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Yvette C. Berisford, Parshall B. Bush,* John I. Blake, and Cassandra L. Bayer

ABSTRACT

Three low-volume mini-sprinklers were tested for their efficacy to strip trichloroethylene (TCE) and tetrachloroethylene (PCE) from water. Deionized water spiked with TCE and PCE was pumped for approximately 1 h at 0.19 to 0.21 MPa (28 to 30 lb in^{-2}) through a mini-sprinkler supported on top of a 1.8-m-tall riser. Water was collected in collection vessels at 0.61 and 1.22 m above the ground on support columns that were spaced at 0.61-m intervals from the riser base, and samples were composited per height and distance from the riser. Overall, air-stripping reduced dissolved concentrations of TCE and PCE by 99.1 to 100 and 96.9 to 100%, respectively, from mean influent dissolved concentrations of 466 to 1675 µg L^{-1} TCE and 206 to 940 µg L^{-1} PCE. In terms of mass removed, the mini-sprinklers removed TCE and PCE at a rate of approximately 1400 to 1700 and 700 to 900 µg L^{-1}, respectively, over a 1-h test period. Mini-sprinklers offer the advantages of (i) easy setup in series that can be used on practically any terrain; (ii) operation over a long period of time that does not threaten aquifer depletion; (iii) use in small or confined aquifers in which the capacity is too low to support large irrigation or purging systems; and (iv) use in forests in which the small, low-impact droplets of the mini-sprinklers do not damage bark and in which trees can help manage (via evapotranspiration) excess waste water.

Trichloroethylene (TCE) and tetrachloroethylene (PCE) are industrial solvents that have been used as cleaning and degreasing agents since the 1930s (McCulloch and Midgley, 1996). The USEPA classified both chemicals as "high production volume chemicals," with production exceeding 454 000 kg (1 million lb) annually in the USA (USEPA, 2000). Because of their widespread use and inappropriate disposal, TCE and PCE are common contaminants in soil and ground water in the USA and are included on at least seven federal regulatory lists (Scorecard, 2001; USEPA, 1998a, 2001; United States Geological Survey, 2001). Some of the present methods used for the remediation of volatile organic chemical compounds (VOCs) from ground water or contaminated soil include phytoremediation (Dietz and Schnoor, 2001; Newman et al., 1997), biodegradation (Leahy and Shreve, 2000; McCarty, 2000; Mihopoulos et al., 2000; van Eckert et al., 2001), in vitro dehalogenation (Chang et al., 2001), dechlorination by metals (Cheng and Wu, 2001), chemical oxidation by potassium permanganate (Schnarr et al., 1998; Schroth et al., 2001; Soel and Schwartz, 2000) and hydrogen peroxide (Gates and Siegrist, 1995), pump and treat technology (USEPA, 1998b), and in situ air-sparging (Adams and Reddy, 1999; Rabideau et al., 1999; Reddy and Adams, 2000; Ryan et al., 2000).

A recent study at the University of Nebraska at Lincoln (Richardson and Sahle-Demessie, 1998) and a follow-up evaluation project by the USEPA SITE Program (in cooperation with USEPA Region 7 and University of Nebraska at Lincoln) at Hastings, NE (USEPA, 1998c) reported that the common agricultural use of sprinkler systems to irrigate crops also reduced the dissolved concentrations of VOCs in the irrigation water by at least 96% without a significant effect on air quality. The studies were prompted by a need for alternative, more economical methods to treat ground water. In both studies, the sprinkler system was a pivoting, self-propelled 80-m-long boom from which ground water (which was already contaminated with VOCs) was pumped through nozzles along the boom at a rate of 4353 L min^{-1} (1150 gal min^{-1}). That irrigation system was not used as a remediation method per se. However, since the ground water had been already contaminated with TCE and PCE and since crops are irrigated with boom-type irrigation systems, the investigation centered on remediation as a side benefit of this type of irrigation system. Although that irrigation system could be effective in remediation, its use would be limited to relatively open and flat terrain (slope < 15°). A major concern about the use of such large sprinkler systems would also be their effect on aquifer depletion in areas affected by overdraft of ground water resources. This is particularly important in considering that ground water is the basic resource for about 40% of the public water supply in the USA, and in some states more than 90% of the water that is used for irrigation is provided by ground water (Cash, 1998; United States Geological Survey, 2000).

The importance of the Nebraska study was that it demonstrated the effectiveness of air stripping by an irrigation sprinkler system. With an emphasis on application to forested land, the present study was conducted to test smaller mini-sprinkler systems that could be set up easily in practically any type of terrain and that could be operated at a substantially smaller risk to ground water depletion. Trees, particularly conifers such as loblolly pine (*Pinus taeda* L.), would provide a means for managing (via evapotranspiration) the excess wastewater during year-round sprinkler operations. The mini-sprinklers have small and low-impact droplets that will not damage the bark of trees, which is a problem with typical impact sprinklers that have a concentrated stream and a rotating head. Another advantage of using mini-sprinklers is that many contaminated aquifers are

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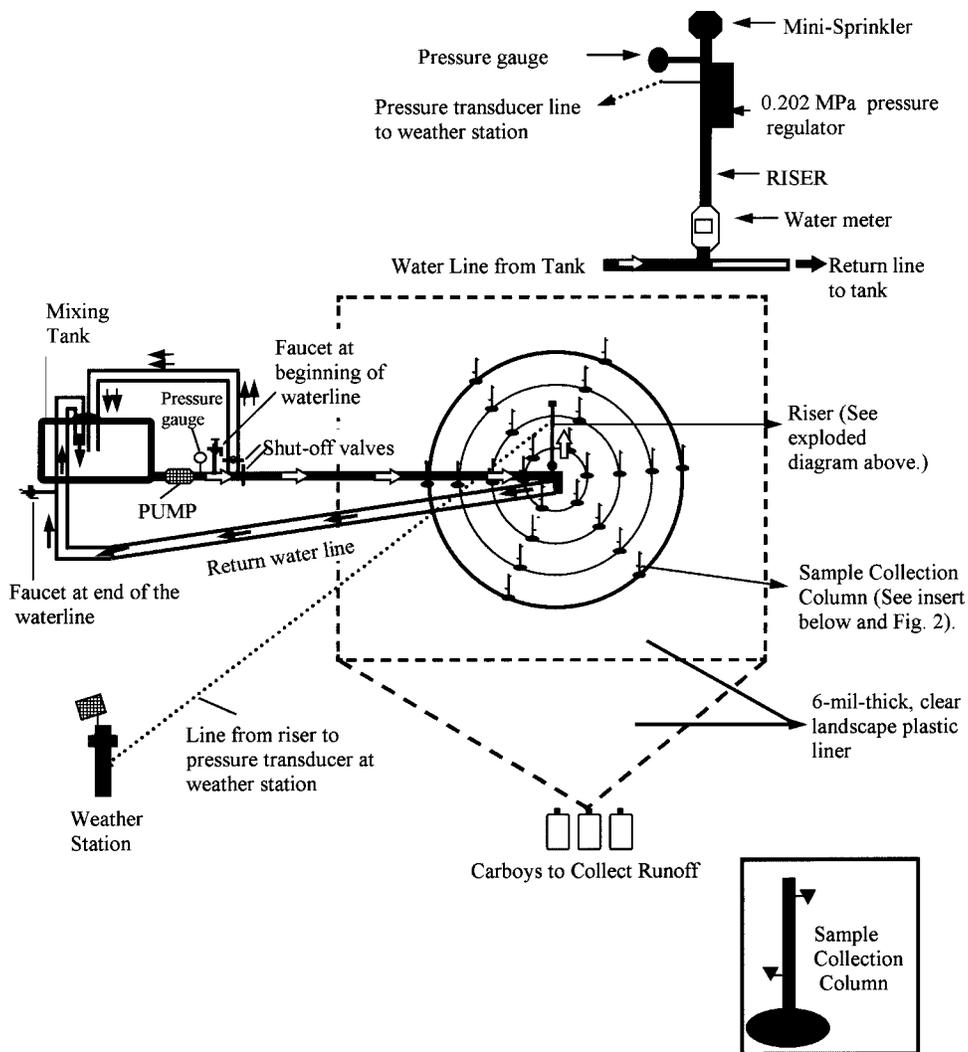
Fig. 1. General layout of the field test area (not drawn to scale). White arrows indicate the flow of water from the mixing tank to mini-sprayer, single black arrows indicate flow of water from the riser to the mixing tank, and double black arrows indicate flow in a bypass loop that was used to mix the water in the tank. Refer to Fig. 2 and 3 for enlargements of the sample collection columns and method of compositing.

small or confined and the wells are shallow so that the capacity is relatively low, and hence does not support large irrigation systems such as the one used in the Nebraska study.

Smaller-scaled irrigation systems, such as those that are used on lawns and in horticultural greenhouses, can be used on practically any terrain and can be set up within a minimum of cleared land area. Additionally, such systems could be quickly set up with materials that are generally available at local gardening and hardware supply outlets, and so offer an additional advantage of quick mobility to address emergency remediation tasks. The current research tested the efficacy of three types of horticulture mini-sprinkler systems to strip TCE and PCE from contaminated water.

MATERIALS AND METHODS

Field Design for Efficacy Testing

The basic design (Fig. 1) consisted of a mixing tank from which deionized water containing TCE (CAS 79-01-6) and

PCE (CAS 127-18-4) was pumped at a pressure of 0.19 to 0.21 MPa (28 to 30 lb in^{-2}) through polyethylene irrigation pipe to a mini-sprinkler that was located 1.8 m high on a riser in the center of a 12.2-m-diameter, circular area. Radiating out from the base of the riser were four concentric circles spaced 0.61 m apart (Fig. 2). Six sample collector columns were evenly spaced on each concentric circle so that six rows of four columns each radiated at approximate 60° intervals from the base of the riser. The entire area of the columns plus a buffer zone (to catch drift) was lined with 6-mil-thick clear polyethylene plastic to contain the contaminated water and collect runoff.

