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Determination of 1,4-Dioxane in the Cape Fear River Watershed by Heated Purge-and-Trap Preconcentration and Gas Chromatography−Mass Spectrometry

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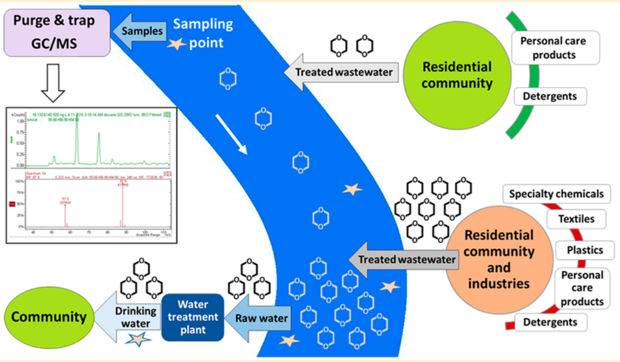
Ⓢ *Supporting Information*

ABSTRACT: Recent U.S. Environmental Protection Agency data show that 1,4-dioxane is frequently detected in U.S. drinking water derived from both groundwater and surface water. 1,4-Dioxane is a likely human carcinogen, and an excess 10^{-6} cancer risk is associated with a drinking water concentration of 0.35 μg/L. To support 1,4-dioxane occurrence investigations, source identification and exposure assessment, a rapid and sensitive analytical method capable of quantifying 1,4-dioxane over a wide concentration range in a broad spectrum of aqueous matrices was developed. The fully automated method is based on heated purge-and-trap preconcentration and gas chromatography/mass spectrometry with selected-ion storage and has a reporting limit of 0.15 μg/L. Quantification of 1,4-dioxane was accomplished by isotope dilution using mass-labeled 1,4-dioxane-d8 as internal standard. Matrix spikes yielded recoveries of 86−115% in drinking water, groundwater, surface water, and wastewater treatment plant (WWTP) effluent. Also, 1,3-dioxane can be distinguished from 1,4-dioxane. The method was applied to investigate 1,4-dioxane occurrence and sources in the Cape Fear River watershed of North Carolina. 1,4-Dioxane concentrations ranged from <0.15 μg/L in nonimpacted surface water to 436 μg/L downstream of a WWTP discharge. In WWTP effluent, 1,4-dioxane concentrations varied widely, with a range of 1.3−2.7 μg/L in one community and 105−1,405 μg/L in another. Discharges from three municipal WWTPs were primarily responsible for elevated 1,4-dioxane concentrations in the Cape Fear River watershed.



INTRODUCTION

The cyclic diether 1,4-dioxane is a solvent stabilizer that commonly co-occurs with chlorinated solvents in contaminated groundwater. While its usage in the context of solvent stabilization has declined,[1] 1,4-dioxane continues to serve as an important industrial solvent in the production of textiles, paper, brominated flame retardants, pharmaceuticals, and other specialty chemicals. It is also a byproduct of manufacturing processes involving ethylene oxide (e.g., production of polyester, polyethylene terephthalate, and surfactants) and is present in numerous consumer products such as detergents, shampoos, and cosmetics.[1−4] The U.S. Environmental Protection Agency (USEPA) included 1,4-dioxane in the third contaminant candidate list (CCL3) and classified it as "likely to be carcinogenic to humans" by all routes of exposure.[5] An excess one-in-a-million cancer risk is associated with lifetime consumption of drinking water containing 0.35 μg/L 1,4-dioxane.[5] While USEPA has not developed a drinking water standard for 1,4-dioxane to date, several states have established guidelines or standards, including California (1 μg/L, drinking water notification level; 35 μg/L, drinking water response level),[6] Massachusetts (0.3 μg/L, drinking water guideline),[7] Maine (4 μg/L, drinking water maximum exposure guideline),[8] New Hampshire (3 μg/L, ambient groundwater quality standard),[9] Colorado (0.35 μg/L, groundwater standard),[10] Florida (3.2 μg/L, groundwater criterion; 130 μg/L, surface water cleanup target level),[11] and North Carolina (3 μg/L, groundwater quality standard;[12] 0.35 μg/L, surface water supply standard[13]).

While the occurrence of 1,4-dioxane in groundwater is well documented,[14−17] reports about its prevalence in wastewater treatment plant (WWTP) effluents, surface water, and drinking water are limited. Occurrence of 1,4-dioxane in surface water and wastewater was assessed in several Japanese studies.[18−22] In a nationwide survey of Japanese drinking water sources, 1,4-dioxane was detected at levels ≥0.05 μg/L in 32 of 80 surface water samples, with an average concentration of 0.20 μg/L.[18] In other studies, 1,4-dioxane concentrations in Japanese rivers ranged from <0.03 to 16 μg/L.[19−22] 1,4-Dioxane was not effectively removed in conventional municipal WWTPs[19] and was detected in WWTP effluents at concentrations ranging

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from 0.8 to 46 μg/L when WWTPs treated domestic wastewater only and 1.0−97 μg/L when WWTPs accepted industrial WWTP effluent and stormwater in addition to domestic wastewater.[22] A study conducted in Germany and Poland confirmed that 1,4-dioxane removal was negligible in municipal WWTPs, and 1,4-dioxane concentrations of up to to 2.2 μg/L were measured in downstream surface water.[23] Results from these studies suggest WWTP effluent can be an important source of 1,4-dioxane in surface water.

