EVALUATION OF A MODIFIED AUTOMATIC SAMPLER FOR THE COLLECTION OF WATER SAMPLES FOR ANALYSIS OF TRACE ORGANIC COMPOUNDS OR SUSPENDED SEDIMENT

By D.Y. Tai, M.E. Jennings, K.D. White and L.A. Garcia

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CONVERSION FACTORS AND ABBREVIATIONS

Multiply	By	To obtain
cubic foot per second (ft^3/s)	0.01093	cubic meter per second
foot (ft)	0.3048	meter
inch (in.)	25.4	millimeter
liter (L)	1.057	quart
milliliter (mL)	0.03382	ounce, fluid
pint (pt)	0.4732	liter
quart (qt)	0.9464	liter
square mile (mi^2)	2.590	square kilometer

Temperature in degrees Celsius (°C) is converted to degrees Fahrenheit (°F) as follows:

$$°F = 1.8 \times °C + 32$$

Abbreviated units used in this report

$\mu g/L$	micrograms per liter
mg/L	milligrams per liter

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EVALUATION OF A MODIFIED AUTOMATIC SAMPLER FOR THE COLLECTION OF WATER SAMPLES FOR ANALYSIS OF TRACE ORGANIC COMPOUNDS OR SUSPENDED SEDIMENT

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ABSTRACT

A commercial automatic water sampler, ISCO Model 2700, was modified to accommodate glass sample-collection containers of 1 liter or larger. This modified sampler was tested for sampling efficiency and cross contamination in the laboratory and in the field. Laboratory tests, using atrazine and 2-chlorophenol in water at concentrations of 5 micrograms per liter and 50 micrograms per liter, showed no absorption of these compounds by the sampling system. No cross-contamination was detected in the sample collection when water-purge cycles were used.

Field tests of the modified automatic water sampler were conducted at two stream sites in Kentucky. Concentrations of diazinon and suspended sediment in water samples collected using the modified autosampler were compared to concentrations in water samples collected using a manual depth-integrated, cross-sectional method. In the diazinon tests, a difference in concentration of less than 10 percent was observed between the two methods. In the sediment tests, however, differences in concentration of 14 to 50 percent were observed but concentrations were within a range of only a few milligrams per liter. These large percentage differences may have been due to the low sediment concentration (less than 10 milligrams per liter). No cross-contamination was detected in the sample collection during the field tests. Test results indicated that the modified autosampler is suitable for the collection of samples for analysis of trace organic compounds but additional testing is needed to evaluate the suitability of the autosampler for sampling suspended sediment.

INTRODUCTION

There has been an increasing need for the collection of multiple water samples during storms as a means of determining the occurrence and relative distribution of trace organic compounds in surface water. Because storms frequently occur during the evening hours and the monitoring sites are usually some distance away from the laboratories or offices, a reliable automatic sampler (autosampler) that would reduce manpower requirements and ensure collection of samples in a timely fashion is needed.

Several criteria need to be considered in the selection of an autosampler for the collection of samples for analysis of organic compounds.

* An autosampler that accommodates 1-liter or larger containers is needed because analytical methods for determining concentration of trace organic compounds require large sample volumes.

* An autosampler with parts made of materials that do not absorb organic compounds is needed to sample water that contains only trace amounts of those compounds.

* An autosampler that incorporates a cleaning cycle between samples is needed to prevent any cross-contamination.

* An autosampler equipped with a pump that can lift water at least 20 ft is needed to facilitate field sample collection.

Although several commercial samplers were available when the need for a sampler that could be used for sampling trace organic compounds first arose, the ISCO Model 2700 autosampler most nearly met the above criteria. However, the volume of the glass sample container in this sampler, 0.35 L, was inadequate for the collection of samples for analysis of organic compounds. This report describes the modification of this autosampler to accommodate glass containers of 1 L or larger. The laboratory test results regarding absorbance and cross-contamination of the modified autosampler system, with atrazine and 2-chlorophenol as the test chemicals, are presented in this report.

The modified autosampler also was tested in the field as part of the Kentucky River basin pilot study of the National Water-Quality Assessment program (NAWQA) of the U.S. Geological Survey (USGS). Field tests were designed to evaluate sampling performance from both quality and quantity perspectives. Samples collected by the autosampler were compared to samples collected by depth-integrated, cross-sectional methods. The purging efficiency of the autosampler was also tested in the field, comparing both air and water purge modes. The results of the field tests are also presented.

INSTRUMENT MODIFICATION

The ISCO Model 2700 autosampler is designed to collect either 24 sequential samples or a single composite sample. This sampler uses a peristaltic pump to transfer water from the source to the sample containers. All materials that come into contact with the sample are either Teflon® or stainless steel except for one 35-inch segment of silicone rubber tubing. The manufacturer indicates that this sampler has a suction lift of 26 ft. The controller can regulate a sampling program, including the time intervals between sample collection, the volume of samples, the length of the purge cycle between each sampling, and the purging time. A water-level actuator that will start the sampling program at a predetermined water level can be interfaced with the ISCO autosampler. A photograph of the ISCO Model 2700 autosampler is shown in figure 1.

The ISCO Model 2700 autosampler satisfied all the criteria for collecting samples for analysis of trace organic compounds except that pertaining to the size of the sample container. This autosampler can collect twenty-four 350-milliliter samples in glass bottles or twenty-four 1-liter samples in polypropylene bottles. However, for trace organic compound analysis, especially for pesticides, 1-liter glass sample bottles are needed. No existing 1-liter glass bottle conforms to the size and shape of the polypropylene bottle currently used in the ISCO Model 2700. Therefore, no available 1-liter glass bottle can fit into the space in the autosampler housing.

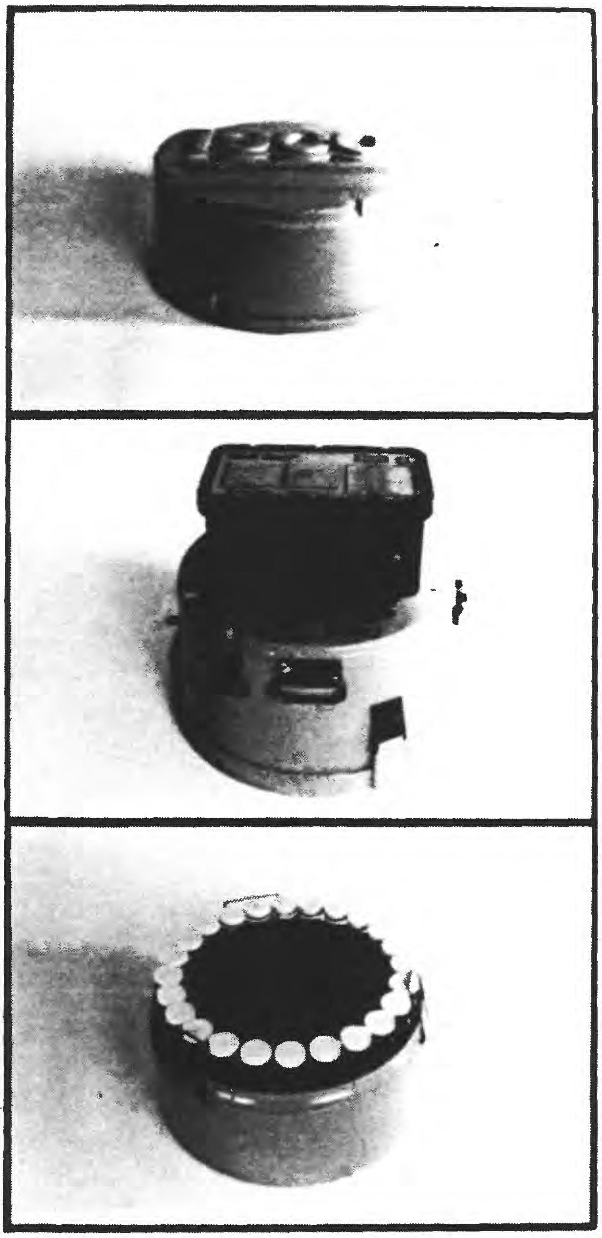

Figure 1.--ISCO Model 2700 autosampler.