The polyethylene irrigation pipe used in this study was selected because of its general availability in hardware and irrigation supply stores throughout the southeastern USA. Of concern was the possible adsorption of TCE or PCE to the inside of or loss through the walls of the polyethylene pipe. Low-density polyethylene has been used as the membrane in vapor diffusion bag samplers for monitoring VOCs in sediment and water without any reported significant adsorption to the polyethylene (Vroblesky 2000, 2001a,b; Vroblesky and Campbell, 2001). Because of the lack of published data on the behavior (adsorption to or diffusion through the pipe walls) of TCE or PCE in the type of polyethylene irrigation
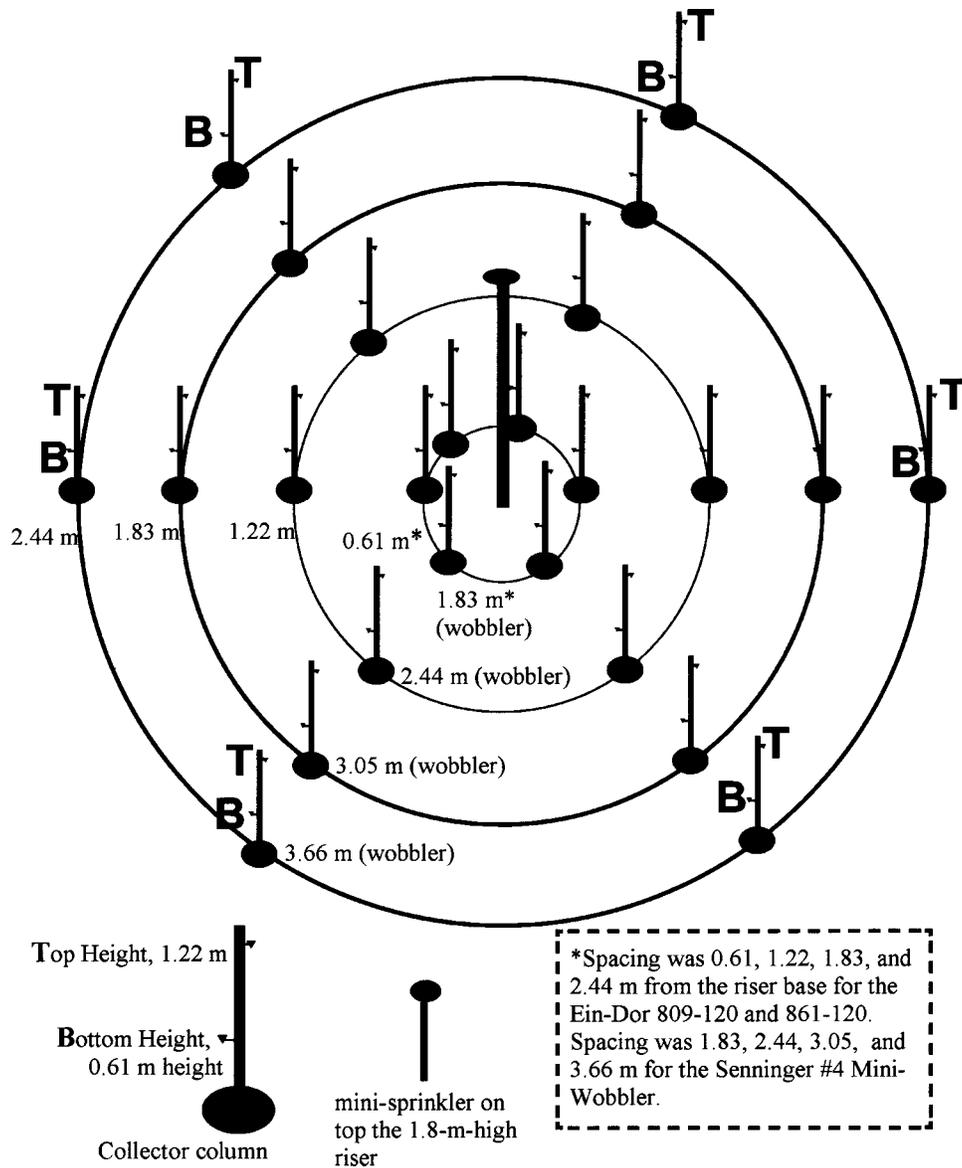
Fig. 2. Location of sample collector columns and method of compositing samples. Water from the bottles at the same height (1.22 or 0.61 m) and distance (i.e., those indicated on the same circle in the diagram) from the riser were composited. For example, water from all T bottles on the 2.44-m circle were composited into one bottle and water from all B bottles on that same circle were composited into another bottle.

pipe used in our study, the concentrations of TCE and PCE in the pipe at points where the contaminated water entered and left the pipe were compared. In Fig. 1, the points of collection are labeled as the faucets at beginning and end of the water line. Samples were collected simultaneously from each faucet at the beginning, end, and each 15 min of each test ($n = 5$ per test). Two tests of each mini-sprinkler system were conducted (total of six tests). Analysis of variance (SAS PROC ANOVA, $\alpha = 0.05$, Duncan's multiple range test) was used to compare the means of dissolved concentrations of TCE and PCE in the samples collected at the beginning and end of the irrigation pipe for each of the six tests (SAS Institute, 2000).

Each collector column (Fig. 3) was made of a 1.37-m-long × 1.27-cm-diameter (54 in × 0.5 in) rebar rod inserted into the center of an X-shaped base that was constructed from two pieces of 5- × 10- × 46-cm (height × width × length) untreated lumber. Two collection funnels were clamped to the rod so that the top of one funnel was 0.61 m and the other was 1.22 m

above the ground. A 1-L amber glass collection bottle was clamped beneath each funnel so that the stem of the funnel extended full length into the bottle and the base of the funnel was seated across the opening of the bottle. The funnels were clamped opposite each other so that they would not obstruct the path of water into each other.

Mini-Sprinkler Setup

Three sprinkler types were tested: Senninger Mini-Wobbler (#4 nozzle; Senninger Irrigation, Orlando, FL) and Ein Dor Model 809-120 and 861-120 mini-sprinklers (Agridor Ltd., Rosh Ha'ayin, Israel). The mini-sprinklers, connectors, pressure regulators, and polyethylene pipe were supplied by ML Irrigation Systems (Laurens, SC). Some of the characteristics of each mini-sprinkler are listed in Table 1. For each test, a mini-sprinkler was attached to a 0.202 MPa (2.0 atm) pressure regulator (Fig. 1) mounted on top of a 1.27-cm-i.d. polyethylene irrigation pipe (see top insert in Fig. 1.). The pipe was
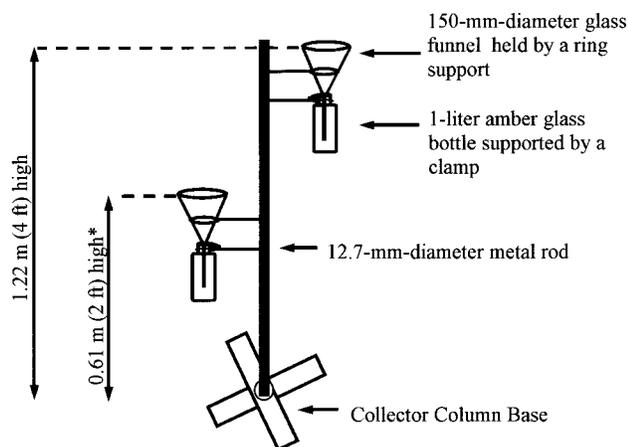
*Height is measured from the ground to the top of the collection funnel.

Fig. 3. Design of a sample collection column.

supported by a metal support stand that held the mini-sprinkler 1.8 m above the ground. The base of the pipe at ground level was attached to a water meter that measured the volume of influent water that flowed into the sprinkler. A centrifugal pump (Sta-Rite 60 Cycle 3/4 hp, Model JHD-62HL; Sta-Rite, Delavan, WI) pumped water from a 1134-L-capacity mixing tank through an approximate 15-m-long × 2.54-cm-i.d. polyethylene irrigation pipe to a T-connector at the base of the water meter. Water that did not enter the sprinkler returned to the tank through another 15-m loop of the irrigation pipe (Fig. 1, black arrows). Faucets were attached at the beginning and end of the water line so that water could be sampled as it entered and left the irrigation pipe. The difference between dissolved TCE and PCE concentrations in the water as it entered and exited the pipe would be used to assess the loss of dissolved concentrations of TCE or PCE within the pipe. Water pressure at the base of the mini-sprinkler was monitored with a manually read pressure gauge and a pressure transducer that was connected to a data logger in a weather station approximately 30 m from the riser. Pressure transducer readings and pressure gauge readings were recorded every 2 and 15 min, respectively, during a test.

Test Conditions

Test conditions that could not be controlled, but which may affect the performance of the mini-sprinkler test systems, were measured on site. Air temperature, percent relative humidity, barometric pressure, solar radiation, and wind speed and direction were recorded every 2 min by the weather station.

Before each test, the mixing tank was rinsed three times with approximately 1134 L of tap water (Athens, GA city water) followed by two rinses with deionized water. Each 1134-L aliquot was circulated in the tank for approximately 1 h, and then the tank was drained and vacuumed to remove all standing water from it. On the evening before a test day,

the tank was filled with deionized water and allowed to vent overnight to remove any free chlorine in the water.

