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Comparison of quarter-hourly on-line dynamic headspace analysis to purge-and-trap analysis of varying volatile organic compounds in drinking water sources

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ABSTRACT

On-line dynamic headspace analysis was refined for the quarter-hourly monitoring of select volatile organic compounds (VOCs) in ground and surface waters, for extended periods of time. Hourly comparisons were made to on-line purge-and-trap analysis, and to purge-and-trap analysis after sample preservation and storage. Variations in VOC concentrations of 6047% biweekly, 222% daily, 97% hourly, and 35% quarter-hourly were observable, with the 15-min cycle of the dynamic headspace analysis. The headspace analyzer had superior retention time stability, required less maintenance, and had 1/4 the analysis time as a typical purge-and-trap–gas chromatograph system used for hourly comparisons.

INTRODUCTION

The temporal monitoring of volatile organic compounds (VOCs) in water sources is important because of contamination (*i.e.* 4000 gallons of VOCs can be dissolved in a single ground water plume[1], or chemicals spilled into surface water), and the transport of contaminants. The maximum safe concentration levels for most VOCs in drinking water range from 1–5 ppb[2,a]. The speed of on-line VOC analyses is especially important at water sources with nearby contamination, or water sources near industrial or commercial operations where sudden accidental releases of VOCs to water supplies are possible.

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[a] Throughout the article the American billion (10^9) is meant.

Water sources have been monitored hourly by on-line purge-and-trap analysis[3] using a Tekmar 6000 process stream sampler (Cincinnati, OH, U.S.A.), Tekmar LSC-2 purge-and-trap–gas chromatographic (GC) system, and integrator system.

This project is the first application of quarter-hourly on-line headspace analysis for monitoring VOC concentrations in surface and ground waters, for extended periods of time[7]. A Siemens (ES Industries, Voorhees, NJ, U.S.A.) P101 dynamic headspace analyzer[4] was refined, and quality assurance was developed, for quarter-hourly analyses. Significant quarter-hourly variations in VOC concentrations in water sources, were observed with headspace analysis. The speed of headspace monitoring is a major advantage over purge-and-trap analysis for temporal monitoring.

EXPERIMENTAL

A Siemens P101 continuous on-line dynamic headspace analyzer was used to quantify VOCs quarter-hourly. The Siemens analyzer differed greatly from two traditional purge-and-trap systems which were used for hourly quality assurance comparisons.

With traditional purge-and-trap systems[5], a 5-ml grab sample is sparged with helium for 11 min. The objective of sparging is to purge the total amount of volatiles to a cool adsorbent trap. During desorption, an injection valve is turned and carrier gas flows through the trap, which is heated for 4 min to desorb VOCs to the GC apparatus.

With the Siemens headspace analyzer (Fig. 1), the sample was heated to 58°C before sparging with helium. Water continuously entered the sparger at 4 l/h, and overflowed through a headspace-free sidearm. (The headspace is the helium, volatile
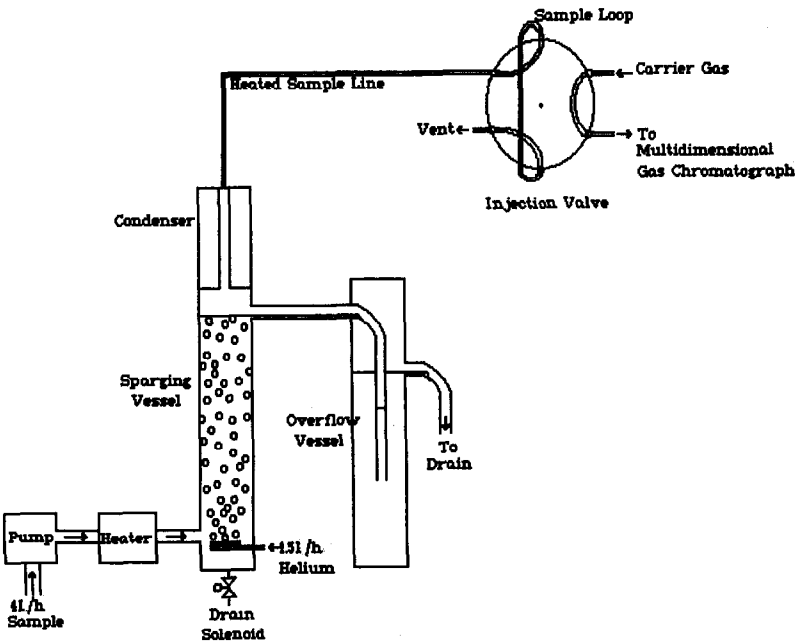