Two major modifications were made to the autosampler so that it would accommodate 1-liter or larger glass sample containers: (1) 24 Teflon® funnels, which deliver the water samples from the distributor to the glass bottles, and a stand were added to the original sampler; (2) the distribution arm was extended to all of the funnels for the delivery of the water samples. The modified autosampler is shown in figure 2. (The modified autosampler will hereafter be referred to in this report as the autosampler.)

In this configuration, the peristaltic pump delivers water from the source through the Teflon® suction line, the 35-inch silicone rubber tubing, the distributor, and finally through the funnel to the sample bottles, which are situated outside of the sampler housing. Bottles of any size or shape and tubing of any length can be used between the funnels and the bottles. If samples require refrigeration, the use of longer tubing to connect the funnels to the bottles will allow the bottles to be placed in a cooler or a refrigerator.

OPERATING PROCEDURES--MODIFIED AUTOSAMPLER

To set up the autosampler for automatic sequential sampling, preset all of the operation parameters on the keypad of the controller, including starting time, length of air prepurge and postpurge, length of water-purge cycle, sample volume, and sampling intervals. The autosampler will go through the following cycles:

1. Air prepurge - When the autosampler starts, the pump rotates in reverse to prepurge the suction line. The air prepurge time is precalibrated on the controller through the controller-calibration mode.

2. Water purge - The water purge cycle flushes the suction line with sample water to eliminate or minimize cross-contamination. In this cycle, the pump rotates in the forward direction and transports water into the suction line up to the inlet of the pump. The water volume is precalibrated through the controller-calibration mode.

3. Air postpurge - The pump again rotates in reverse direction, pumping out the purge water from the suction line. The air postpurge time is also precalibrated through the controller-calibration mode.

4. Multiple water purge cycles - If more than one water purge cycle is needed, steps 2, 3, and 4 may be repeated as many as four times.

5. Fill sample - The pump rotates to the forward position, fills the suction line, then continues to rotate and deliver water through the distributor, into the Teflon® funnel and tubing, and, finally, into the sample bottle. The sample volume is also precalibrated through the controller-calibration mode.

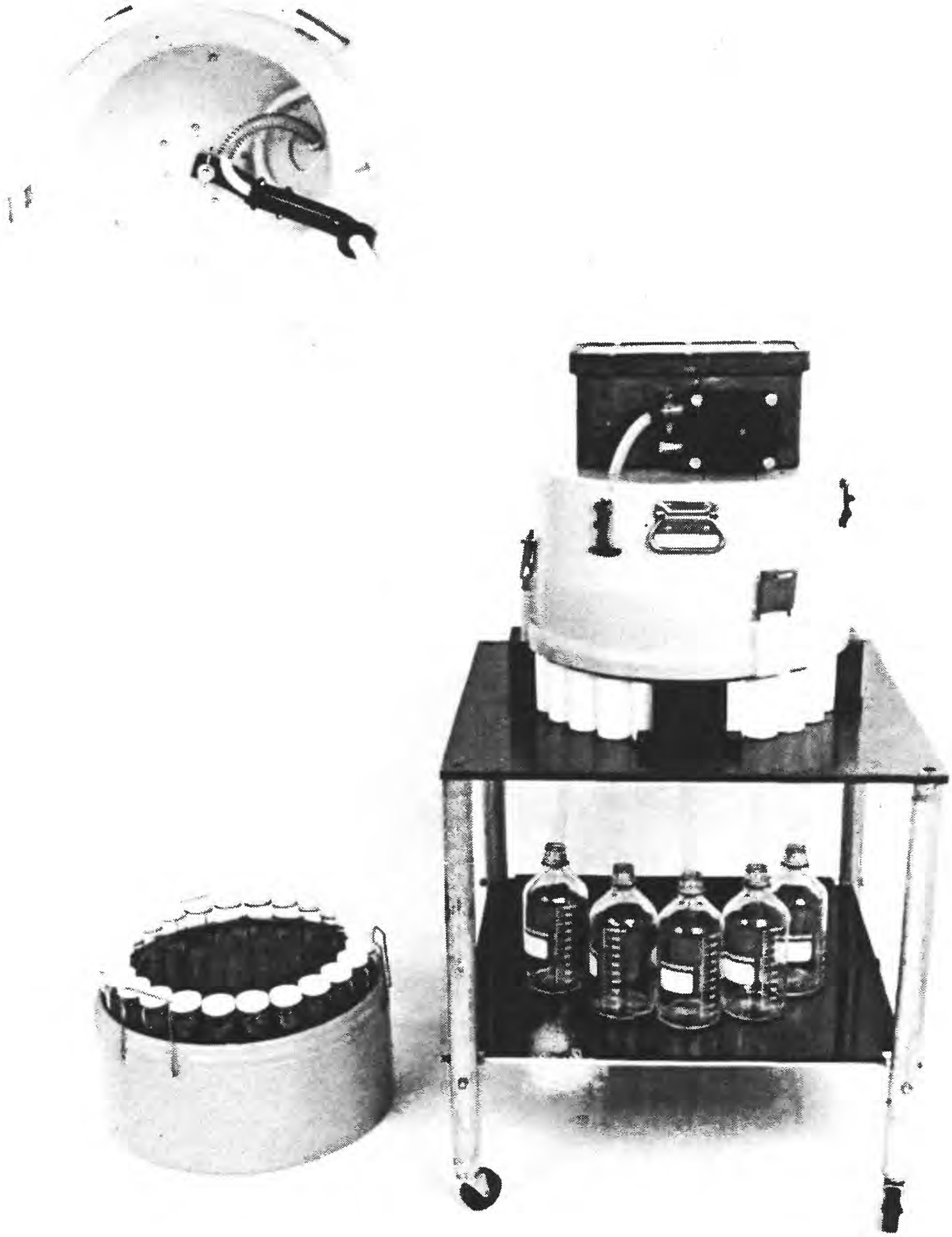

Figure 2.--Modified ISCO Model 2700 autosampler. Insert: Bottom view of distributor.

6. Air postpurge - The pump resets to reverse direction and purges out all the residual water from the suction line.

7. Distributor - The distributor will automatically move to the next position and the next cycle will start from step 1 after the preset time interval. One sampling cycle is completed when all seven of the preceding steps have been performed.

The details of setting up the sampling program are given in the instruction manual for the ISCO Model 2700 sampler (ISCO, Inc., 1987).

LABORATORY TESTS

Two tests were performed at the laboratory: (1) the absorption test--checking for absorption of organic compounds to the suction line and the pump tubing of the autosampler and (2) the purge-efficiency test--checking for carry-over of the sample between cycles, which can cause cross-contamination.