On a test day, the water volume in the tank was adjusted to 1134 L to compensate for overnight evaporation. The water was mixed for 1 h, then 1 mL each of TCE and PCE in 600 mL of methanol was added to the tank, and the solution was mixed for an additional 1 h before turning on the mini-sprinkler. The TCE (stabilized, 99.5+% purity, ACS reagent-grade) and PCE (99+% purity, ACS reagent-grade) were obtained from J.T. Baker (Phillipsburg, NJ) and Sigma-Aldrich Chemical Company (Milwaukee, WI), respectively.

Each mini-sprinkler test system was run for approximately 1 h for each of two tests on the same day. The 1-h test time was needed so that a sufficient volume of water for a primary, duplicate, and matrix spike sample could be collected in the bottles on the collection columns. The Senninger Mini-Wobbler was tested on 14 Mar. 2001 from 0737 to 0852 and 1004 to 1105 h. The Ein Dor 809-120 model was tested on 23 Mar. 2001 from 0735 to 0838 and 1307 to 1407 h, and the Ein Dor 861-120 model was tested on 23 Mar. 2001 from 0916 to 1018 and 1127 to 1227 h.

Field blanks of tap water, deionized water, and mixing tank water (before the addition of TCE and PCE) were each placed in 250-mL beakers and exposed to the field conditions in an area near the test site that precluded exposure to the TCE and PCE solution that was sprayed into the air by the mini-sprinklers.

Sampling

The locations of the sampling stations and their frequency of sampling are listed in Table 2. Samples were collected from the mixing tank, faucets at the beginning and end of the water line, collectors on the columns, beakers on the ground within the test area, runoff, and field blanks. Water from the collector bottles on the columns was composited per height and distance from riser base (Fig. 2).

At each sampling station, three samples (primary, duplicate, and matrix spike samples) were collected in prelabeled 60-mL vials (clear borosilicate glass vials [Kimble/Kontes, Vineland, NJ] for USEPA water analysis). Vials were completely filled to overflowing to eliminate head space before capping with teflon-lined tops. Each vial contained 1 g of phosphate buffer and ammonium chloride preservative (1.2 g ammonium chloride to 2 g dibasic sodium phosphate to 198 g monobasic potassium phosphate) to lower the sample pH to 4.8 to 5.5 and convert free chlorine to monochloramine.

Samples were placed in ice chests within 5 min after collection. Each ice chest contained triplicate blanks (three vials each of tap water, deionized water, and mixing tank water) and a calibrated, digital thermometer that measured current, minimum, and maximum temperatures. Temperatures in the chests were maintained at 1 to 5°C. Each set of field samples was accompanied by a chain of custody form and transferred to a laboratory refrigerator (≤4°C) within 2 h after sampling.

Table 1. Characteristics of the mini-sprinklers that were used in the tests.

Mini-sprinkler	Flow rate†	Droplet size	Wetting diameter‡	Special feature
	L h⁻¹ (gal h⁻¹)		m (ft)	
Senninger Mini-Wobbler	141 (37)	medium	10.4 (34–35)	large wetting diameter at low pressures
Ein Dor 809-120	120 (32)	fine	4.2 (13.8)	provides a mist of very fine droplets
Ein Dor 861-120	120 (32)	medium	9.6 (31.5)	ideal for irrigation beneath trees

† At 0.21 MPa (30 lb in⁻²).
‡ At 0.21 MPa (30 lb in⁻²) and a 1.8-m height.

Table 2. Sampling stations and frequency of sampling.

Sampling station	Frequency and location
Mixing tank	Sampled before addition of trichloroethylene (TCE) and tetrachloroethylene (PCE) and before and after each test.
Faucets	Sampled at the beginning, end, and every 15 min during a test.
Collectors (0.61 m)†	Sampled at the end of the test period. Composited per distance from the riser (Fig. 2).
Collectors (1.22 m)†	Sampled at the end of the test period. Composited per distance from the riser (Fig. 2).
Runoff	Sampled at the end of the test.
Ground level	Composite from six 250-mL beakers placed on ground 0.61 m from riser.
Field blanks	Tap, tank, and deionized water, each in a 250-mL beaker, sampled at the end of each test day.
Triplicate blanks	Tap, tank water, and deionized water in vials were placed in each ice chest that was used to transport samples.‡

† These are the bottles on the collector columns.
‡ A set of three vials (primary, duplicate, and matrix spike) of each type of water was placed in each ice chest.

Field Design to Test the Effect of Compositing and Exposure to Air on Dissolved Concentrations of Tri- and Tetrachloroethylene

Since TCE and PCE are volatile, the physical process of pouring water from bottles on the collector columns to make a composite may have resulted in the loss (via volatilization) of dissolved concentrations of TCE or PCE in the composite. Also, during the approximate 1-h test of each mini-sprinkler system, water in the uncapped collection bottles and ground-level beakers was exposed to air; hence, this prolonged exposure during the sample accumulation period could also have caused a loss of dissolved concentrations of TCE or PCE in the samples. Either of these potential losses could be mistaken for losses due to stripping by the mini-sprinklers and would result in a greater-than-actual stripping efficiency of the mini-sprinkler systems. Therefore, an experiment was conducted to determine if such losses could occur under field conditions similar to those of the mini-sprinkler tests.

Three replications, each consisting of six collector columns that were evenly spaced in a 1.22-m-diameter circle, were set up in the same experimental area where the mini-sprinkler tests had been conducted (Fig. 4). The same techniques that were used in the mini-sprinkler tests to clean, fill, mix, and add TCE and PCE to the mixing tank and to collect samples in triplicate were used in this experiment. After the TCE and PCE had been mixed in the tank for 1 h, the faucet at the beginning of the water line was purged for 5 min, and then each of sixty 1-L amber glass bottles was filled with approximately 300 mL of water from this faucet and capped with teflon-lined caps. The bottles were randomly allocated into five sets of 12 bottles each: Replication 1, Replication 2, Replication 3, Time 0 Min, and Time 60 Min. For Replications 1 through 3 (Fig. 4), two bottles were clamped on the collector columns so that the bottles were approximately opposite each other and 1.22 m high on the column. One member of each pair of bottles on each column was allocated for preparing the composite sample, and the other bottle was allocated for individual sampling (noncomposite). The Time 0 Min and Time 60 Min bottles were placed on a lab cart near the collector columns. After all bottles had been clamped on the collector columns, their caps were removed. The completion of this removal process marked Time 0 or the beginning of the 60-min time period. At this time, samples were collected from the Time 0 Min bottles. Water from six Time 0 Min bottles was used to make three composites (100 mL of water from each bottle), and the other six of the Time 0 Min bottles were sampled individually. At the end of 60 min (from Time 0), similar composites and individual samples were collected from each replication and the Time 60 Min bottles.

Within each replication and Time 60 Min group, the effect of compositing on dissolved concentrations of TCE and PCE was analyzed by comparing the mean dissolved concentration levels in noncomposited ($n = 6$) vs. composited samples ($n = 3$) (Fig. 5). For statistical analysis of variance within groups, SAS PROC GLM ($\alpha = 0.05$, Duncan's multiple range test) was used (SAS Institute, 2000).

The loss of dissolved concentration levels of TCE and PCE during the 60-min period while samples in collection bottles were exposed to air was assessed by comparing mean dissolved concentrations in the noncomposited samples that had been exposed to air (Replications 1, 2, and 3; $n = 6$ per replication) with those in the noncomposited samples that had not been exposed to air (Time 0 Min and Time 60 Min; $n = 6$ per group) (Fig. 6). Analysis of variance (SAS PROC ANOVA, $\alpha = 0.05$, Duncan's multiple range test) was used to compare the means (SAS Institute, 2000).

Sample Extraction and Gas Chromatography Analysis

All of the primary samples and 10% of the duplicates and matrix spike samples were analyzed. A computer program, based on Microsoft Excel's random number generator (Microsoft Corporation, 2000), was used to randomly select the duplicate and matrix spike samples for analysis. The relative percent difference (RPD) for each set of field duplicates was calculated as $100 \times$ (difference between the two values/mean of the two values). The RPD should not exceed 25% for any one analyte and the RPD for 90% of the analytes must be less than 20% (USEPA, 1995). The matrix spike samples were spiked with 1.0 mL of an analytical standard that contained 10 mg L^{-1} of both TCE and PCE. The percent recovery in the matrix spikes should fall between 75 and 125% and the percent recoveries of at least 90% of those spikes must be 80 to 120% (USEPA, 1995). All samples were extracted within their 14-d holding times.

The TCE, PCE, decafluorobiphenyl (DFB), and p-bromofluorobenzene (BFB) analytical standards were obtained from AccuStandard (New Haven, CT). Decafluorobiphenyl and p-bromofluorobenzene were used as the surrogate and internal standards, respectively. Samples were extracted in methyl-*tert* butyl ether (MTBE) according to USEPA Method 551.1 (USEPA, 1995), except that Eppendorf pipettes instead of syringes were used to add solvents and standards into the vials. Two lab spikes (one in deionized and the other in tap water) and two lab blanks (deionized water and tap water) were extracted and analyzed with each batch of field samples. Previous testing in our lab had detected a false peak in tap water that could be mistaken for a TCE peak in the field samples; therefore, since field samples could contain residual tap water that was used to clean the mixing tank, two sets of extraction batch blanks and spikes, triplicate blanks, and field blanks were made (one set from tap water and another set from deionized water).