Fig. 1. Schematic diagram of the continuous headspace analyzer.

gases, and water vapor above the sample). The objective of sparging is to obtain a steady state concentration of volatiles in the headspace. Moisture is removed from the headpace by a condenser. The headspace exits through an injection valve. Once every 15 min, 10 μl of headspace are injected into the Siemens GC apparatus. Although the air–water partitioning of VOCs depends on Henry's constants, Henry's constants do not have to be known to make calibration curves on a dynamic headspace analyzer. Water entered the sparger at 4 l/h, and the overflowing sparger holds 330 ml of liquid. The headspace volume above the sparger is 80 ml. Helium purge flowed into the sparger at 1.5 l/h, and exited the sample loop at 1.5 l/h. The phase ratio (water–headspace volume ratio) was approximately 4:1, and the water–headspace flow ratio was approximately 3:1.

With the Siemens analyzer, the oven was run isothermally at 67°C, and three capillary columns with valveless column switching were available for multidimensional analysis. The primary column, a 15 m × 0.32 mm I.D., 1-μm OV-1710 capillary column, gave sufficient resolution for all compounds under study; secondary columns for multidimensional analysis were not used. Because the Siemens analyzer has no trap and runs isothermally, a 15-min analysis cycle was possible for all compounds analyzed.

On the Siemens analyzer, aqueous sample is continuously pumped into the sparging vessel, even when the sparger drains between analyses. Between analyses, the sparging vessel is drained, and influent is quickly blown down through the sparger with 70 kPa (10 p.s.i.) helium. The Siemens analyzer can be programmed to open one of fifteen different influent solenoids to analyze up to fifteen different sample streams. If the influent to the sparger is switched to a different sample stream during the beginning of the 1.2 min drain cycle, there usually is no noticeable carry over between successive 15-min samples from streams with different VOC concentrations. Influent streams were regulated to 10 p.s.i. with a pressure regulator, and solids were removed with a glass wool filter.

Quality assurance

Continuous internal standard injection was added to the Siemens analyzer for quality assurance. Dilute aqeuous fluorobenzene was pumped into the analyzer, along with the water sample, to give a 15 ppb final internal standard concentration. A Fluid Metering (Oyster Bay, NY, U.S.A.) lab pump, and lab pump junior were used for the sample and internal standard, respectively. Effluents from the sample and internal standard pumps were mixed in a 1/8 in. PTFE "T" mounted on the effluent of the internal standard pump.

The Siemens analyzer was quality assured using blanks, replicate analyses, calibration standards, other internal standards, field duplicates, lab duplicates, splits, blinds, intralaboratory comparison and interlaboratory comparison. Also, instrument maintenance was carefully evaluated.

RESULTS AND DISCUSSION

Calibration

Absolute peak areas from the injected fluorobenzene internal standard had a 5% relative standard deviation (R.S.D.). When a large homogeneous batch sample of 51

ppb tetrachloroethene (PCE) was analyzed 21 times, peak areas had 1.8% R.S.D. Duplicate analyses of other target compounds, such as chloroform, were reproducible with less than 5% R.S.D. Therefore, we decided that it would be more precise to use absolute areas of target compound peaks, without dividing by the internal standard peak areas. Internal standards peak areas were monitored, however, as additional quality assurance that the sensitivity of the Siemens analyzer did not change after thousands of injections or after being transported hundreds of kilometers to four different sites.