Test Procedures

Two organic compounds, atrazine and 2-chlorophenol, were selected as the test chemicals. These organic compounds were analyzed using solid phase extraction and high performance liquid chromatography methods (Analytical International, Varian Associated, Inc., 1987).

Absorption Test

The test for absorption of organic compounds by the autosampler consisted of circulating a dilute solution of atrazine of known concentration through the sampler and monitoring the change in concentration of the atrazine solution. In the test setup, 25 ft of Teflon® suction line connected the supply containers to the pump; the suction lift was 9 ft. The length of Teflon® tubing between the funnel and sample bottle was 1 ft. Because there were only trace concentrations, it would have been difficult to observe any change after just one cycle. So that the effect of any absorption would be enhanced, 3 L of atrazine solution of 50 mg/L concentration was pumped through the system for ten cycles.

Water collected in the sample bottle and the water used in the purge cycle were collected from the first sampling port and then returned to the original supply bottle. The water was then recycled and collected from the next sampling port and so on through the tenth sampling port. Duplicate experiments were performed. The control sample was collected from the original supply bottle before starting the experiment. The results of the absorption test are presented in table 1.

Table 1.--*Absorption test results*

[µg/L, micrograms per liter]

Experiment number	Concentration of atrazine Control (µg/L)	 Sample (µg/L)	Percent difference[1]
1	50.4	50.3	-0.2
2	49.7	48.9	-1.6
Mean	50.0	49.6	-0.9

[1] [(Sample-control)/control] x 100

Purging-Efficiency Tests

This autosampler has two modes of purging: (1) air purge and (2) water purge. Both purging modes were tested for their ability to minimize cross-contamination of samples.

Air Purge

Air purge includes air prepurge and air postpurge. The procedures followed in this test are shown schematically in figures 3 and 4. In these procedures, atrazine solution (and, in separate runs, 2-chlorophenol solution) and water were placed in two separate containers and alternately collected through the sampler. Carry-over, or cross-contamination, due to any incomplete purge would have caused either the dilution of the atrazine solution or the introduction of atrazine into the water sample or both. Each run comprised two cycles. All steps were programmed through the controller pad. The cycles and procedural steps in each were as follows:

First cycle - Atrazine sampling (fig. 3)

Step 1: Air prepurge to waste.
Step 2: Atrazine solution (volume precalibrated) pumped from atrazine supply bottle to sample bottle.
Step 3: Air postpurge to waste.
Step 4: Distributor automatically advanced to the next sampling port.

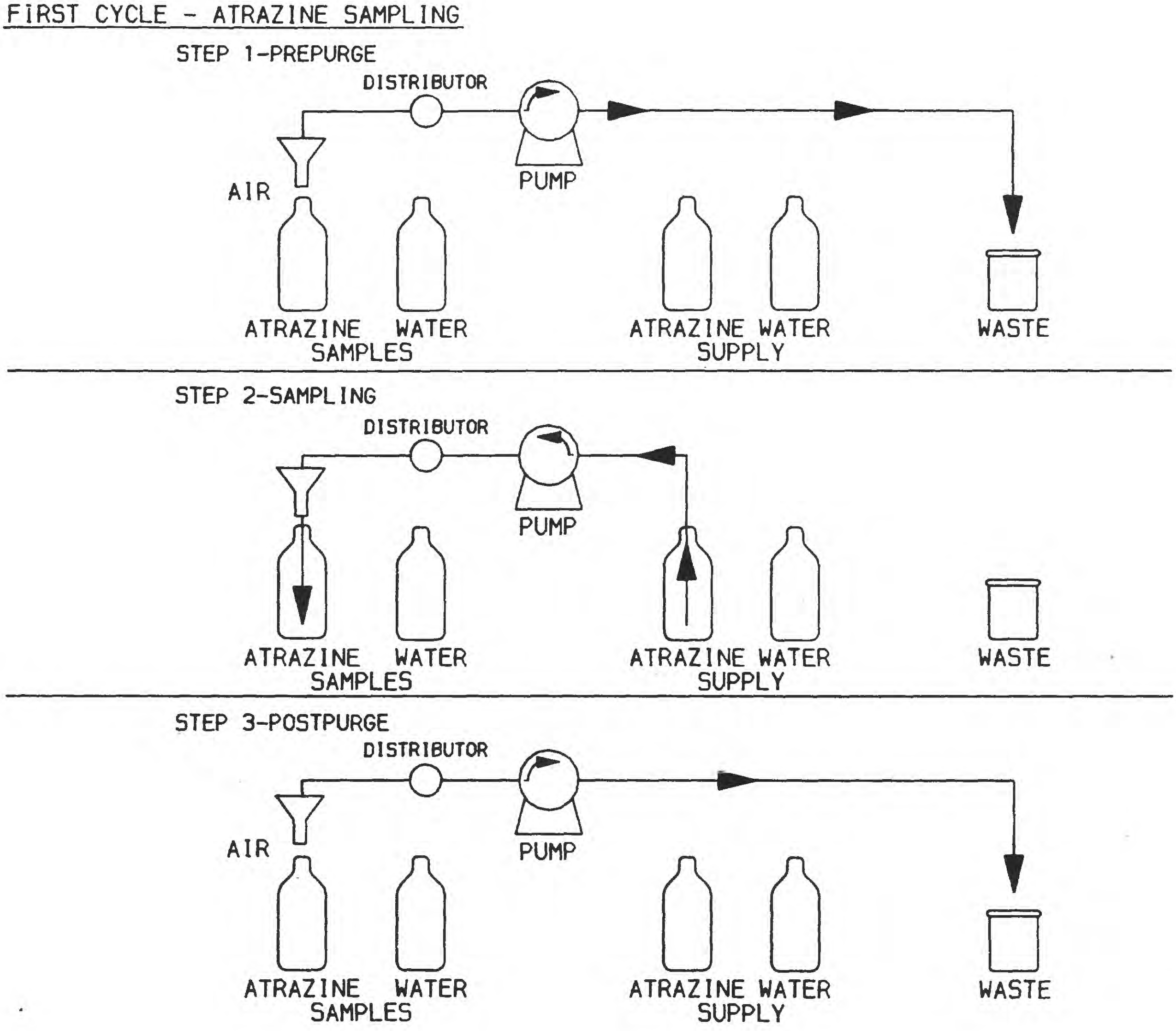

Figure 3.--Air-purge procedure used in atrazine (and 2-chlorophenol) sampling cycle.