Extracts were analyzed within their 14-d holding time on a Tremetrics Model 9001 gas chromatograph (Finnigan Corp., Austin, TX) equipped with an electron detector and an Rtx-1 30-m length × 0.25-mm-i.d. Crossbond 100% dimethyl polysiloxane column (Restek Corporation, Bellefonte, PA). The temperature program was first oven temperature = 40°C, hold
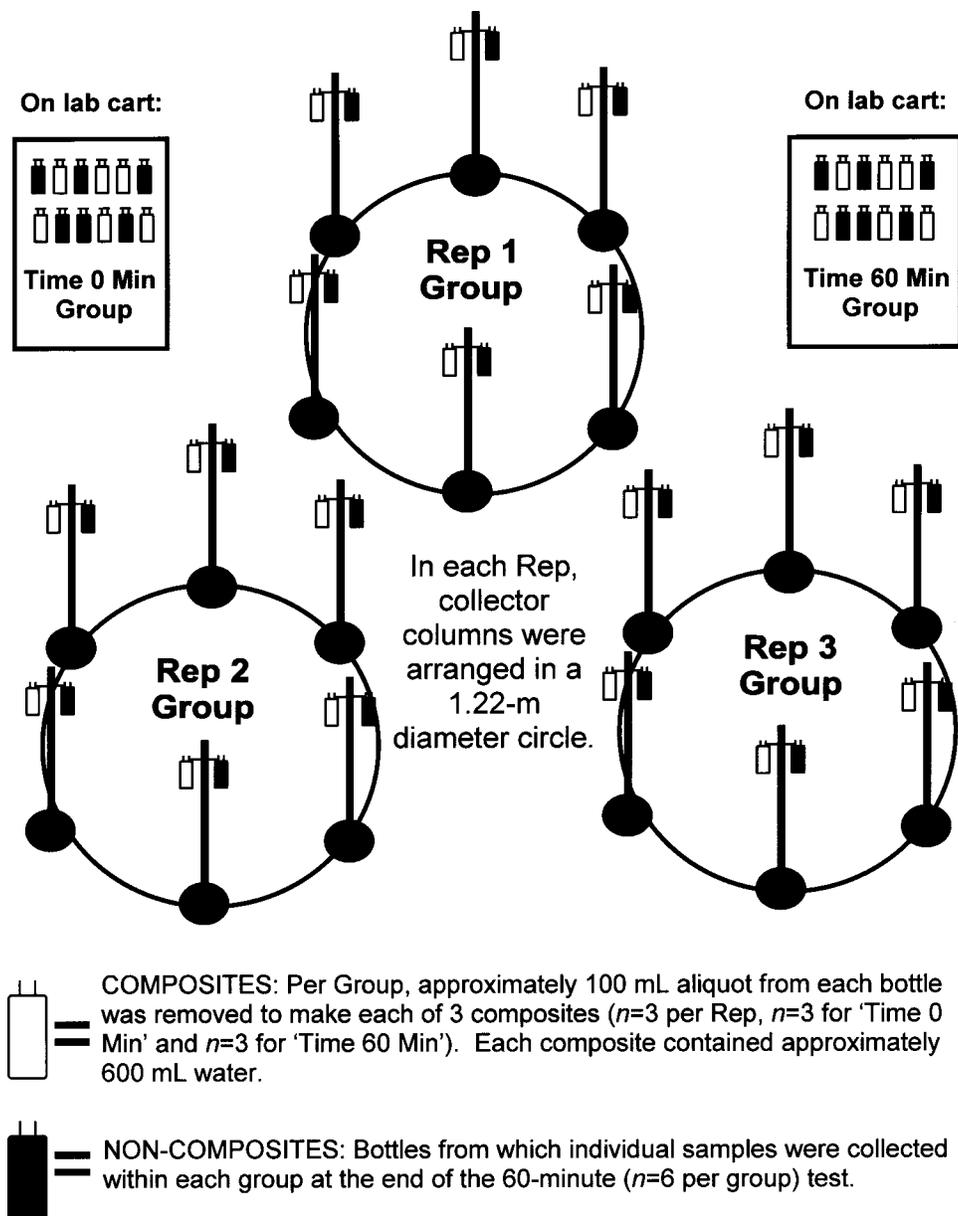
Fig. 4. Field setup for testing the loss of dissolved concentrations of trichloroethylene (TCE) and tetrachloroethylene (PCE) during sample compositing or from exposure to air for 60 min. For illustration purposes, bottles are illustrated as black or white; however, in the actual field test, all bottles were 1-L amber glass. Bottles on the lab carts were capped until sampled. Bottles on the collector columns were uncapped throughout the 60-min test period.

7 min, increase to 165°C at 10° min^{-1}, final hold 2 min. Peaks were integrated on a Model 3394A integrator (Hewlett-Packard, Palo Alto, CA). Five-point standard calibration curves (0.01–5.0 mg L^{-1}) were run for TCE and PCE.

Before running samples on the gas chromatograph, the following criteria had to be met:

1. The correlation coefficients of five-point standard curves of TCE and PCE had to be at least 0.99.
2. For precision or repeatability, the relative standard deviation of three successive injections of 2 μL of a 0.1 mg L^{-1} TCE standard had to be less than 20%. The relative standard deviation was calculated as 100 × (standard deviation of the peak areas of the three injections/mean of the peak areas of the three injections).

3. For relative response, the ratio of the peak area of a 2-μL injection of a 0.1 mg L^{-1} TCE standard to the peak area of a 2-μL injection of a 0.1 mg L^{-1} p-bromofluorobenzene standard had to agree within 20% of the same relative response of the current standard curve.
4. For instrument calibration verification with a midrange standard, the absolute value of the percent difference between the instrument's value for a midrange standard containing TCE, PCE, decafluorobiphenyl, and p-bromofluorobenzene and its label value for these compounds had to be within 15%.
5. The instrument blank (methyl-*tert* butyl ether) could not contain any peaks of TCE, PCE, decafluorobiphenyl, or p-bromofluorobenzene.
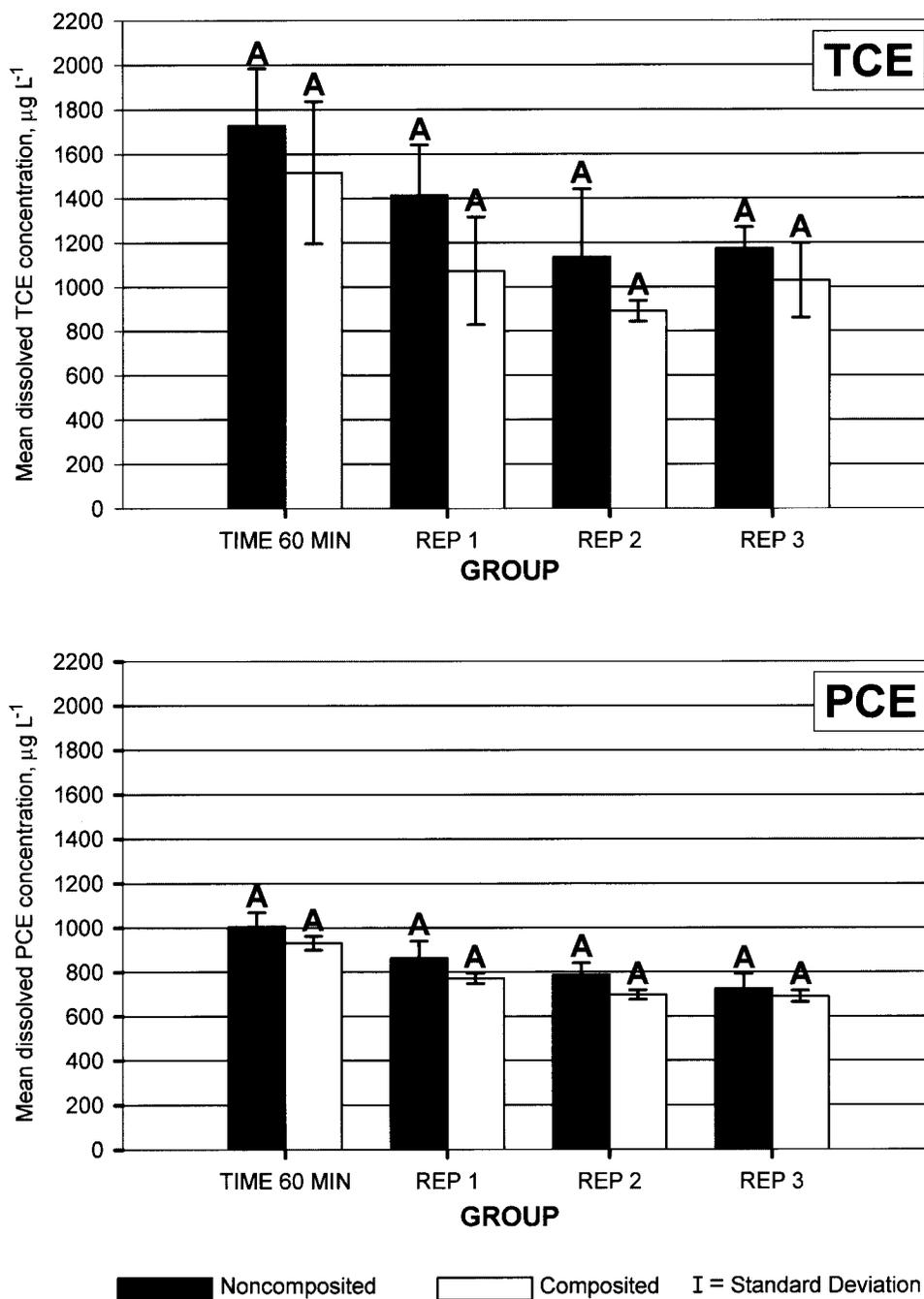
Fig. 5. Effect of compositing on dissolved concentrations of trichloroethylene (TCE) and tetrachloroethylene (PCE). Within each group, bars with the same letters are not significantly different from each other ($n = 6$ for noncomposited samples; $n = 3$ for composited samples; SAS PROC GLM, Duncan's multiple range test, $\alpha = 0.05$).