Occurrence data for 1,4-dioxane in US surface water are lacking, but the possible impact of WWTP discharges on 1,4-dioxane concentrations at downstream drinking water intakes was recently estimated.[24] On the basis of measured 1,4-dioxane concentrations in the effluents of 40 U.S. WWTPs (median: 1.13 μg/L, maximum: 3.30 μg/L) and dilution factors associated with receiving waters, Simonich et al.[24] concluded that the probability of 1,4-dioxane concentrations exceeding 0.35 μg/L at downstream drinking water intakes is negligible. However, data from the third unregulated contaminant monitoring rule (UCMR3) conducted by USEPA illustrate that 1,4-dioxane does occur at elevated concentrations in US drinking water derived from surface water. As of October 2015, UCMR3 data show 1,4-dioxane detections in 11.6% of 32,740 analyzed samples and concentrations ≥0.35 μg/L in 3.1% of analyzed samples; of the 1008 drinking water samples with 1,4-dioxane concentrations ≥0.35 μg/L, 22% were of surface water origin.[25] Overall, 1,4-dioxane concentrations in 26 UCMR3 samples of surface water origin exceeded the maximum WWTP effluent value of 3.30 μg/L reported by Simonich et al.,[24] suggesting that some WWTP effluents contain 1,4-dioxane at substantially higher levels than previously reported. In North Carolina (NC), 60 out of 63 UCMR3 samples with 1,4-dioxane concentrations ≥0.35 μg/L were derived from surface water. Furthermore, 6 of the 12 highest 1,4-dioxane concentrations in the UCMR3 database were measured in drinking water produced from the Cape Fear River (CFR) in NC (up to 13.3 μg/L).[25]

In this study, the CFR watershed, the largest watershed in NC, was selected as a test bed to investigate 1,4-dioxane occurrence and sources. To assess the contribution of WWTP discharges to 1,4-dioxane occurrence in surface water and drinking water, a versatile method for the analysis of drinking water, surface water and wastewater was needed. Currently available methods were designed for specific matrices, and none were sufficiently sensitive and/or validated across the range of water matrices that needed to be analyzed in this study. Therefore, a rapid and sensitive analytical method suitable for the determination of 1,4-dioxane in a wide range of aqueous matrices was developed for this study.

The analysis of 1,4-dioxane presents a technical challenge because of the high affinity of 1,4-dioxane for water. USEPA has published several standard methods for the analysis of 1,4-dioxane in environmental samples including drinking water, soil, and municipal sludge.[26−31] Different laboratories have modified these standard methods to achieve higher sensitivity. In Table S1 of the Supporting Information (SI), both standard methods and modifications are summarized. Liquid−liquid and solid phase extraction are the most commonly used sample preparation methods to achieve reporting limits below 1 μg/L,[16,17,32−38] a level of sensitivity not easily achieved via other sample preparation techniques. However, extraction is time- and labor-intensive, requires large sample volumes, and generates solvent waste. Solid phase microextraction (SPME) is an alternative option[39−43] but requires expensive fibers with limited lifetime. Another sample preparation method, purge-and-trap (P&T), is generally considered ineffective for 1,4-dioxane enrichment, and reporting limits are typically at least one order of magnitude higher than those achieved with solid phase or liquid−liquid extraction.[3,32,34,36,44] Some P&T methods are capable of determining 1,4-dioxane concentrations as low as 1 μg/L by either purging for extended periods of time (20 min) at room temperature[45] or shorter times (5 min[46] - 11 min[47]) at elevated temperature; however, no information about method performance is available for applying these methods to different aqueous matrices. Similar to heated P&T, heated headspace sampling also promotes volatilization of 1,4-dioxane from aqueous solution for quantification at subμg/L levels, but without active purging, the extraction time can be as long as 30 min.[42]

Objectives of this study were to (1) develop a rapid analytical method capable of quantifying aqueous 1,4-dioxane concentrations below the one-in-a-million cancer risk level of 0.35 μg/L; (2) assess method performance in a wide range of aqueous matrices using matrix spikes; (3) compare method performance to that of two EPA standard methods; and (4) apply this method to determine instream 1,4-dioxane concentrations in the CFR watershed of NC and to assess the importance of WWTP discharges as sources of 1,4-dioxane. Also, because of the growing concern about 1,4-dioxane occurrence and toxicity, it is possible that 1,3-dioxane may become a substitute as no water quality standards or guidelines have been developed for the latter. Therefore, a final objective of this research was to determine whether the developed analytical method can separate these two isomers.