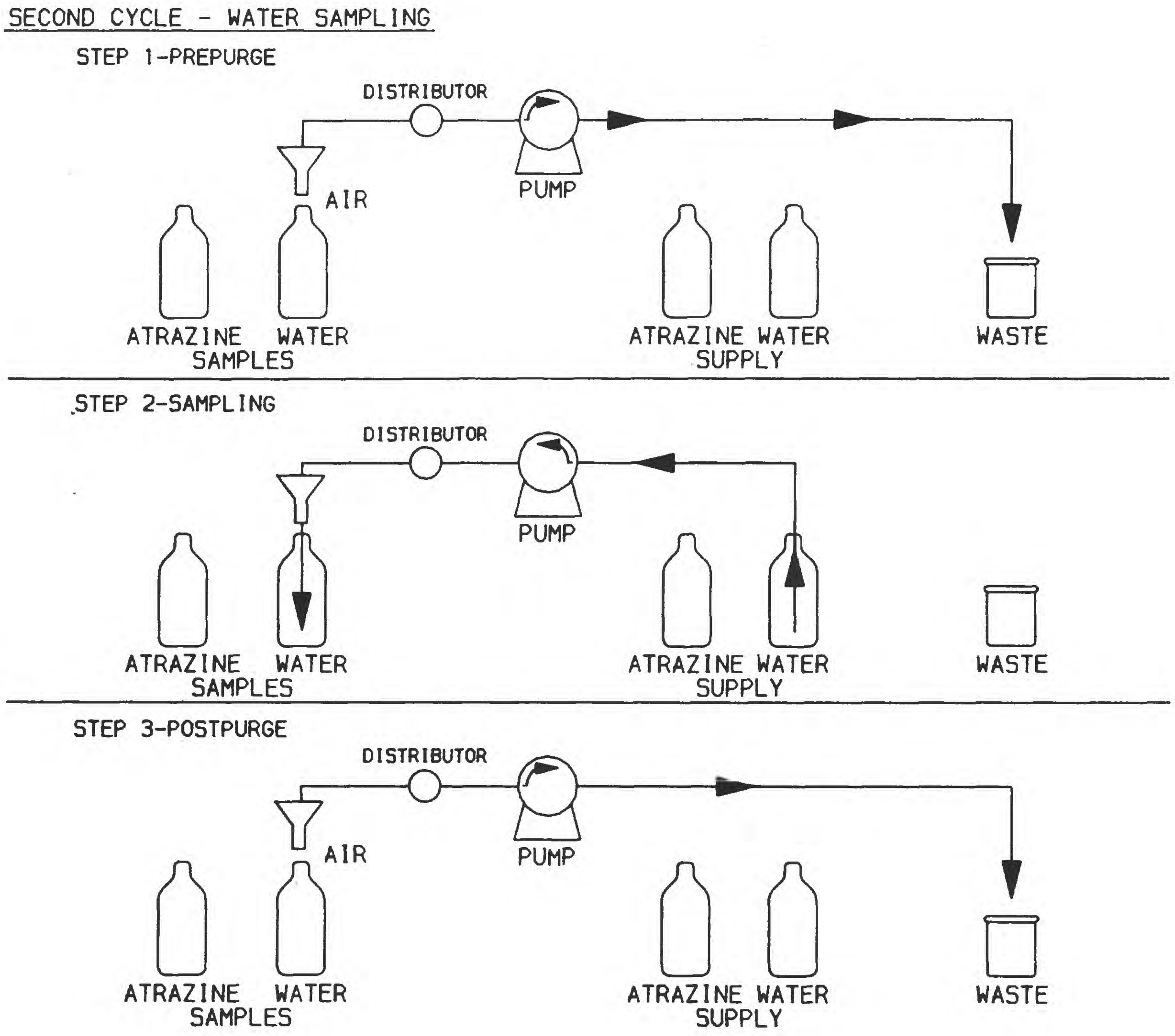

Figure 4.--Air-purge procedure used in water sampling cycle.

Second cycle - Water sampling (fig. 4)

Step 1: Air prepurge to waste
Step 2: Water (volume precalibrated) pumped from water supply bottle to water sample bottle.
Step 3: Air postpurge to waste
Step 4: Distributor automatically advanced to the next sampling port.

Two experiments were performed in duplicate. The first experiment consisted of a single run that completed the above two cycles. The test results for experiments using atrazine and 2-chlorophenol at two concentrations each are listed in table 2. The second experiment consisted of four consecutive runs that enhanced the effect of carry-over. An atrazine solution with a concentration of 50 μg/L was used in this experiment. After one run, the contents of the sample bottles were poured back into their respective original supply bottles. This process was repeated three more times, collecting the test solution sample through ports 1, 3, 5, and 7 and the water sample through ports 2, 4, 6, and 8. The test results for this experiment, which used only atrazine, are listed in table 2.

Table 2.--*Purge-efficiency test results--air purge*

[μg/L, micrograms per liter]

Experiment	Control concentration (μg/L)	Sample concentration (μg/L)	Percent difference[1]	Concentration in water (μg/L)
		ATRAZINE		
Single run	5.0	4.9	- 2.0	0
	5.0	4.8	- 4.0	0
Single run	50.1	47.9	- 4.4	trace
	49.9	48.1	- 3.6	trace
Four repetitive runs	50.4	43.1	-14.5	4.2
	49.7	42.6	-14.3	5.4
		2-CHLOROPHENOL		
Single run	10.2	8.0	-21.6	0
	9.9	9.4	- 5.1	0
Single run	49.2	49.2	0.0	2.5
	50.8	45.9	- 9.6	2.5

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[1] [(Sample-control)/control] x 100

Water Purge

The water-purge mode includes air prepurge, water purge, and air postpurge. A repeat of the water-purge cycle, which will flush the suction line between samplings and further reduce possible cross-contamination, may also be programmed into the water-purge mode. The volume needed for the flushing, from the tip of the suction line to the inlet of the pump, may be precalibrated. In this operation, water was pumped (suctioned) from the source to the inlet of the pump and then discharged before samples were collected. A maximum of four water-purge cycles may be entered through the controller pad. For this study, only two cycles were used. The sampling operation is shown schematically in figures 5 and 6.

Placing supplies of atrazine solution, water, and rinse water in separate containers and collecting samples of each made it possible to observe the effect of this water-purge mode. The procedural steps in each cycle were as follows:

First cycle - Atrazine sampling (fig. 5)

Step 1: Air prepurge, rinse-water purge, and then air postpurge rinse water.
Step 2: Repeat step 1.
Step 3: Atrazine solution pumped from the supply container to the sample bottle.
Step 4: Air postpurge to waste.
Step 5: Distributor automatically advanced to the next sampling port.

Second cycle - Water sampling (fig. 6)

Step 1: Air prepurge, rinse-water purge, then air postpurge rinse water.
Step 2: Repeat Step 1
Step 3: Water pumped from the supply container to the water sample bottle.
Step 4: Air postpurge to waste.
Step 5: Distributor automatically advanced to the next sampling port.

Two experiments were performed in duplicate. The first was a single run that completed the above two cycles. The second consisted of three consecutive runs, the purpose of which was to enhance the effect of any carry-over. After one run, the contents in the sample bottles were poured back into their respective original supply containers. This process was repeated two more times. The test solution sample was collected through ports 1, 3, and 5 and the water sample through ports 2, 4, and 6. The study of water purge was originally scheduled for four consecutive runs. However, due to an unintentional overflow of rinse water, the experiment was terminated at the end of the third run. The test results for these experiments are listed in table 3 and discussed in the next section.