The method detection limits (MDL) of TCE and PCE in deionized water were determined according to USEPA (1985).

RESULTS AND DISCUSSION

The standard curves for TCE and PCE were linear from 0.01 to 5 mg L^{-1}. The MDLs were 2.29 μg L^{-1} for TCE and 2.01 μg L^{-1} for PCE. Dissolved concentrations below the MDLs are reported as nondetectable. The mean percent recovery in matrix spike samples was 111.5 ± 12.8% ($n = 12$) for TCE and 96.3 ± 10.2%

($n = 12$) for PCE. These percent recoveries satisfied the analytical method requirement that the percent recovery in the matrix spikes should fall between 75 and 125% and that the recoveries in at least 90% of these spikes must be 80 to 120% (USEPA, 1995). The relative percent difference (RPD) for the duplicate samples was less than 20% in 91.8% of the duplicates for both TCE (range of 0.0–16.6%, $n = 12$) and PCE (range of 0.0–16.5%, $n = 12$). This satisfied the analytical method requirement that the RPD for 90% of the samples must
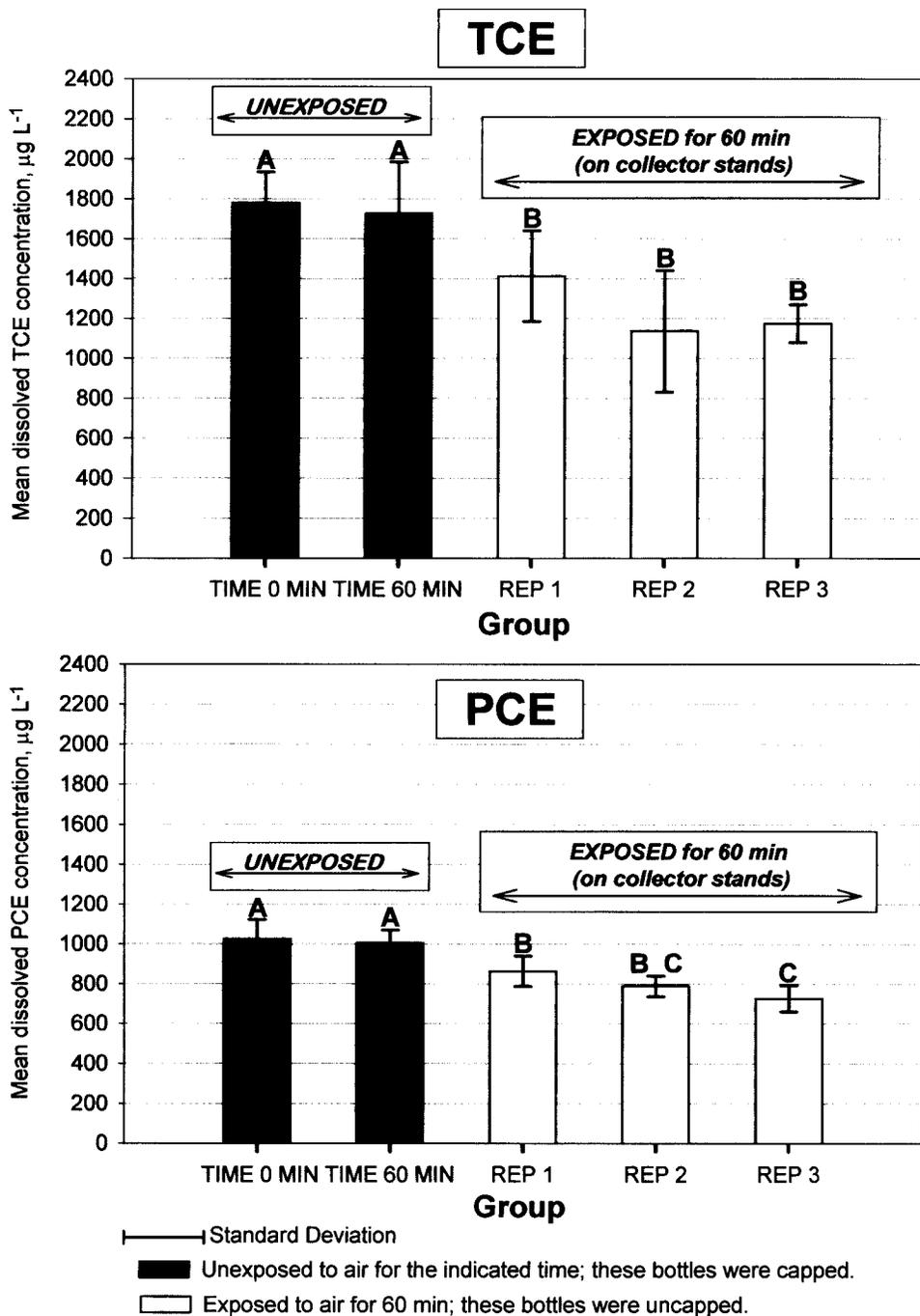
Fig. 6. Effect of exposing contaminated water to air in bottles for 60 min. In the exposed groups, the collection bottles were open during the experiment. Bars with the same letters are not significantly different from each other (SAS PROC GLM, Duncan's multiple range test, $\alpha = 0.05$).

not exceed 25% for any analyte (USEPA, 1995). The RPD exceeded 20% in one duplicate set for both TCE (RPD = 31.5%) and PCE (RPD = 34.3%). The mean percent recovery of the surrogate (decafluorobiphenyl) for the study was 66.7 ± 10.8% ($n = 209$).

Compositing did not have a statistically significant effect on the dissolved concentration levels of TCE or PCE (Fig. 5); however, statistically significant losses were incurred during the lag time of approximately 1 h during which contaminated water was exposed to air inside the collection bottles (Fig. 6). Overall, the mean

dissolved TCE concentrations were 28.2% lower in the exposed water than in the unexposed water. Similarly, mean PCE concentrations were 21.2% lower in the exposed water. The overall percent loss was calculated as the percent difference between mean dissolved concentrations in the water from bottles that had been unexposed to air for 60 min (Unexposed, Time 60 Min group, $n = 6$; Fig. 6) and the mean dissolved concentrations in water that had been exposed in bottles for 60 min (Exposed, Replications 1–3, $n = 18$; Fig. 6). The mean dissolved concentrations of TCE in exposed vs. unex-

Table 3. Minimum efficiency† of the mini-sprinkler test systems to strip trichloroethylene (TCE) from influent water.

Mini-sprinkler	Test	Influent concentration‡	Highest concentration in collectors	Loss in collectors§	Highest concentration corrected for percent loss	Efficiency¶
		μg L^{-1}		%	μg L^{-1}	%
Senninger Mini-Wobbler	1	1675 ± 151	7.2	28.2	10.0	99.4
Senninger Mini-Wobbler	2	728 ± 84	0.0	28.2	0.0	100.0
Ein Dor 809-120	1	1502 ± 118	9.5	28.2	13.2	99.1
Ein Dor 809-120	2	466 ± 34	0.0	28.2	0.0	100.0
Ein Dor 861-120	1	1392 ± 297	2.7	28.2	3.8	99.7
Ein Dor 861-120	2	630 ± 171	0.0	28.2	0.0	100.0

† This is the minimum efficiency since it is based on the highest dissolved concentration in any sample.
‡ Mean dissolved concentrations from faucet samples ($n = 5$) at the beginning of the waterline, sampled each 15 min of each test.
§ Calculated as $100(A - B)A$, where $A = 1736 ± 256$ (mean from samples that were unexposed to air as shown in Fig. 6, Time 60 Min, $n = 6$); $B = 1246 ± 231$ (mean of samples that were exposed to air for 60 min as shown in Fig. 6, Replications 1–3, $n = 18$).
¶ Within each test, this is calculated as $100(C - D)/D$, where C is the mean dissolved influent concentration and D is the highest dissolved concentration corrected for percent loss.

Table 4. Minimum efficiency† of the mini-sprinkler test systems to strip tetrachloroethylene (PCE) from influent water.

Mini-sprinkler	Test	Influent concentration‡	Highest concentration in collectors	Loss in collectors§	Highest concentration corrected for percent loss	Efficiency¶
		μg L^{-1}		%	μg L^{-1}	%
Senninger Mini-Wobbler	1	940 ± 134	4.3	21.2	5.5	99.4
Senninger Mini-Wobbler	2	450 ± 84	0.0	21.2	0.0	100.0
Ein Dor 809-120	1	766 ± 56	18.6	21.2	23.6	96.9
Ein Dor 809-120	2	206 ± 31	0.0	21.2	0.0	100.0
Ein Dor 861-120	1	734 ± 70	0.0	21.2	0.0	100.0
Ein Dor 861-120	2	407 ± 74	0.0	21.2	0.0	100.0

† This is the minimum efficiency since it is based on highest dissolved concentration in water in any sample.
‡ Mean dissolved concentrations from faucet samples ($n = 5$) at the beginning of the waterline, sampled each 15 min of each test.
§ Calculated as $100(A - B)A$, where $A = 1005 ± 64$ (mean from samples that were unexposed to air as shown in Fig. 6, Time 60 Min, $n = 6$); $B = 792 ± 84$ (mean of samples that were exposed to air for 60 min as shown in Fig. 6, Replications 1–3, $n = 18$).
¶ Within each test, this is calculated as $100(C - D)/D$, where C is the mean dissolved influent concentration and D is the highest dissolved concentration corrected for percent loss.

posed water were 1246 ± 231 μg L^{-1} vs. 1736 ± 256 μg L^{-1}, respectively. For PCE, the values were 792 ± 84 μg L^{-1} vs. 1005 ± 64 μg L^{-1}, respectively, in exposed vs. unexposed water.