■ MATERIALS AND METHODS

Chemicals. 1,4-Dioxane (99.5%), 1,3-dioxane (98%), methanol (purge-and-trap grade), and anhydrous sodium sulfite (ACS grade) were purchased from Thermo Fisher Scientific (Waltham, MA). A commercial 1,4-dioxane standard (1 mg/mL in methanol) was purchased from Absolute Standard (Hamden, CT) to prepare quality control (QC) solutions. Deuterium-labeled 1,4-dioxane-d8 (99 atom % D) and anhydrous sodium bisulfate (technical grade) were purchased from Sigma-Aldrich (St. Louis, MO).

Purge-and-Trap Settings. Analytes and internal standard (IS) were extracted from aqueous samples by a Stratum AQUATEK 100 P&T system (Teledyne Tekmar, Mason, OH). For each analysis, 1 μL of 20 mg/L 1,4-dioxane-d8 in methanol was automatically added as IS into 5 mL sample. The mixture was purged with helium at 60 °C for 12 min, followed by dry purge at 20 °C for 6 min and desorbed at 250 °C for 1 min. The parameters were optimized to maximize sensitivity and minimize moisture carryover. Detailed P&T settings are listed in Table S2 of the SI. The purged chemicals were concentrated on a Teledyne Tekmar #9 trap for analysis.

Gas Chromatography/Mass Spectrometry (GC/MS). Upon desorption from the trap, analytes and IS were transferred to a gas chromatograph and ion trap mass spectrometer (CP-3800 GC coupled with Saturn 2200 MS, Agilent, Santa Clara, CA). A VF-624ms column (30 m × 0.25 mm × 1.4 μm, Agilent) was used for compound separation. The MS was operated in electron ionization (EI) mode with selected-ion storage (SIS). Detailed settings of the GC/MS are summarized in Table 1.

Table 1. GC/MS Settings

split ratio	40
inlet temperature	200 °C
carrier gas	1 mL/min helium
oven temperature	started at 30 °C, held for 1.0 min, ramped at 20 °C/min to a final temperature of 200 °C and held for 10.0 min
MS detector on	4.5 to 6.5 min
multiplier offset	200 V
emission current	100 μA
scan time	0.6 s
SIS mass range	55–66, 86–90 and 94–98
ion storage level	48.0 *m*/*z*
ion time factor	100%
ion trap temperature	190 °C
manifold temperature	60 °C
transfer line temperature	220 °C

Calibration Standards and Quality Control Samples. A stock standard solution (SSS) (1 mg/mL) was prepared by dissolving neat 1,4-dioxane in ultrapure water and stored at 4 °C. A primary dilution standard (PDS) was prepared from the SSS at 2000 μg/L in ultrapure water on the day of calibration curve preparation. Duplicate calibration standards (0.15–300 μg/L) were prepared from the PDS to build a nine-point calibration curve. Calibration standards were analyzed at the beginning and end of each sample batch. QC solutions (1 and 100 μg/L in ultrapure water) were prepared from a standard solution obtained from a second source (1 mg/mL in methanol). To validate the calibration and method stability, a QC sample was analyzed after every 10–15 unknown samples.

Environmental Samples for Matrix Spikes. To validate the developed analytical method in different environmental matrices, matrix spike experiments were conducted in one drinking water sample, two surface water samples, and two WWTP effluents collected in the CFR watershed, NC. In addition, one drinking water sample from another watershed in NC as well as groundwater from AZ and IL were used for matrix spike experiments. Sodium sulfite (50 mg/L, to remove free and combined chlorine) and sodium bisulfate (1 g/L, to inhibit microbial activities) were added to all samples at the time of sample collection as directed by EPA Method 522. Samples were kept at 4 °C and analyzed within 28 days of collection.

Surface Water Samples for Occurrence and Source Identification. To investigate the occurrence of 1,4-dioxane in the CFR watershed, surface water samples were collected monthly from October 2014 to July 2015. Sampling sites were selected to bracket 8 WWTP discharge points. Samples were collected in 500 mL precleaned and baked amber glass bottles (VWR International, Philadelphia, PA) as described in EPA Method 522. Bridge samplers developed in our laboratory (shown in Figure S1 of the SI) were used to collect samples. No 1,4-dioxane sorption to or release from the sampling devices was detected in preliminary experiments. Sample preservation and storage methods were the same as described above. A trip blank (to check for contamination during sample