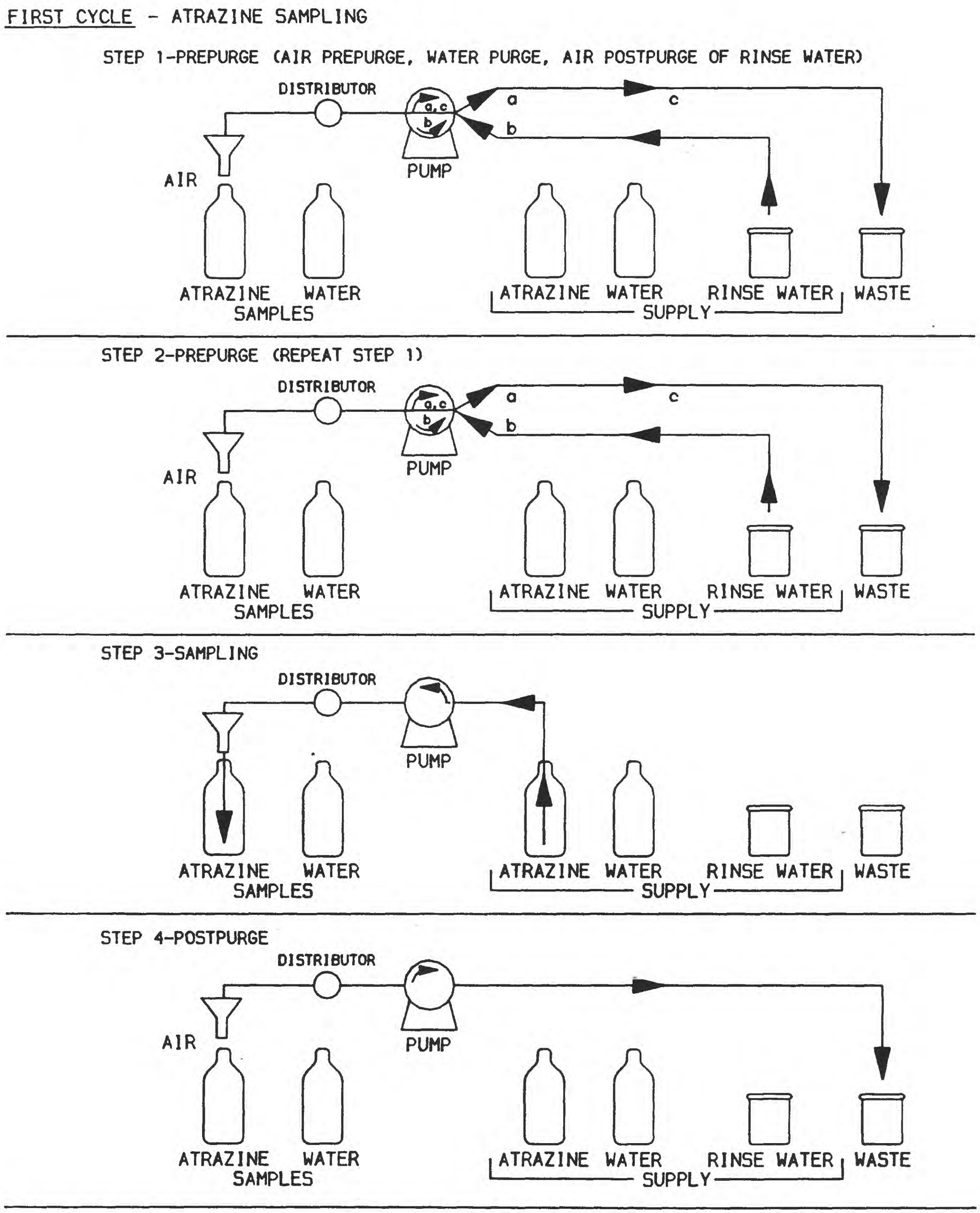

Figure 5.--Air-purge and water-purge procedures used in atrazine sampling cycle.

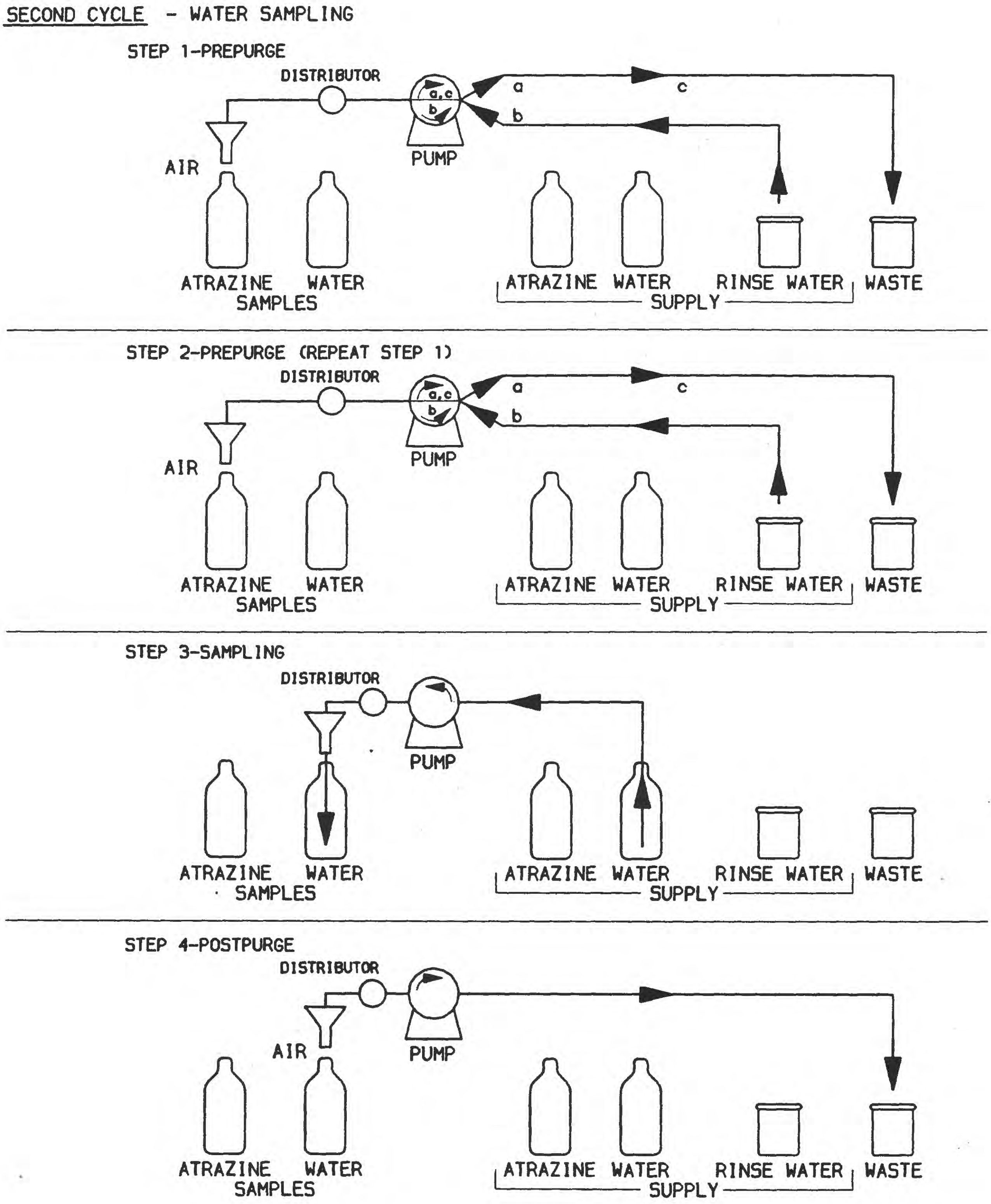

Figure 6.--Air-purge and water-purge procedures used in water sampling cycle.

Table 3.--*Purge-efficiency test results--water purge*

[µg/L, micrograms per liter]

Experiment	Control concentration (µg/L)	Sample concentration (µg/L)	Percent difference[1]	Concentration in water (µg/L)
ATRAZINE				
Single run	49.5	45.9	- 7.3	0
	50.5	48.9	- 3.2	0
Triple run	50.4	49.1	- 2.6	0
	49.6	47.4	- 4.4	0

[1] [(Sample-control)/control] x 100

Test Results and Discussion

Absorption Test

The difference between the concentration of atrazine in the control and that in the sample averaged less than 1.0 percent (table 1). Therefore, no appreciable absorption of atrazine had occurred after 10 cycles. Because the autosampler normally uses only one cycle, the absorption of atrazine and probably most organic compounds by the autosampler can be considered negligible.