The EPA method detection limits[6] calculated from the Siemens analyzer, with a flame ionization detector, were: chloroform 2.8 ppb, fluorobenzene 2.0 ppb, PCE 2.3 ppb, and toluene 1.4 ppb. These compounds had similar method detection limits on a Tekmar LSC-2 purge-and-trap–Varian 3300 GC system with a flame ionization detector. Method detection limits equal the absolute standard deviation of >6 replicate determinations multiplied by the 99% t-value corresponding to the number of replicates[6]. For example, 21 Siemens analyzer determinations of a large standard had 0.89 ppb standard deviation; thus the method detection limit is 0.89 ppb × 2.53 = 2.3 ppb.

Precision

The precision of the Siemens analyzer and two different purge-and-trap systems were compared by analyzing hourly tap water samples using all three systems. Fig. 2 shows the chloroform concentrations in Philadelphia tap water (treated surface water) from each hour. ▲ symbols represent chloroform concentrations determined by 15-min composite samples on the Siemens analyzer. Five min before the headspace from each composite sample was injected into the Siemens GC, two VOC bottles (with hydrochloric acid and ascorbic acid as preservatives) were filled with tap water from the same inlet. ■ symbols represent the chloroform concentrations determined from one VOC bottle which was immediately analyzed at Drexel University (intra-laboratory comparison) by a Tekmar LSC-2 purge-and-trap–Varian 3300 GC system
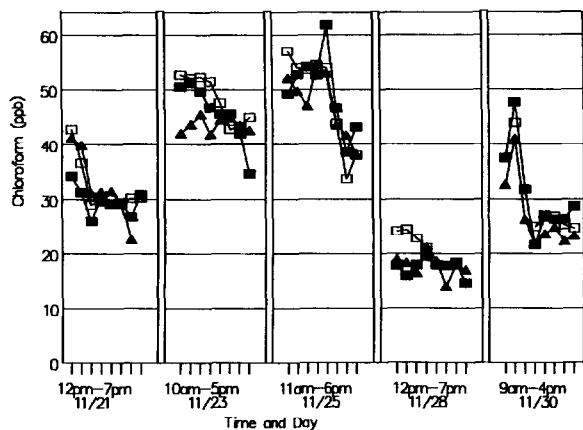

Fig. 2. System comparison plot of determinations of chloroform in Philadelphia tap water *vs*. date and hour water was sampled. ▲ = 15-min composite headspace analyses on Siemens analyzer; ■ = Grab samples analyzed immediately on Tekmar LSC-2 purge-and-trap–Varian 3300 GC system; □ = samples preserved and analyzed on purge-and-trap system at National Environmental Testing, Thorofare, NJ, U.S.A.
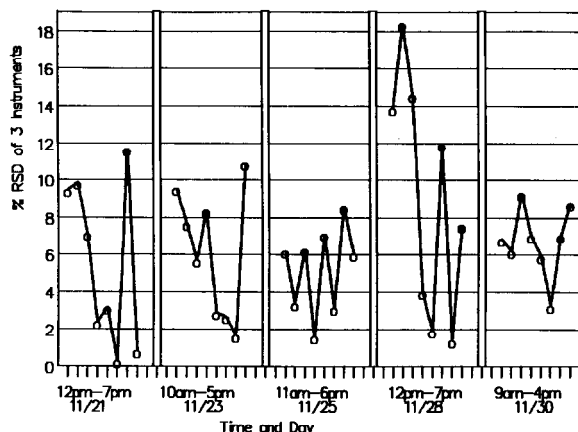
Fig. 3. System comparison plot of relative standard deviation of the determinations from 3 instruments *vs.* date and hour water was sampled.

with flame ionization detector. □ symbols represents chloroform concentrations determined from the other preserved VOC bottles, which were refrigerated and analyzed by National Environmental Testing Inc. (Thorofare, NJ, U.S.A.) by a purge-and-trap system (as interlaboratory comparison).

Fig. 3 shows that the R.S.D. of chloroform concentrations determined by the three instruments for each hour, averaged 6%, and did not exceed 18%. The Siemens analyzer and the two purge-and-trap systems had similar precision for chloroform, fluorobenzene, PCE, and toluene.