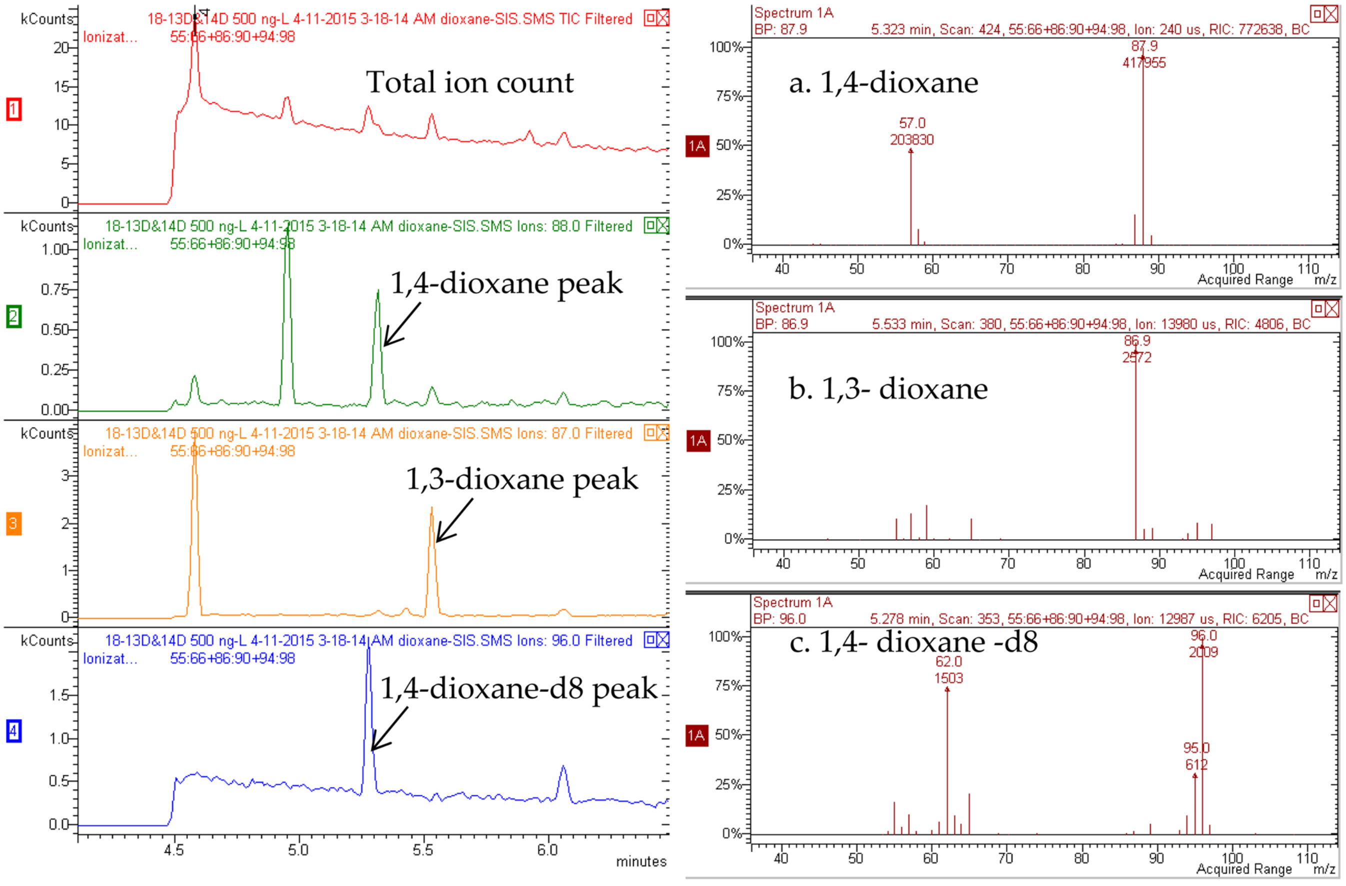

Figure 1. Example total ion chromatogram, mass chromatograms, and associated SIS mass spectra for 1,4-dioxane (a), 1,3-dioxane (b), and 1,4-dioxane-d8 (IS) (c) in ultrapure water spiked at concentrations of 0.7, 0.6, and 4 μg/L, respectively.

collection), a storage blank (to check for contamination during sample storage), and a field QC (to check for loss during sample collection and storage) were included in each sampling event and analyzed together with the field samples. No contamination was detected in blanks (>95% of blanks were $<^1/_3$ the minimum reporting level) and no changes were detected in field QCs. Duplicate samples were taken at sites selected at random to check method reproducibility. Selected field samples were quantified as collected and after fortification (spiked with the PDS) as required by EPA Method 522. 1,4-Dioxane recoveries of fortified samples were within 70−130% of theoretical values when the fortified concentration (5 μg/L) was at least 10% of the background 1,4-dioxane concentration. In addition, split samples were collected and sent to two commercial laboratories for analysis by two standard EPA methods, and results were compared with those obtained by the method described herein.