Purge-Cycle Efficiency Tests

Air purge

At the lower test concentration of 5 µg/L, the concentrations of atrazine in the samples and in the control (the original stock solution of atrazine) in the single-run tests were essentially the same (table 2). Differences that were detected (less than 5 percent) can be attributed, in part, to analytical variability. No atrazine was detected in the water samples in these tests. At the higher test concentration of 50 µg/L, the difference between the concentration in the sample and that in the control was within experimental error. A trace amount of atrazine was detected in the water. It was estimated to be 0.2 µg/L, which is below the analytical quantitation limit of 0.5 µg/L.

Four consecutive runs were performed in the laboratory, the purpose of which was to enhance the carry-over effect. Under these extreme experimental conditions, which are unlikely to occur in the field, the atrazine concentration in the sample decreased from the control level (from about 50 to 43 µg/L) and the water sample showed a cumulative carry-over of about 5 µg/L.

For the 2-chlorophenol test, at a concentration of about 10 µg/L, no appreciable carry-over was observed. At a concentration of 50 µg/L, one run showed no decrease in the concentration while the other run showed a decrease from 50.8 to 45.9 µg/L. The water sample contained a small amount of 2-chlorophenol (2.5 µg/L).

Water purge

Single and triple runs, designed to evaluate the efficiency of the water-purge system, indicated little measurable cross-contamination (table 3). Although small differences in atrazine concentrations between the control and the sample were noted, no atrazine was detected in the water collected during the sampling operation. This indicates that the water-purge system is effective in eliminating cross-contamination of atrazine and probably many other organic compounds.

FIELD TEST

Field testing of the autosampler was conducted to (1) evaluate whether the sample collected by the autosampler is representative of the stream; (2) test the purging efficiency of the autosampler--air purge as opposed to water purge; and (3) evaluate the pumping capability of the autosampler at various heights above the stream level. Stream samples were analyzed for either the synthetic organophosphorus insecticide diazinon or suspended sediment.

Test Procedures

Two stream sites in Kentucky were targeted for sampling. A stream site in the Kentucky River basin with a history of pesticide contamination was chosen to evaluate the autosampler for its capacity to collect samples with representative concentrations of organic compounds. An urban stream in Louisville was chosen to evaluate the autosampler for its capacity to collect samples with representative concentrations of suspended sediment. Sampling was performed during baseflow conditions in September 1989.

First, the representativeness of samples collected by the autosampler was evaluated. Several paired samples were collected. The two samples in each pair were collected simultaneously--one by the autosampler, a point sample of stream conditions, and the other by manual sampling using traditional USGS depth-integrated cross-sectional sampling techniques. The performance of the autosampler was measured by the difference between the concentrations in the two samples in each pair.

Second, the purging efficiency of the autosampler was evaluated. The testing compared air and water purges of the system between samplings. Four paired samples were collected and analyzed for diazinon; six paired samples were collected and analyzed for suspended sediment. As in the representativeness testing, the two samples in each pair were collected simultaneously--one by the autosampler, a point sample of stream conditions, and the other by manual sampling techniques. The performance of the autosampler was similarly measured by the difference between the concentrations in the two samples in each pair.

Third, the pumping capability of the autosampler at various heights above the stream level was evaluated. This capability was evaluated on the basis of the amount of time required to pump 900 mL of sample with the pump at various heights above the stream. The pumping test was limited by the standard 25-foot length of Teflon® tubing supplied with the autosampler.

Site Description

Sampling for organic compounds was evaluated at a site on South Elkhorn Creek at Midway, Kentucky (USGS station number 03289300), which drains part of the city of Lexington (1988 estimated population--300,000) and is downstream from one of the city's two major wastewater treatment facilities (fig. 7).

Figure 7.--South Elkhorn Creek sampling site.

Some low-intensity agricultural land uses are also included within the 105-square-mile drainage area of this sampling location. As part of the Kentucky River basin NAWQA study, this site was sampled for organic compounds on a seasonal basis from May 1988 to June 1989. Because diazinon was detected in all samples collected at this location, it was chosen as the "target" compound for use in evaluating the autosampler. Site characteristics are listed in table 4.

Table 4.--*Characteristics of sampling sites used for field tests*

[USGS, U.S. Geological Survey; mi^2, square mile; ft^3/s, cubic foot per second]

USGS station name	USGS station number	Drainage area (mi^2)	Average discharge (ft^3/s)
South Elkhorn Creek at Midway, Kentucky	03289300	105	152
Middle Fork Beargrass Creek at Louisville, Kentucky	03293000	18.9	25.4

Suspended sediment sampling was evaluated at a site on Middle Fork Beargrass Creek, an urban stream in Louisville, Kentucky (fig. 8). At this site (USGS station number 03293000), the stream drains about 19 mi^2 in the metropolitan Louisville area. Downstream from the sampling site, Middle Fork Beargrass Creek converges with two other small streams and flows into the Ohio River. Because of the availability of sediment record, this site was chosen for use in evaluating the performance of the autosampler in collecting water samples containing suspended sediment. Site characteristics are listed in table 4.

Sample Collection

At each location, two stream samples were collected simultaneously--one sample by the autosampler and one sample using a hand-held DH-75-Q sediment sampler retrofitted with a Teflon® gasket and a brass nozzle. The equal-transit-rate, equal-width-increment (EWI) method was used with the DH-75-Q sediment sampler. This method, described in detail by Guy and Norman (1970), results in a cross-sectional, depth-integrated sample. The autosampler with the intake located at mid-channel and mid-depth results in a point sample. Flow conditions during sampling were typically low (baseflow, which is normal for September) and the streams were considered well mixed. Figure 9 shows an autosampler in use.


89 2 16

Figure 8.--Middle Fork Beargrass Creek sampling site.

Figure 9.--Autosampler in use.

Sample collections by the autosampler are shown schematically in figures 10 and 11. Before sampling began, the autosampler suction line, pump, and output fixture were purged--first with approximately 10 L of distilled water, then with approximately 10 L of native stream water, and, finally, with air. The DH-75-Q sediment sampler was rinsed three times with hexane and allowed to dry; this process removed any organic contaminants. The autosampler collected samples for analysis of organic compounds in 1-liter, narrow-mouthed amber bottles, which had been baked at 450 °C for 2 hours; the DH-75-Q collected samples for analysis of organic compounds in 1-quart, widemouthed glass jars, which had been baked at 450 °C for 2 hours. Samples for analysis of sediments were collected by the autosampler in standard 1-pint glass milk bottles and by the DH-75-Q in 1-quart, widemouthed glass jars.

After a clean, baked, 1-quart glass jar was fitted onto the hexane-rinsed sampler head and nozzle of the DH-75-Q, five verticals, equally spaced over the 40-foot-wide stream cross section, were sampled. Approximately 1 L of water from each was collected by the EWI method. Coincident with the sampling of the middle vertical, the automatic sampler collected a 0.9-liter sample. The intake to the autosampler was positioned at mid-channel and mid-depth (about 1 ft below the water surface). After all five verticals had been collected, the autosampler was automatically purged either with air or with 3 L of native stream water, depending on the experiment.