Accuracy

The accuracy of the Siemens analyzer was determined by analyzing blinds (spiked standards with expected concentrations) on the Siemens analyzer and a purge-and-trap system. Table I shows the results of analyzing chloroform blinds on the Siemens analyzer and NET's purge-and-trap system.

TABLE I

CHLOROFORM BLINDS

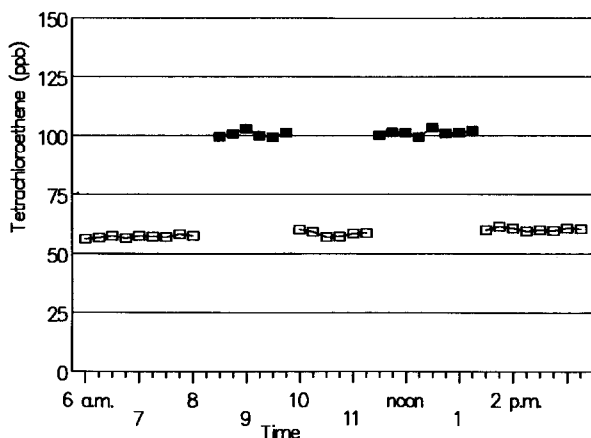| Expected (ppb)	Instrument	Analysis Time	Determined (ppb)
6.7	Siemens	on-line	9.1
6.7	Siemens	on-line	8.9
6.7	NET purge-and-trap system	within 2 weeks	7.8
13.0	Siemens	on-line	14.0
13.0	Siemens	on-line	14.0
13.0	NET purge-and-trap system	within 2 weeks	16.0
27.0	Siemens	on-line	24.0
27.0	Siemens	on-line	24.0
27.0	Siemens	on-line	28.0
27.0	NET purge-and-trap system	within 2 weeks	37.0

Fig. 4. Quarter-hourly headspace analyses of two adjacent wells with different tetrachloroethene concentrations, using Siemens analyzer. ■ = Raw water from well A2; □ = raw water from well A1. No memory effects were apparent when switching between samples of different concentrations.

Retention times

Retention times on the Siemens analyzer remained within ±0.02 min per week, even with 100-fold changes in concentration. Retention times on the Tekmar LSC-2–Varian 3300 purge-and-trap system varied ±0.30 min between a few analyses, with 100-fold changes in concentration.

Instrument variability

Before evaluating the variability of VOCs in water sources, it was determined that all compounds studied could be reproducibly determined on the Siemens analyzer with <5% R.S.D. This was done by replicate analyses of large homogenous spiked standards (12–51 ppb concentrations).

Carry over between samples

It also was determined that the Siemens analyzer could switch between two sample streams during its drain cycle, with little carry over between successive 15-min samples from different streams. Fig. 4 shows switching between analyses of two adjacent wells, well A1 and well A2. Although the wells had different PCE concentrations, both wells had fairly constant concentrations on this day, and the analyzer did not show any carry over when switching between the two wells. Automatic switching between sample and calibration standards also worked well. The Siemens analyzer can be programmed to switch between fifteen sample streams, using solenoids.