■ RESULTS

Chromatogram and Mass Spectrum. An example total ion chromatogram as well as the 1,4-dioxane, 1,3-dioxane, and 1,4-dioxane-d8 (IS) mass chromatograms and corresponding mass spectra are shown in Figure 1. Peaks of all three compounds were obtained within 5.5 min, symmetrical and clearly separated from one another as well as from background noise/other compounds in the samples. Ions with m/z of 88 and 96 served as quantitation ions (Q-ion) for 1,4-dioxane and 1,4-dioxane-d8, respectively. The ratio of secondary ion (57 for 1,4-dioxane, 62 for 1,4-dioxane-d8) to the Q-ion was constant across calibration solutions, QC solutions and environmental samples (relative standard deviation (RSD) < 20% for 1,4-dioxane and <10% for 1,4-dioxane-d8). No 1,3-dioxane peak was detected in any of the environmental samples and thus no further quantitative analysis was performed. If 1,3-dioxane quantification is needed in other studies, m/z 87 could serve as Q-ion. The total program run times for the P&T and GC were 31 and 19.5 min, respectively. Since the sample preparation (P&T) and quantification (GC/MS) operate in parallel, the average analytical time required per sample was 35 min.

Method Calibration. 1,4-Dioxane calibration curves covered a concentration range of 0.15−300 μg/L, which was based on preliminary investigations of 1,4-dioxane concentrations in water matrices of interest. An example calibration curve is shown in Figure 2, and corresponding response factors and relative response factors are summarized in Table S3 in the SI. The calibration curve was essentially linear for concentrations spanning more than three orders of magnitude. When the response factor and relative response factor (also referred to as calibration factor and response factor, respectively, in some references such as EPA Method 8000D[48]) are constant (RSD < 20% according to EPA Method 8000D[48]), use of the linear model is generally considered appropriate over the calibration range.[48] However, in this study, a power regression was found to produce smaller errors than linear regression when comparing concentrations back-calculated through the regression equation to the theoretical values (SI Table S3). Thus, power regression was used for calibration in this study.

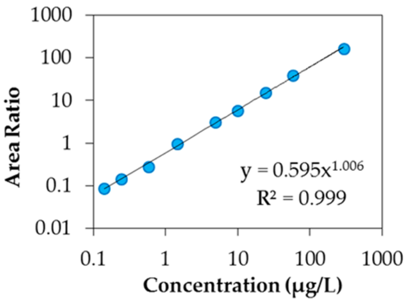

Figure 2. Calibration curve for 1,4-dioxane (0.15−300 μg/L) with 1,4-dioxane-d8 as the internal standard (4 μg/L).

Minimum Reporting Level and Detection Limit. The minimum reporting level (MRL) and detection limit (DL) for the developed method were determined as described in EPA Method 522. Briefly, the MRL was calculated using seven replicates of 1,4-dioxane-fortified ultrapure water at the proposed MRL (0.15 μg/L). The half range for the prediction interval of results (HR_{PIR}) was determined using eq 1, where S is the standard deviation, $t_{(n-1,\,1-\alpha\,=\,0.99)}$ is the Student's t value at the 99% confidence level with n-1 degrees of freedom (t = 3.707), and n is the number of replicates (n = 7).

$$HR_{PIR} = S \times t_{(n-1,1-\alpha=0.99)} \times \sqrt{1 + \frac{1}{n}} \tag{1}$$

Then the upper and lower limits of the Prediction Interval of Results (PIR = mean ± HR_{PIR}) were calculated. The Upper PIR must be ≤150% recovery and the Lower PIR must be ≥50% recovery, as shown in eqs 2 and 3

$$\text{Upper PIR} = \text{Mean} + HR_{PIR}(\leq 150\% \times \text{Fortified concentration}) \tag{2}$$

$$\text{Lower PIR} = \text{Mean} - HR_{PIR}(\geq 50\% \times \text{Fortified concentration}) \tag{3}$$

With seven replicates of solution fortified at 0.15 μg/L, the calculated upper and lower PIR values were 98 and 78% recovery, respectively, both meeting the criteria above. Thus, the MRL for this method was determined to be 0.15 μg/L, which is lower than the excess one-in-a-million cancer risk level of 0.35 μg/L. The MRL is also lower than that of all previously reported P&T methods and compares well with that of solid phase and solvent extraction methods shown in Table S1 of the SI.

The DL was determined with seven replicates of ultrapure water fortified with 0.1 μg/L 1,4-dioxane and was calculated using eq 4, where S, $t_{(n-1,\,1-\alpha\,=\,0.99)}$ and n are the same as defined for eq 1. The DL calculated for this method is 0.056 μg/L.

$$DL = S \times t_{(n-1,1-\alpha=0.99)} \tag{4}$$

Precision and Accuracy. The reliability of this method was evaluated by analyzing samples of ultrapure water fortified with 1,4-dioxane at concentrations of 1 and 100 μg/L. Precision and accuracy were determined by the RSD and percent recovery, respectively. Seven fortified samples at each concentration were analyzed. RSDs were 6% at both concentrations, and recoveries were 112% and 101% of the spiked values at 1 and 100 μg/L, respectively, suggesting the method is both precise and accurate.

