.0735	<.0735	<.0735
Flumensulam, Filtered, Recov. (g/L)	<.0866	<.0866	<.0866	<.0866
Fluometuron, Filtered (g/L)	<.0617	<.0617	<.0617	<.0617
Fonofox, Filtered, Recov.	<.0027	<.0027	<.0027	<.0027
Hydroxyatrazine (g/L)	<.1927	<.1927	<.1927	<.1927
Imazaquin, Water (g/L)	<.103	<.103	<.103	<.103
Imazethapyr, Water (g/L)	<.0879	<.0879	<.0879	<.0879
Imidacloprid, Filtered, Recov. (g/L)	<.106	<.106	<.106	<.106
Lindane, Dissolved (g/L)	<.004	<.004	<.004	<.004
Linuron, Filtered (g/L)	<.0695	<.0695	<.0695	<.0695
Linuron, Filtered @ 0.7- m (g/L)	<.035	<.035	<.035	<.035
Malation, Dissolved (g/L)	<.027	<.027	<.027	<.027
MCPA, Filtered (g/L)	<.0585	<.0585	<.0585	<.0585
MCPB, Filtered (g/L)	<.0625	<.0625	<.0625	<.0625
Metalaxyl, Water (g/L)	<.0571	<.0571	<.0571	<.0571
Methiocarb, Filtered (g/L)	<.0795	<.0795	<.0795	<.0795
Methomyl Oxime, Filtered (g/L)	<.0102	<.0102	<.0102	<.0102
Methomyl, Filtered (g/L)	<.0768	<.0768	<.0768	<.0768
Methyl Azinophos (g/L)	<.05	<.05	<.05	<.05
Methyl Parathion (g/L)	<.006	<.006	<.006	<.006
Metolachlor, Water (g/L)	<.013	<.013	<.013	<.013
Metribuzin, Water, Dissolved (g/L)	<.006	<.006	<.006	<.006
Metsulfuron-Meth (g/L)	<.1138	<.1138	<.1138	<.1138
Molinate, Filtered @ 0.7- m (g/L)	<.0016	<.0016	<.0016	<.0016
Napropamide, Filtered (g/L)	<.007	<.007	<.007	<.007
Neburon, Filtered (g/L)	<.0747	<.0747	<.0747	<.0747
Nicosulfuron, Water (g/L)	<.0653	<.0653	<.0653	<.0653
Norflurazon, Filtered (g/L)	<.0774	<.0774	<.0774	<.0774
Oryzalin, Filtered (g/L)	<.0711	<.0711	<.0711	<.0711

Appendix A. Organic parameters determined in the blank samples and source water—Continued
 [µg/L, micrograms per liter; E, estimated]

Parameter	First Liter	Seventh Liter	Tenth Liter	Source Water
Oxamyl Oxime, Water (g/L)	<.0644	<.0644	<.0644	<.0644
Oxamyl, Filtered (g/L)	<.016	<.016	<.016	<.016
P,P' DDE, Dissolved (g/L)	<.0025	<.0025	<.0025	<.0025
Parathion, Dissolved (g/L)	<.007	<.007	<.007	<.007
Pebulate, Filtered @ 0.7- m (g/L)	<.0016	<.0016	<.0016	<.0016
Pendimethalin, Filtered (g/L)	<.01	<.01	<.01	<.01
Permethrin, Filtered (g/L)	<.006	<.006	<.006	<.006
Phorate, Filtered @ 0.7- m (g/L)	<.011	<.011	<.011	<.011
Picloram, Filtered (g/L)	<.0712	<.0712	<.0712	<.0712
Prometon, Filtered, Recov. (g/L)	<.015	<.015	<.015	<.015
Pronamide, Filtered @ 0.7- m (g/L)	<.0041	<.0041	<.0041	<.0041
Propachlor, Dissolved (g/L)	<.01	<.01	<.01	<.01
Propanil, Filtered @ 0.7- m (g/L)	<.011	<.011	<.011	<.011
Propargite, Filtered (g/L)	<.023	<.023	<.023	<.023
Propham, Filtered (g/L)	<.0717	<.0717	<.0717	<.0717
Propiconazole, Filtered (g/L)	<.0643	<.0643	<.0643	<.0643
Propoxur, Filtered (g/L)	<.0594	<.0594	<.0594	<.0594
Siduron, Filtered (g/L)	<.0933	<.0933	<.0933	<.0933
Simazine, Dissolved, Recov. (g/L)	<.011	<.011	<.011	<.011
Sulfometuron Me (g/L)	<.0388	<.0388	<.0388	<.0388
Tebuthiuron, Filtered (g/L)	<.016	<.016	<.016	<.016
Terbacil, Dissolved, Recov. (g/L)	<.0954	<.0954	<.0954	<.0954
Terbacil, Filtered @ 0.7- m (g/L)	<.034	<.034	<.034	<.034
Terbufos, Filtered @ 0.7- m (g/L)	<.017	<.017	<.017	<.017
Thiobencarb, Filtered (g/L)	<.0048	<.0048	<.0048	<.0048
Triallate, Filtered @ 0.7- m (g/L)	<.0023	<.0023	<.0023	<.0023
Tribenuron, Filtered, Recov. (g/L)	<.0678	<.0678	<.0678	<.0678
Triclopyr, Filtered (g/L)	<.1008	<.1008	<.1008	<.1008
Trifluralin, Filtered (g/L)	<.009	<.009	<.009	<.009
3,4 Chlorphnl Methyl (g/L)	<.0915	<.0915	<.0915	<.0915