Variability of VOCs in water sources

Fig. 5 shows quarter-hourly determinations of PCE and 1,1,1-trichloroethane in raw well water B. Quarter-hourly variations in PCE concentrations were observable, due to the speed of headspace analysis. On this day, PCE concentrations varied as much as 25% between successive 15-min analyses (between 8:30 and 8:45 a.m.), and varied as much as 97% per hour (from 8:15 to 9:15 a.m.). For this entire day, PCE
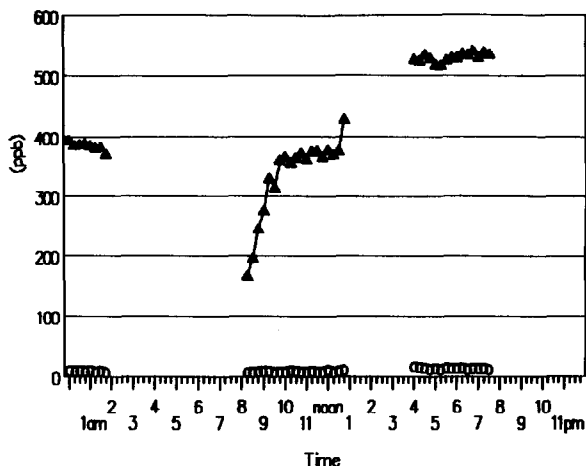
Fig. 5. Quarter-hourly headspace analyses of tetrachloroethene and 1,1,1-trichloroethane in raw well water B using Siemens analyzer (different site than Fig. 4). ▲ = tetrachloroethane; ○ = 1,1,1-trichloroethane. Tetrachloroethene concentrations varied as much as 97% per hour (between 8:15 a.m. and 9:15 a.m.) and 35% between successive 15 minute analyses (8:30 a.m. and 8:45 a.m.). 1,1,1-trichloroethane concentrations ranged from 10 to 22 ppb during this day.

concentrations varied 222% (from 168 to 541 ppb). On other days, PCE concentrations varied as much as 35% between successive 15-min analyses. Fig. 4 shows analyses of raw well water B, before it passed through granular activated carbon contactors to remove VOCs, and was chlorinated, for use as drinking water.

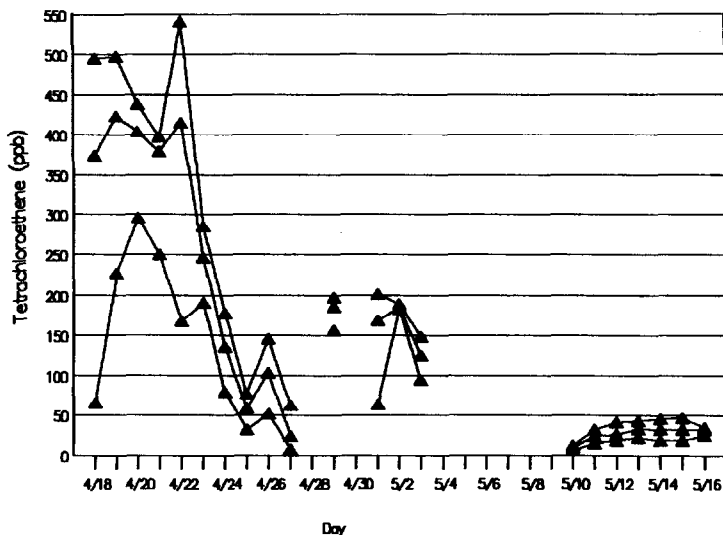Fig. 6 shows minimum, average, and maximum daily PCE concentrations in raw

Fig. 6. Minimum, average, and maximum daily PCE concentrations in raw well water B determined by quarter-hourly headspace analyses from April 18 (4/18) to May 16 (5/16). Notice 6047% decrease in PCE concentrations between April 22 and May 10, due to dilution by rain. Analyses were not made between May 4 and 9.

well water B, determined by quarter-hourly analyses for approximately 1 month. PCE concentrations decreased 6047% in 2½ weeks (from 541 ppb to 9 ppb), apparently due to dilution by rains. Although large variability was seen in this well, no contamination was detected in a well just 1.6 km away.

Maintenance

Maintenance required by Siemens analyzer was minimal. The sparging vessel was disassembled monthly and rinsed out with water to remove solids. A 8 m³ (300 foot³) cylinder of zero grade air was replaced once every 9 days. A 6 m³ (200 foot³) cylinder of high-purity helium was replaced every 18 days. A 6 m³ cylinder of high-purity hydrogen would last approximately 6 months. Paper for a Hewlett-Packard 3390 integrator (added to the Siemens analyzer) would last for more than a week. Seals on the injection valve were still good after approximately 15 000 injections. The major sampling problem was the removal of solids from the water before it entered the analyzer. Large amounts of solids would appear when a well was turned on, and had to be filtered out with glass wool, which had to be replaced frequently. The traps in our Tekmar LSC-2 purge-and-trap had to be replaced every few months.

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