Comparison with Standard Methods. An interlaboratory comparison was performed to confirm the accuracy of the developed method. Surface water samples collected in the CFR watershed were sent to two commercial laboratories for 1,4-dioxane quantification, and results were compared with those obtained by the method described herein. For sample preconcentration, Lab A used liquid−liquid extraction (Standard Method SW 846/EPA Method 8270, MRL = 3 μg/L) and Lab B used solid phase extraction (EPA Method 522, MRL = 0.07 μg/L). Among all 64 samples with results > MRL (Figure 3), the RSDs for interlaboratory results ranged from 0 to 32%, and the average RSD was 10% (data listed in Table S4 in SI). The agreement between data acquired using this method and other standard methods provides further validation of the analytical approach developed herein.

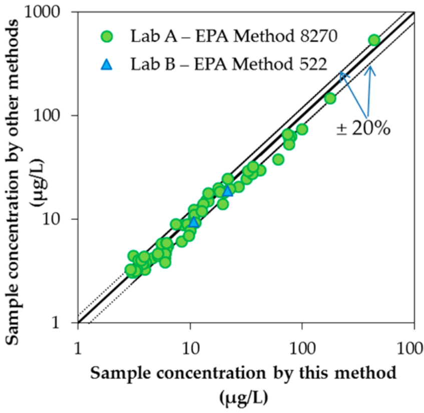

Figure 3. Comparison of 1,4-dioxane concentration data obtained with the analytical method described herein and standard methods. Thick solid line represents perfect agreement.

Method Application to Environmental Samples. An important objective of this research was to develop an analytical method that can accurately quantify 1,4-dioxane concentrations in a wide range of aqueous matrices. To demonstrate the capabilities of the method, matrix spike experiments were conducted with drinking water, groundwater, surface water, and WWTP effluent samples. Within each water matrix, background 1,4-dioxane concentrations were elevated in one sample and negligible/low in the other. Water quality characteristics of the matrices are summarized in Table S5 in the SI. Each matrix was analyzed for its background 1,4-dioxane concentration, and then spiked at two 1,4-dioxane concentrations as shown in Table 2. For all matrices, RSDs were ≤9%, and recoveries of matrix spikes ranged from 86 to 115% with no discernible differences among the tested aqueous matrices. It should be noted that the recoveries for matrices with background 1,4-dioxane concentrations below the MRL of 0.15 μg/L are reported by assuming the background concentration is either zero or MRL/2. The results shown in Table 2 suggest that the developed analytical method can be applied with confidence in a wide range of water quality contexts.

1,4-Dioxane Occurrence in the CFR Watershed, NC. Surface water samples were collected upstream and downstream of eight WWTP discharge locations (labeled 1−8 in Figure 4) in the CFR watershed of NC. Although 1,4-dioxane concentration data at each sampling location varied from month to month, the distribution pattern between upstream and downstream locations bracketing individual discharge points remained the same. As shown in Figure 4, WWTP

Table 2. Precision and Accuracy for 1,4-Dioxane Determinations in Spiked Water Samples

matrix		spiked concentration (μg/l)	average measured concentration (μg/l) (n = 4)	RSD	recovery[a]
drinking water	A	0.00	< 0.15		
		0.37	0.39	4%	106%/86%
		0.75	0.71	5%	95%/85%
	B	0.00	8.72	5%	
		5.02	13.38	4%	93%
		9.91	17.90	2%	93%
groundwater	A	0.00	< 0.15		
		0.36	0.35	5%	97%/76%
		0.73	0.70	9%	95%/85%
	B	0.00	1.36	6%	
		2.02	3.10	2%	86%
		4.89	6.02	2%	95%
surface water	A	0.00	< 0.15		
		0.37	0.43	7%	115%/95%
		0.73	0.77	8%	104%/94%
	B	0.00	58.08	3%	
		51.22	116.92	2%	115%
		99.71	165.82	3%	108%
wastewater	A	0.00	2.15	9%	
		0.88	3.01	5%	99%
		1.87	3.99	5%	99%
	B[b]	0.00	118.45	5%	
		49.71	169.88	2%	103%
		99.53	230.66	4%	113%

[a] When background concentrations were < MRL (i.e., < 0.15 μg/L), recovery is reported using two values: the first was calculated assuming a background concentration of zero, and the second was calculated assuming a background concentration of MRL/2 (= 0.075 μg/L). [b] The background 1,4-dioxane concentration in wastewater B was beyond the calibration range, thus wastewater B was diluted 5 times and then used for the matrix spike tests.