The efficiency of each mini-sprinkler test system was calculated in Tables 3 and 4. Efficiency refers to percent of TCE or PCE that each system stripped from the influent water. The efficiencies take into account the estimated loss of TCE and PCE during the 1-h exposure of water in sample collection bottles as explained in the previous paragraph. Dissolved concentrations of TCE and PCE were not detected in the second test of each mini-sprinkler system (Tables 3 and 4). In the first tests, the Senninger Mini-Wobbler system was efficient in reducing dissolved concentrations of both TCE and PCE by 99.4%. Similarly, the Ein Dor 809-120 was 99.1% (TCE) and 96.9% (PCE) efficient. The Ein Dor 861-120 reduced TCE concentrations by 99.7% and PCE was not detected in any sample collector in that system. Efficiencies were 100% for the tests in which TCE or PCE were not detected. In these cases, efficiency seems to be 100%; however, that may be a reflection of the lower dissolved concentrations of TCE and PCE in the influent water for these tests (T1 vs. T2 in Fig. 7 and 8). An important factor to consider about the lack of detectable TCE or PCE in the second tests is that the initial dissolved concentrations in the influent water in the second tests were 45 to 74% less than those in the first tests (T1 vs. T2 in Tables 3 and 4); hence the total dissolved mass of TCE or PCE in each second test may have been below the stripping capacity of that test sys-

tem (Table 5). Table 5 shows the total dissolved mass of TCE and PCE in the influent water volume that was subject to stripping during each approximate 1-h test. If the total dissolved mass of TCE and PCE in each first test were to represent the stripping capacity of that test system, then there was insufficient dissolved mass in the second test of any system to challenge that capacity. Hence, neither TCE nor PCE should be detected in the second tests as was the case in this study. For example, if the dissolved mass of TCE in the first Senninger Mini-Wobbler test were reduced by 99.4% (from Table 3), then that system had the capacity to remove a total mass of 287 037 μg of TCE. The total dissolved mass removed was calculated as (stripping efficiency from Table 3) $\times$ (TCE mass in the influent water volume from Table 5). In the second test of that same system, only 82 555 μg was present in the influent water volume (Table 5). This amount was below the 287 037 μg stripping capacity of the system and therefore 100% stripping (above the method detection limit of 2.29 μg L^{-1}) of the TCE would be expected.

The reduction in the initial dissolved concentrations of TCE and PCE in the influent water in the second tests of each mini-sprinkler system were most probably due to volatilization in the mixing tank, and not to any significant loss in the polyethylene irrigation pipe. Three factors that support this probability are (i) the spiked water in the mixing tank was not replaced before the second test of any mini-sprinkler system, (ii) the tank contained a large headspace that would have allowed for volatilization loss between tests, and (iii) there was
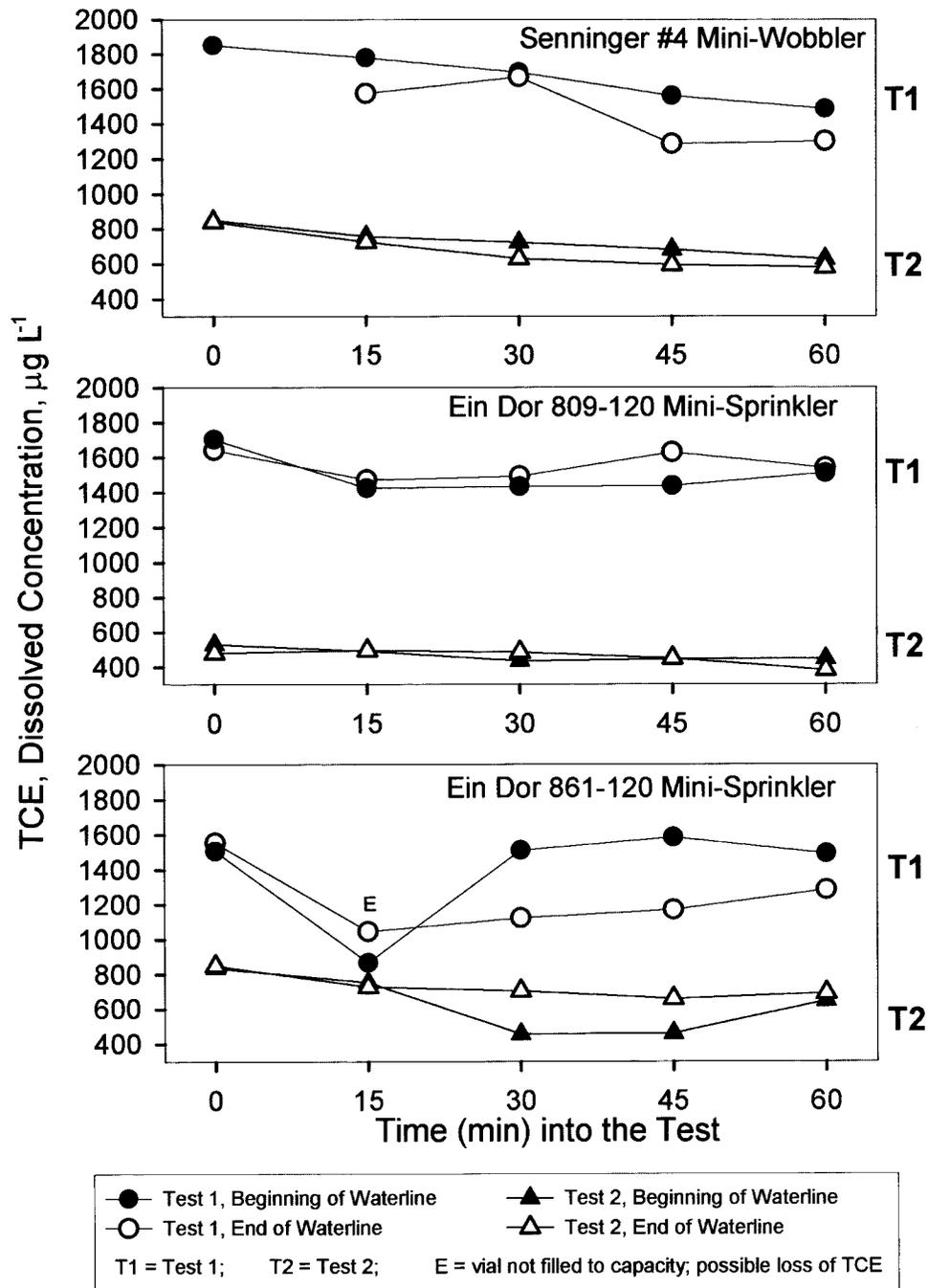
Fig. 7. Comparison of dissolved concentrations (μg L^{-1}) of trichloroethylene (TCE) in water sampled every 15 min from faucets at the beginning and end of the waterline.

no significant loss in dissolved concentrations in the waterline (Fig. 7–9).

Another factor to consider in the lack of detectable TCE or PCE in the second tests of each mini-sprinkler system is that as a test day progressed from early morning through early afternoon (refer to Table 6 for test dates and times), meteorological conditions changed to enhance volatilization, evaporation, and drift. Temperature, wind speed, and solar radiation increased and percent relative humidity generally decreased during the day. For the tests that began before 1000 h, the temperature, solar radiation, wind speed, and percent relative

humidity ranged from 6.7 to 13.9°C, 180 to 850 W m², 0 to 11.26 km h⁻¹ (0 to 7 mi h⁻¹), and 49 to 79%, respectively, compared with 15.0 to 19.4°C, 400 to 1080 W m², 1.61 to 14.48 km h⁻¹ (1 to 9 mi h⁻¹), and 29 to 47% for the tests that began after 1000 h.