The EWI samples to be analyzed for diazinon were transferred from the widemouthed jars to clean, narrow-mouthed amber bottles and placed on ice. The autosampler sample for diazinon also was placed on ice. The sampling procedure was then repeated within 10 minutes using clean sample containers.

Samples collected for analysis of diazinon were shipped on ice overnight to the USGS laboratory in Colorado, where the samples were analyzed using gas chromatography methods. Samples collected for the analysis of suspended sediment were analyzed in the USGS sediment laboratory in Louisville, Kentucky.

Test Results and Discussion

Diazinon Sampling

Results of the paired sampling (EWI and autosampler) for diazinon are presented in table 5. Precision was excellent for samples collected using the EWI method. The mean diazinon concentration of the four EWI samples, which were collected approximately 10 minutes apart, was 0.26 μg/L and concentrations ranged from 0.25 to 0.26 μg/L. Precision was similar for samples collected with the autosampler. The mean diazinon concentration of the four autosampler samples was 0.26 μg/L and concentrations ranged from 0.25 to 0.27 μg/L. Slightly higher diazinon concentrations (0.02 and 0.01 μg/L) were detected in samples 2 and 4 than in samples 1 and 3. These differences might have been caused by contamination due to inadequate purging with air or water between the cycles but might also reflect analytical variability or differences between samples collected a few minutes apart.

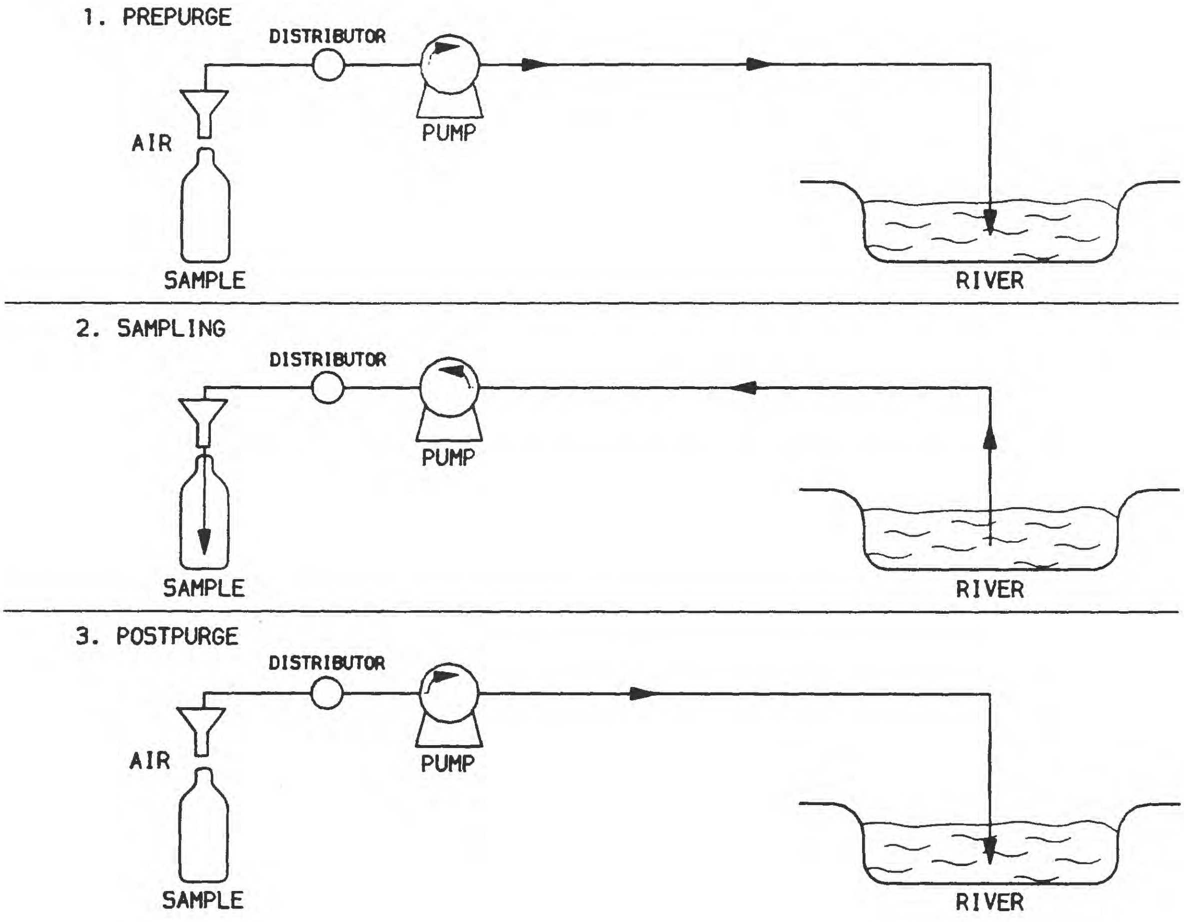

Figure 10.--Air-purge procedure used in field test.

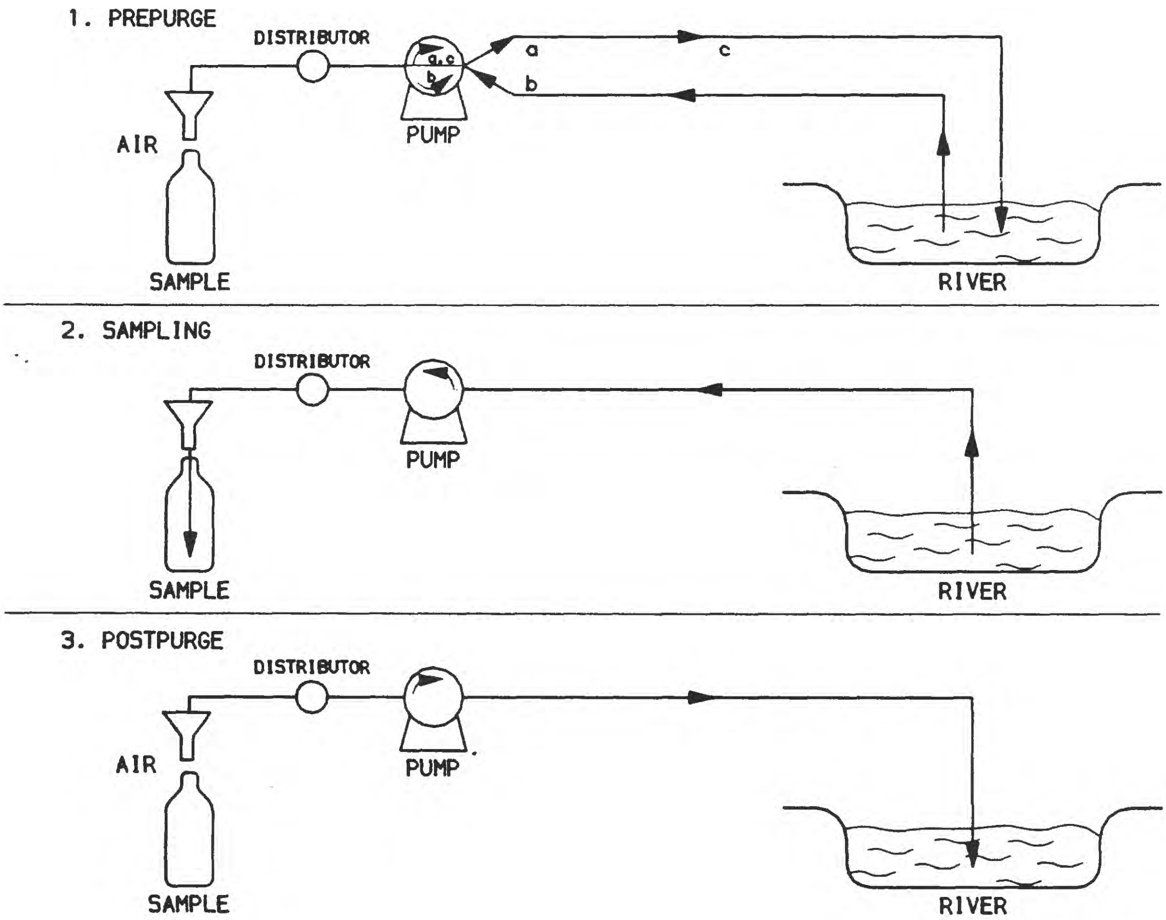

Figure 11.--Air-purge and water-purge procedures used in field test.