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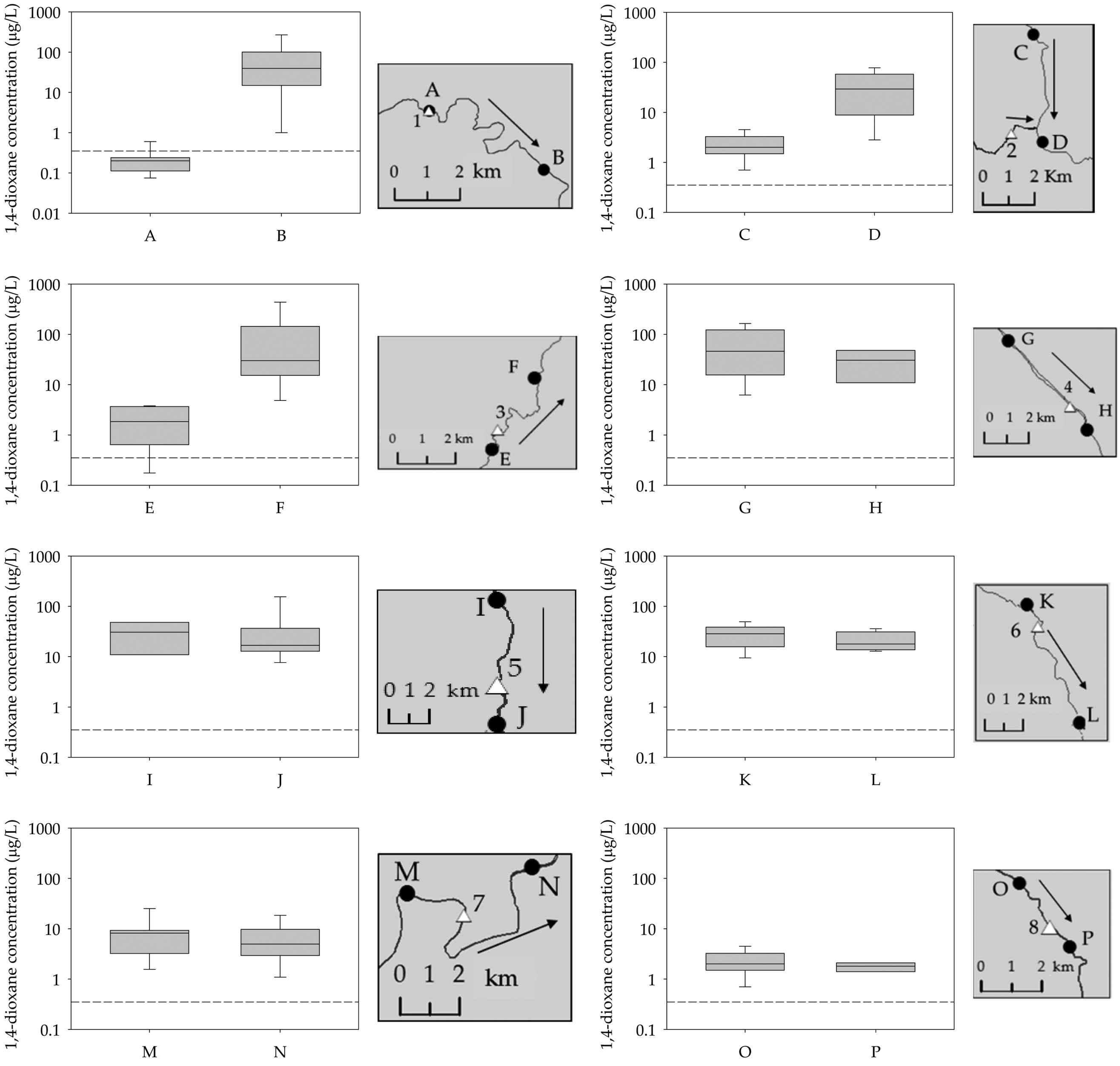

Figure 4. Instream 1,4-dioxane concentrations upstream and downstream of wastewater treatment plant (WWTP) discharges in the CFR watershed, NC. Monthly samples were collected from October 2014 through July 2015. Dashed lines show the 10^{-6} excess cancer risk level/NC surface water quality standard for drinking water supplies (0.35 μg/L). Solid circles with lettered labels represent sampling locations, and open triangles with numbered labels represent WWTP discharge points. Arrows indicate river flow direction. Data < MRL for point A were assigned a value of MRL/2 (= 0.075 μg/L).

discharges 1, 2, and 3 were important contributors to elevated instream 1,4-dioxane concentrations. Upstream concentrations were relatively low for all three discharge points (<MRL to 0.6 μg/L at site A, 0.7–4.5 μg/L at site C, and 0.2–3.8 μg/L at site E). However, downstream of the discharge points, 1,4-dioxane concentrations were one to two orders of magnitude higher (1.0–268 μg/L for site B, 2.8–78 μg/L for site D, and 4.8–436 μg/L for site F). The results for sampling points A-F illustrate that WWTP discharges can be important point sources that contribute to elevated instream 1,4-dioxane concentrations.