Meteorological conditions cannot be controlled, but may have a significant effect on the stripping efficiency of the mini-sprinklers. The effects of meteorological conditions on the observed stripping efficiencies would be greatest at elevated temperatures, wind speeds, solar radiation, and lower relative percent humidity. To test this in our study, the Ein Dor 809-120 sprinkler system
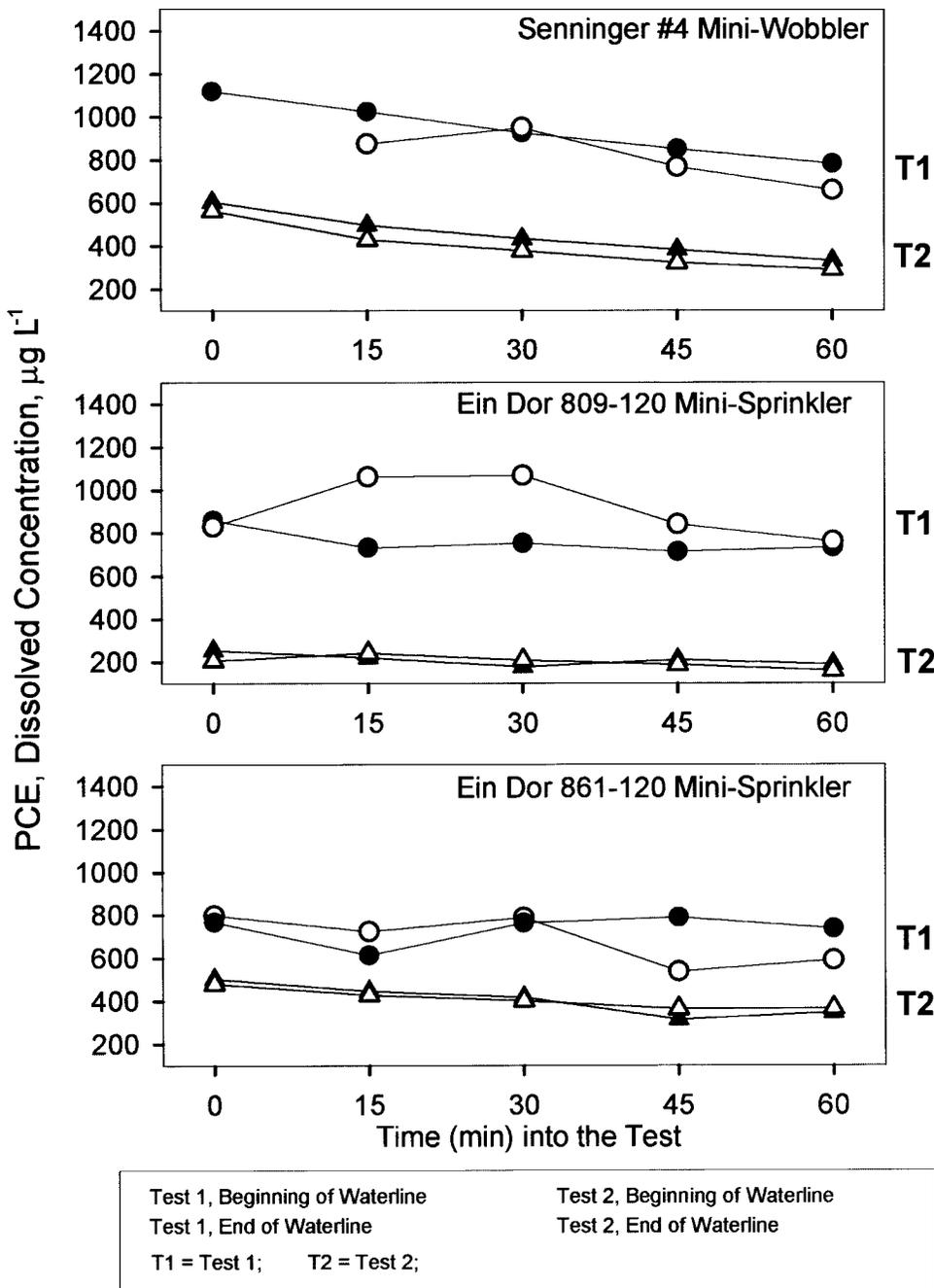
Fig. 8. Comparison of dissolved concentrations (μg L^{-1}) of tetrachloroethylene (PCE) in water sampled every 15 min from faucets at the beginning and end of the waterline.

was tested during the morning (0735–0838 h) and afternoon (1307–1407 h) (Table 6). The test times were chosen to depict a relative "worst-case scenario" for volatilization of the VOCs during early morning hours and a "better-case scenario" later in the afternoon when air temperatures, wind speed, and solar radiation were higher and percent relative humidity was lower. The "best-case scenario" would have been mid- to late-afternoon hours; however, all tests were conducted during conditions that minimized drift from the test site. As seen in Table 6, the percent runoff volume for the Ein Dor 809-120 morning test was approximately twice (55 vs. 28%) that of its afternoon test, and the percent unaccounted water volume was approximately 20% less (42 vs. 69%) in the morning test. The most obvious factors that accounted for these differences would include loss of runoff volume due to drift and evaporation. The Ein Dor 809-120 produced a visibly very fine mist that was observed to drift offsite; the other mini-sprinklers did not produce such a mist. Drift (which may contain other undesirable contaminants) to sensitive offsite areas would be a major factor to consider in using mini-sprinklers and may regulate the operating conditions under which the sprinkler systems could be

Table 5. Total mass of trichloroethylene (TCE) and tetrachloroethylene (PCE) in influent water during a 1-h test of each test system.

Mini-sprinkler	Test	TCE		PCE	
		Mass†	Percent of Test 1	Mass†	Percent of Test 1
		µg	%	µg	%
Senninger Mini-Wobbler	1	288 770		162 056	
Senninger Mini-Wobbler	2	82 555	29	51 030	31
Ein Dor 809-120	1	193 007		98 431	
Ein Dor 809-120	2	45 109	23	19 941	20
Ein Dor 861-120	1	132 658		69 950	
Ein Dor 861-120	2	61 929	47	40 008	5

† Calculated as (total volume of water dispensed) × (mean dissolved concentration), where the first term is the total number of liters dispensed through the sprinkler during a test (Table 2), and the second term is the mean dissolved concentration (µg L^{-1}) that was dispensed through the sprinkler during the test. For each test, the mean was calculated from the concentrations in the five samples that were collected at 15-min intervals from the faucet located at the beginning of the waterline (Fig. 7 and 8). See Fig. 1 for faucet location.
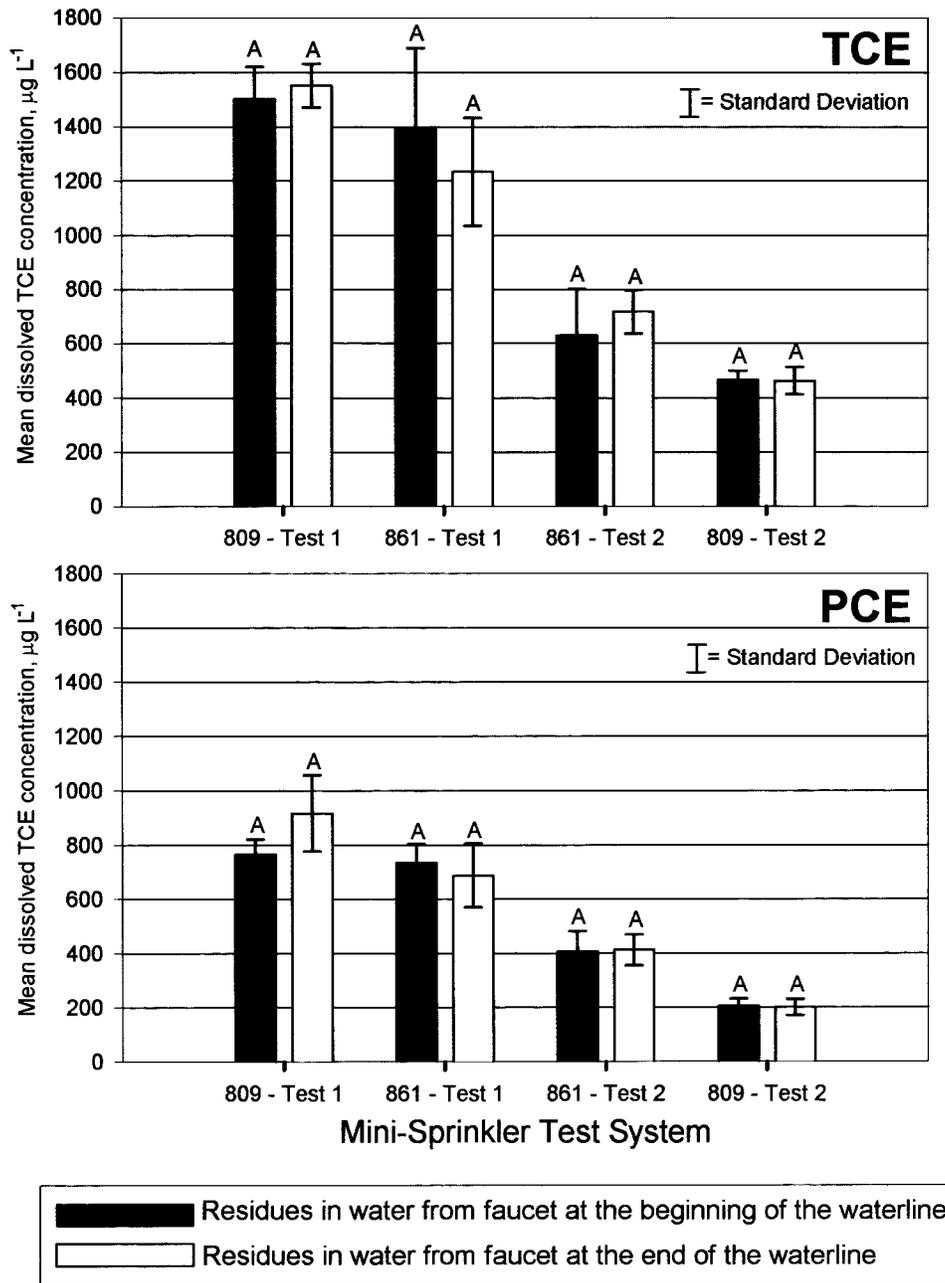
Fig. 9. Stability of trichloroethylene (TCE) and tetrachloroethylene (PCE) in the polyethylene irrigation pipe (waterline). The first test of each mini-sprinkler was begun before 1000 h; the second tests were begun after 1127 h. Within each test, bars with the same letter are not significantly different from each other (SAS PROC ANOVA, Duncan's multiple range test, α = 0.05).

Table 6. Water balance table, with influent, runoff, collector, and unaccounted water volumes for the 2001 test dates.