Appendix B. Inorganic parameters determined in the blank samples

[µg/L, micrograms per liter; mg/L, milligrams per liter; µS/cm, microsiemens per centimeter; E, estimated]

Parameter	First Liter	Seventh Liter	Tenth Liter	Source Water
pH, WH, LAB (standard units)	7.58	6.85	6.43	6.34
Nitrogen Ammonia (mg/L as N)	<.002	<.002	<.002	0.002
Nitrogen, nitrite (mg/L as N)	<.001	<.001	<.001	<.001
Nitrogen Ammonia + Organic (mg/L as N)	E.061	<.1	<.1	<.1
Nitrogen Ammonia + Organic (mg/L as N)	E.046	<.08	<.08	<.08
NO ₂ + NO ₃ , Dissolved (mg/L as N)	0.006	0.006	0.005	<.005
Phosphorus, Total (mg/L as P)	<.0037	E.002	E.002	<.0037
Phosphorus, Dissolved (mg/L as P)	<.006	<.006	<.006	<.006
Phosphorus, Ortho (mg/L as P)	<.007	<.007	<.007	<.007
Dissolved Organic Carbon (mg/L as C)	<.15	<.15	<.15	<.15
Calcium, Dissolved (mg/L as Ca)	<.011	<.011	0.1821	<.011
Magnesium, Dissolved (mg/L as Mg)	<.008	<.008	0.1804	<.008
Sodium, Dissolved (mg/L as Na)	<.06	<.06	<.06	<.06
Potassium, Dissolved (mg/L as K)	<.24	<.24	<.24	<.24
Chloride, Dissolved (mg/L as Cl)	E.04	<.08	<.08	<.08
Sulfate, Dissolved (mg/L as SO ₄)	<.11	<.11	<.11	<.11
Fluoride, Dissolved (mg/L as F)	<.16	<.16	<.16	<.16
Silica, Dissolved (mg/L as SiO ₂)	<.09	<.09	<.09	<.09
Arsenic, Dissolved (g/L as As)	<.18	<.18	<.18	<.18
Barium, Dissolved (g/L as Ba)	<1.	<1.	<1.	<1.
Beryllium, Dissolved (g/L as Be)	<.06	<.06	<.06	<.06
Boron, Dissolved (g/L as B)	<7.	<7.	<7.	<7.
Cadmium, Dissolved (g/L as Cd)	<.037	<.037	<.037	<.037
Chromium, Dissolved (g/L as Cr)	<.8	<.8	<.8	<.8
Cobalt, Dissolved (g/L as Co)	<.015	<.015	<.015	<.015
Copper, Dissolved (g/L as Cu)	<.23	<.23	<.23	<.23
Iron, Dissolved (g/L as Fe)	<10.	<10.	<10.	<10.
Lead, Dissolved (g/L as Pb)	<.08	<.08	<.08	<.08
Manganese, Dissolved (g/L as Mn)	0.376	0.393	0.179	0.115
Thallium, Dissolved (g/L as Tl)	<.041	<.041	<.041	<.041
Molybdenum, Dissolved (g/L as Mo)	<.2	<.2	<.2	<.2
Nickel, Dissolved (g/L as Ni)	<.06	<.06	<.06	0.066
Silver, Dissolved (g/L as Ag)	<1.	<1.	<1.	<1.
Strontium, Dissolved (g/L as Sr)	<.08	<.08	<.08	<.08
Vanadium, Dissolved (g/L as V)	<.21	<.21	<.21	<.21
Zinc, Dissolved (g/L as Zn)	<1.	<1.	<1.	<1.
Antimony, Dissolved (g/L as Sb)	<.048	<.048	<.048	<.048
Aluminum, Dissolved (g/L as Al)	<1.	<1.	<1.	<1.
Lithium, Dissolved (g/L as Li)	<.3	<.3	<.3	<.3
Selenium, Dissolved (g/L as Se)	<.33	<.33	<.33	<.33
Uranium, natural (g/L as U)	<.018	<.018	<.018	<.018
UV Absorbance (units/cm)	0.0002	0.0006	0.0001	0.0005
Absorbance, 280 (units/cm)	0.001	0.0012	0.0009	0.0013
Dissolved Residue at 180 ° C (mg/L)	10	<10.	<10.	<10.
Specific Conductance (S/CM)	E2.32	E1.71	E1.74	E1.57