However, not all WWTP discharges led to increases in instream 1,4-dioxane concentrations. As illustrated in Figure 4, upstream and downstream of WWTP discharge points 4–8, 1,4-dioxane concentrations were similar. For the case of WWTP discharges 4–7, both upstream and downstream concentrations were high; while for WWTP discharge 8, both upstream and downstream concentrations were relatively low (median concentrations of 2 and 1.8 μg/L at points O and P, respectively). Results of *t* tests ($\alpha = 0.05$) showed that there were statistically significant differences between the 1,4-dioxane concentrations upstream and downstream of WWTP discharges 1–3, whereas no statistically significant differences existed between 1,4-dioxane concentrations at sampling points bracketing WWTP discharges 4–8. It should be noted that in the CFR watershed, neither community size nor fraction of industrial wastewater flow[49] influenced whether or not a WWTP discharge elevated instream 1,4-dioxane concentrations.

The impact of WWTP discharges 1−3 on downstream drinking water is substantial because all three discharges are located in the headwater region of the CFR basin. The CFR watershed provides water to more than 120 public water systems serving almost 1.5 million North Carolinians.[50] Among them, over 1 million live downstream of WWTP discharges 1−3 and receive drinking water impacted by elevated levels of 1,4-dioxane.[51]

Because of the widespread existence of 1,4-dioxane in consumer products,[3] its occurrence in domestic wastewater is not surprising. Based on the results of Simonich et al.,[24] 1,4-dioxane concentrations ranging from <0.30 ug/L to 3.30 ug/L can be expected in the effluent of WWTPs that receive primarily domestic wastewater. However, the results of our study show that some WWTP discharges must contain 1,4-dioxane concentrations that greatly exceed those observed by Simonich et al. To illustrate this point more clearly, WWTP discharge samples were collected in two communities located in the CFR watershed. Community 1 has two WWTPs (1-A and 1-B) while community 2 has one. Concentrations of 1,4-dioxane in WWTP effluents of the two communities are compared in Figure 5. The two WWTP effluents of community 1 had relatively low 1,4-dioxane concentrations (1.3−2.7 μg/L in WWTP 1-A and 1.3−2.5 μg/L in WWTP 1-B) that fell into the concentration range reported by Simonich et al.[24] In contrast, WWTP effluent of community 2 had much higher 1,4-dioxane concentrations (154−1405 μg/L), suggesting that one or more industrial sources overshadowed the 1,4-dioxane contribution that can be expected from the use of consumer products. The median concentration in the WWTP discharge in community 2 was 147 times that of community 1, illustrating the different impacts WWTP discharges can have on instream 1,4-dioxane concentrations.

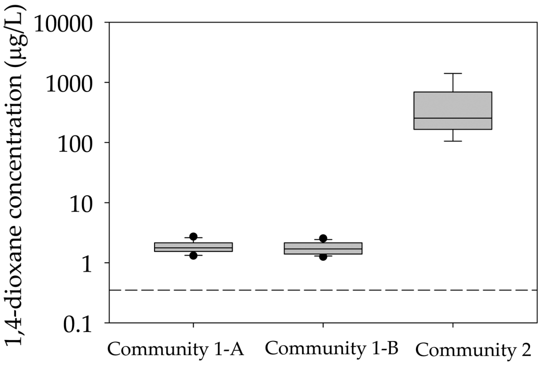

Figure 5. 1,4-Dioxane concentrations in wastewater treatment plant (WWTP) effluents from two NC communities (community 1 has two WWTPs). Data for community 1 were from 7 weeks of weekly sampling and data for community 2 were from nine months of monthly sampling. The dashed line shows the 10^{-6} excess cancer risk level/NC surface water quality standard (0.35 μg/L).

Overall, the new analytical method described herein demonstrated high sensitivity, accuracy and precision. Compared to solid phase and solvent extraction methods, the fully automated heated P&T preconcentration step requires minimal sample volume, analysis time and labor, and produces no hazardous waste. The MRL for aqueous 1,4-dioxane was lowered to a level not previously achieved by published P&T methods, and the method was shown to accurately determine 1,4-dioxane concentrations in a wide range of environmental matrices. Thus, it has great potential to be applied in 1,4-dioxane occurrence and source identification studies, exposure assessment, fate and transport investigations, and treatment process evaluations. Here, the method was applied to demonstrate that three municipal WWTP discharges were primarily responsible for elevated instream 1,4-dioxane concentrations in the CFR watershed of NC.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b05875.

> A table summarizing available methods for aqueous 1,4-dioxane quantification, a table summarizing P&T system settings, a table listing response factors and relative response factors for the calibration curve shown in Figure 2, a table summarizing the data shown in Figure 3, a table summarizing background water quality parameters for the matrix spike samples, and a picture of the bridge sampling device developed for this research (PDF)

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Notes

The authors declare no competing financial interest.

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