Mini-sprinkler	Test	Test date	Test time	Influent†	Runoff	Collectors‡	Unaccounted§
			h		L (% of influent water volume)		
Senninger Mini-Wobbler	1	14 March	0737–0852	172.4	112.3 (65)	1.7 (1)	58.2 (34)
Senninger Mini-Wobbler	2	14 March	1004–1105	113.4	74.1 (65)	1.0 (1)	38.2 (34)
Ein Dor 809-120	1	23 March	0735–0838	128.5	70.3 (55)	4.7 (4)	53.7 (42)
Ein Dor 809-120	2	23 March	1307–1407	96.8	26.8 (28)	3.1 (3)	66.9 (69)¶
Ein Dor 861-120	1	23 March	0916–1018	95.3	74.1 (78)	1.5 (2)	19.7 (21)
Ein Dor 861-120	2	23 March	1127–1227	98.3	76.4 (78)	1.6 (2)	20.4 (21)

† The volume of water was measured on a flow meter at the base of the riser.
‡ Total volume in collectors is the total volume intercepted by all collectors on all columns during the test.
§ Volume that includes drift and loss due to evaporation.
¶ Wind gusts (4.83–19.31 km h^{-1} or 3–12 mi h^{-1}) during the test caused drifting from the area of the collectors; therefore, the drift water was part of the unaccounted volume of water. The temperature of one of the composite water samples from the collectors at the end of the test was 22°C. The temperature taken on the surface of the plastic liner of the experimental area was 31°C at 1437 h.

operated. Although much drifting of the water from the Ein Dor 809-120 system was observed, a downward direction of the drift pattern was also visible. This downward drifting resulted in nearly two to five times as much water volume in the sample collectors for this system as compared with the Ein Dor 861-120 and Senninger Mini-Wobbler systems (Table 6). For the Ein Dor 861-120 and Senninger Mini-Wobbler systems, there were only slight differences (within each system) in the percent of runoff water volume or percent volume of water in collectors or percent unaccounted water volume between tests in the early or late morning hours (Table 6, values in parentheses). The slight differences as opposed to the major differences for the Ein Dor 809-120 tests were probably due to a combination of droplet sizes emitted by the mini-sprinklers and the much more divergent meteorological conditions between the Ein Dor 809-120 morning and afternoon tests.

We detected TCE and PCE in 12 of the 62 samples collected from water that flowed through the mini-sprinklers. Of these 12, 8 ($n = 24$) were from the 1.22-m-high collectors, 1 ($n = 24$) from a 0.61-m-high collector, 2 from beakers on the ground ($n = 6$), and 1 from runoff ($n = 8$). The dissolved concentrations of TCE were significantly higher in the 1.22-m-high collectors (mean = 2.892 ± 3.292 µg L^{-1}, $n = 24$) than in the 0.61-m-high collectors (mean = 0.275 ± 0.953 µg L^{-1}, $n = 24$) (SAS PROC ANOVA, $\alpha = 0.05$), but not significantly different at different distances from the base of the riser (SAS PROC GLM, $\alpha = 0.05$). Among the three mini-sprinkler systems, mean dissolved concentrations of TCE were significantly higher in the Ein Dor 809-120 system (mean = 3.175 ± 4.104) than in the Ein Dor

861-120 system (mean = 0.338 ± 0.955), but there were no significant differences in the dissolved concentrations between the Senninger Mini-Wobbler system (mean = 1.237 ± 1.331 µg L^{-1}) and either of the other two mini-sprinkler systems. Mean dissolved concentrations of PCE were not significantly different among the mini-sprinkler systems, distances from the base of the riser, or between the 0.61- and 1.22-m heights on the collector columns.

The masses of TCE and PCE removed from the influent water for each mini-sprinkler and the agricultural boom-type irrigation sprinkler used in the Nebraska study (Richardson and Sahle-Demessie, 1998; USEPA, 1998c) are compared in Tables 7 (for TCE) and 8 (for PCE). In terms of total mass removed (Column D in the tables), the larger boom-type sprinkler removed 590 to 1044 times more TCE and 14 to 28 times more PCE as did the mini-sprinklers. However, the total influent volume in the boom-type sprinkler was 1894 to 2832 times greater than that of the mini-sprinklers and the initial dissolved concentrations of TCE and PCE were approximately 5 and 100 times less, respectively, than those for the mini-sprinkler tests. This made comparison of the two types of irrigation systems unequal. For a more equitable comparison, the mean influent concentration of the boom-type system was "adjusted" to reflect that of the mini-sprinklers by setting the mean influent concentration of the mini-sprinklers (from Column A in the Tables 7 and 8) as the mean influent concentration for the boom-type sprinkler. These adjusted values are shown in parentheses in Tables 7 and 8. With the adjusted concentration value, the boom-type sprinkler still removed more mass of TCE and PCE

Table 7. Comparison of the mass of trichloroethylene (TCE) removed in 1 h by the mini-sprinklers and an agricultural boom-type irrigation sprinkler. All figures are on a per hourly basis.

Test system	Mean influent concentration†, Column A	Influent water volume, Column B	TCE mass in influent water‡, Column C	TCE mass stripped§, Column D	TCE mass stripped per L influent water¶, Column E
	µg L^{-1}	L	µg		µg L^{-1}
Boom-type	530 ± 26.6	261 165	139 × 10^6	136 × 10^6	519
Boom-type (adjusted)#	(1 523)	261 165	(398 × 10^6)	(390 × 10^6)	(1 493)
Senninger Mini-Wobbler	1 675 ± 151	137.9	230 983	229 597	1 665
Ein Dor 809-120	1 502 ± 118	122.4	183 845	182 190	1 488
Ein Dor 861-120	1 392 ± 297	92.2	127 881	127 497	1 383

† The TCE mean dissolved concentration from Table 3. Data for the boom sprinkler are from the Nebraska study cited in this paper.
‡ Column A × Column B.
§ Column C × % removal.
¶ Column D/Column B.
# Values in this row are adjusted to reflect the initial mean concentration in the mini-sprinklers.

Table 8. Comparison of the mass of tetrachloroethylene (PCE) removed in 1 h by the mini-sprinklers and an agricultural boom-type irrigation sprinkler. All figures are on a per hourly basis.

Test system	Mean influent concentration†, Column A	Influent water volume, Column B	PCE mass in influent water‡, Column C	PCE mass stripped§, Column D	PCE mass stripped per L influent water¶, Column E
	$\mu g\ L^{-1}$	L		μg	$\mu g\ L^{-1}$
Boom-type	7.6 ± 0.17	261 165	1.98×10^6	1.92×10^6	7
Boom-type (adjusted)#	(813)	261 165	(212×10^6)	(205×10^6)	(789)
Senninger Mini-Wobbler	940 ± 134	137.9	129 600	128 800	934
Ein Dor 809-120	766 ± 56	122.4	93 800	93 200	761
Ein Dor 861-120	734 ± 70	92.2	67 700	67 700	734

† The PCE mean dissolved concentration from Table 3. Data for the boom sprinkler are from the Nebraska study cited in this paper.
‡ Column A × Column B.
§ Column C × % removal.
¶ Column D/Column B.
# Values in this row are adjusted to reflect the initial mean concentration in the mini-sprinklers.

than did the mini-sprinklers; however, the mass of TCE or PCE that the boom-type sprinkler removed per liter of influent water (Column E in Tables 7 and 8) was within the range of that removed by the mini-sprinklers. Both systems (mini-sprinklers and boom-type) remove comparable levels of TCE and PCE per liter per hour.

The mini-sprinkler systems have merit for use in the cleanup of TCE and PCE in contaminated ground water. Although the mass of TCE and PCE removed per liter per hour was comparable with that removed by a large agricultural boom-type sprinkler, the mini-sprinklers would have to run approximately 1600 to 3000 times longer to strip the same total mass as the boom-type sprinkler removed in 1 h. This equates to 66 to 125 d for each hour that the boom-type sprinkler is operated. This difference, however, does not exclude the use of mini-sprinklers for remediation purposes. In steep areas in which the boom-type sprinklers cannot be used or in areas in which the removal of large ground water volumes (consider that the boom-type sprinkler in the Nebraska study removed 4353 L min^{-1} or 1150 gal min^{-1}) is prohibited, the mini-sprinklers could be installed in sufficient numbers to regulate the daily volume of ground water that it removes to an "acceptable" level while at the same time strip TCE and PCE from the water. The acceptable level would depend on the dissolved concentrations of TCE and PCE in the ground water, the size of the contaminated plume, the time-frame for the remediation process, and other site conditions such as soil saturation and concern for off-site drift and leaching of other contaminants in the soil. Agriculture is under increasing pressure from the general public and government agencies to regulate the volume of ground water that its large boom-type irrigation systems use. In some areas, ground water has been removed at a rate that approaches or exceeds the recharge rate. This process has resulted in the imposing of strict or no-water usage by both nonagricultural consumers and farmers. Smaller mini-sprinklers such as the ones used in this study may provide a means to help remediate some VOCs from ground water while at the same time protecting the ground water volume against depletion beyond its recharge rate.

CONCLUSIONS

This study investigated the potential for mini-sprinkler systems to strip TCE and PCE from ground water.

Each mini-sprinkler system reduced dissolved concentrations of TCE by 99 to 100% and PCE by 96 to 100% in water that contained 466 to 1675 $\mu g\ L^{-1}$ TCE and 206 to 940 $\mu g\ L^{-1}$ PCE. This percent reduction was based on the highest level of TCE or PCE detected in any one sample for each test system and was adjusted for the percent loss during a 1-h sample accumulation period. Adjusting for this percent loss, the highest dissolved concentration of TCE or PCE detected in any collection vessel was 13.2 and 23.6 $\mu g\ L^{-1}$, respectively.

Mini-sprinklers offer the advantages of easy setup in series that could be used on practically any terrain, operation over a long period of time that would not threaten aquifer depletion, use in small or confined aquifers in which the capacity is too low to support large irrigation or purging systems, and use in forests in which the small, low-impact droplets of the mini-sprinklers would not damage bark. In forests, trees could help manage (via evapotranspiration) excess waste water. In loblolly and other pine forests that are common in the southeastern USA, the mini-sprinklers could be operated nearly year-round.

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