Table 5.--*Comparison of diazinon concentrations in samples collected by the EWI method and the autosampler (using two purging modes)*

[μg/L, micrograms per liter; EWI, equal width increment]

Sample number	Autosampler purging mode	Diazinon concentration (μg/L) EWI method	Diazinon concentration (μg/L) Autosampler	Percent difference[1]
1	air purge	0.26	0.25	-3.8
2	air purge	.25	.27	8.0
3	water purge	.26	.25	-3.8
4	water purge	.26	.26	0

[1] [(Autosampler-EWI)/EWI] x 100

The difference between each paired sample was quantified by calculating a percent difference, where $[C]_{EWI}$ is taken as the standard value, as expressed by the formula:

$$\text{Percent difference} = \frac{[C]_a - [C]_{EWI}}{[C]_{EWI}} \times 100,$$

where

$[C]_a$ is the constituent concentration in the autosampler sample and
$[C]_{EWI}$ is the constituent concentration in the EWI sample.

The percent differences in diazinon concentrations between the paired samples (EWI and autosampler) ranged from -3.8 to 8.0 percent. No obvious differences were detected when the air-purge mode in table 5 was compared with the water-purge mode. These results indicate that the autosampler is capable of collecting a stream sample for analysis of trace organic compounds that is comparable to a sample collected by EWI methodology, provided the stream is well mixed.

Suspended-Sediment Sampling

Results of the paired sampling (EWI and autosampler) for suspended sediment are presented in table 6. The mean suspended-sediment concentration for the six EWI samples was 5 mg/L and concentrations ranged from 4 to 9 mg/L. The mean suspended-sediment concentration for the six autosampler samples was 5 mg/L and concentrations ranged from 2 to 8 mg/L.

Table 6.--*Comparison of suspended-sediment concentrations in samples collected by the EWI method and the autosampler (using two purging modes)*

[mg/L, milligrams per liter; EWI, equal width increment]

Sample number	Autosampler purging mode	Sediment concentration (mg/L) EWI method	Sediment concentration (mg/L) Autosampler	Percent difference[1]
5	air purge	7	8	14
6	air purge	9	8	-11
7	air purge	4	4	0
Mean		7	7	
8	water purge	4	2	-50
9	water purge	4	4	0
10	water purge	4	3	-25
Mean		4	3	

[1] [(Autosampler-EWI)/EWI] x 100

As before, the difference between each paired sample was quantified by calculating a percent difference. Percent differences in suspended-sediment concentrations among the pairs ranged from -50 to 14 percent. Although this percent difference range seems large, some variations could be explained by the low concentrations and the single-significant-digit reporting convention. Actual concentration differences between the paired samples were small (0 to 2 mg/L). The mean sediment concentration of samples 5, 6, and 7 is higher than the mean concentration of samples 8, 9, and 10 for both EWI and autosampler methods. This could represent actual variations in suspended sediment concentrations in the stream during sampling and might not be related to differences between the water-purge and air-purge modes.

These results indicate that the autosampler is capable of collecting a suspended-sediment sample that is representative of actual stream conditions and reasonably comparable to an EWI-collected sample, at least for very low concentrations of suspended sediment (less than 10 mg/L). However, some concern is warranted because the percent differences between concentrations in samples collected by the autosampler and those in samples collected by the EWI method were, in some cases, large. As mentioned, some of the differences could be attributed to the small concentrations sampled and to the lack of analytical sensitivity. Further testing is needed, particularly with high suspended-sediment concentrations, to adequately evaluate the capability of the autosampler to collect representative samples for suspended-sediment analysis.

Pumping Capability

The pumping capability of the autosampler was evaluated by determining the time required to collect 900 mL of sample with the sampler placed at various heights above the stream. When fitted with a 25-foot length of 3/8-inch suction line, the autosampler collected 900 mL of sample in 1 minute when placed at 5 ft and at 15 ft above the stream water surface. Heights greater than 15 ft were not tested, but the manufacturer indicates that the pump can lift water as high as 26 ft. The length of the intake line can also affect pump efficiency. For installations requiring lengths of suction line much greater than 25 ft, friction between the water and the suction-line tubing can adversely affect the performance of the pump. Many gage houses are situated at horizontal and vertical distances from the normal stream edge that require a suction line length greater than 25 ft. The sampling of non-dissolved constituents, such as suspended sediment, may not be particularly efficient under these conditions and may result in samples that are not representative of the stream. Further testing with longer lengths of suction line and greater heights is needed.

SUMMARY AND CONCLUSIONS

Two major modifications were made to the ISCO Model 2700 autosampler so that it could be used with 1-liter or larger glass sample containers: (1) 24 Teflon® funnels with a support stand were added and (2) the distributor arm was extended to deliver water through the funnels to large glass sample containers. The modified autosampler is capable of collecting 24 large volume samples in glass containers, which are required for the determination of trace organic compounds.

Laboratory tests examined the possible absorption of two organic compounds by the autosampler and the possible cross-contamination of samples between sampling and purging cycles. Atrazine and 2-chlorophenol were used for the tests. The absorption test indicated a concentration difference of less than 1 percent between the control and samples that had been recycled through the autosampler 10 times. The purge-efficiency test indicated that there was no cross-contamination during regular sampling with water purging. Based upon these results, absorption and cross-contamination of organic compounds probably is not a problem with the modified sampler.

Field tests were performed at two stream sites in Kentucky. At one site, which had a history of pesticide contamination, the autosampler was evaluated with respect to sampling for diazinon. Paired samples were collected by the modified autosampler and by the traditional USGS depth-integrated, cross-sectional sampling technique. Comparison of the concentration of diazinon in water samples collected by the two methods showed a difference of less than 10 percent. The autosampler was evaluated with respect to suspended-sediment sampling at the other site. Concentration differences of -50 to 14 percent were observed for suspended-sediment samples collected by the two methods, but concentrations generally were within a range of a few milligrams per liter.

These differences may be partly due to the low concentrations (less than 10 mg/L) of suspended sediment. Further tests at higher suspended-sediment concentrations and with longer intake lines are needed, but, based on test results to date, the autosampler is suitable for collecting water samples for analysis of trace organic compounds where suspended-sediment concentrations are low.

The pumping capability of the autosampler was also evaluated. The pump could collect a 900 mL sample at a suction lift of 15 ft. Although the manufacturer specifies maximum suction lift at 26 ft, further testing for suction lift higher than 15 ft is needed.

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