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Sampling trace organic compounds in water: A comparison of a continuous active sampler to continuous passive and discrete sampling methods

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HIGHLIGHTS

- Continuous active sampling method was compared to continuous passive and discrete sampling methods.
- Trace organic compounds in surface water were sampled by the three methods.
- Continuous active sampling method detected the most compounds but at lower concentrations.
- All three methods detected compounds across a wide polarity range.
- Results were dependent on discharge, loading, compound type, and method performance.

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ABSTRACT

A continuous active sampling method was compared to continuous passive and discrete sampling methods for the sampling of trace organic compounds (TOCs) in water. Results from each method are compared and contrasted in order to provide information for future investigators to use while selecting appropriate sampling methods for their research. The continuous low-level aquatic monitoring (CLAM) sampler (C.I.Agent® Storm-Water Solutions) is a submersible, low flow-rate sampler, that continuously draws water through solid-phase extraction media. CLAM samplers were deployed at two wastewater-dominated stream field sites in conjunction with the deployment of polar organic chemical integrative samplers (POCIS) and the collection of discrete (grab) water samples. All samples were analyzed for a suite of 69 TOCs. The CLAM and POCIS samples represent time-integrated samples that accumulate the TOCs present in the water over the deployment period (19–23 h for CLAM and 29 days for POCIS); the discrete samples represent only the TOCs present in the water at the time and place of sampling. Non-metric multi-dimensional scaling and cluster analysis were used to examine patterns in both TOC detections and relative concentrations between the three sampling methods. A greater number of TOCs were detected in the CLAM samples than in corresponding discrete and POCIS samples, but TOC concentrations in the CLAM samples were significantly lower than in the discrete and (or) POCIS samples. Thirteen TOCs of varying polarity were detected by all of the three methods. TOC detections and concentrations obtained by the three sampling methods, however, are dependent on multiple factors. This study found that stream discharge, constituent loading, and compound type all affected TOC concentrations detected by each method. In addition, TOC detections and concentrations were affected by the reporting limits, bias, recovery, and performance of each method.

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1. Introduction

The need to accurately detect a diverse array of trace organic compounds (TOCs) in natural waters is rapidly intensifying. In the past, waters have predominantly been sampled for TOCs by collecting a discrete (grab) volume of water, and field and laboratory methods for discrete samples are well established (e.g. Kolpin et al., 2002; Lewis and Zaugg, 2003, chap. A5; Zaugg et al., 2007a,b, chap. B4; Richardson and Ternes, 2011; U.S. Environmental Protection Agency, 2013). Discrete samples typically consist of a ≤1-L volume of water collected at one point in space and time, and thus represent only the TOCs present in the water at the time and place of sampling. Discrete sampling might miss episodic events that can dramatically alter TOC concentrations. In addition, the limited volume of discrete samples might lead

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to concentrations of TOCs in the sample or sample extract that are below the detection limits of the applied analytical method.

Advances in sampling technologies over the past few decades provide alternative options to discrete sampling for identifying TOCs in water. Use of in-situ continuous passive sampling methods has become increasingly common (e.g. Vrana et al., 2005; Greenwood et al., 2007; Stephens and Müller, 2007; Lohmann et al., 2012). Passively collected samples represent time-weighted averages of concentrations in water over the period of deployment. Passive samples typically have a larger sample volume than discrete samples, and the integrative nature of passive samplers accumulates TOCs and increases the probability that TOC concentrations will be above method detection limits. In-situ continuous active sampling methods have the same benefits as passive sampling methods, and have been used for several decades with varying success (e.g. Rantalainen et al., 1998; Roe utvik et al., 1999; Stephens and Müller, 2007; Zarnadze and Rodenburg, 2008). Previous studies of continuous active samplers have shown that these samplers can successfully detect TOCs in water, and that the results from continuous active samplers are similar to those of continuous passive samplers (Rantalainen et al., 1998; Roe utvik et al., 1999; Ellis et al., 2009).

One continuous passive sampler, the polar organic chemical integrative sampler (POCIS), was developed by the USGS to sample a variety of TOCs in water (Alvarez et al., 2004; Petty et al., 2004; Alvarez, 2010), and its use has grown in popularity (e.g. Di Carro et al., 2010; Li et al., 2010; Rosen et al., 2010; Lissalde et al., 2011; Miege et al., 2012; Morin et al., 2012; Kolpin et al., 2013). The POCIS provides an integrated sample over an extended period of time (several weeks to months) and a range of hydrologic conditions. The volume of water sampled during a POCIS deployment is a function of the sampling rate for a particular TOC and the sampling duration. Studies have shown, however, that TOC concentrations for POCIS samples are strongly controlled by the POCIS sampling rate for the TOC, which can be difficult to define because of many variables, including water velocity, water temperature, and biofouling (Alvarez, 2010; Morin et al., 2012).

The continuous low-level aquatic monitoring (CLAM) sampler (C.I.Agent® Storm-Water Solutions; http://www.ciagent-stormwater.com; commercial introduction in 2007) is a submersible, low-flow-rate sampler that continuously and actively draws water through filtration and solid-phase extraction (SPE) media. The extraction disk(s) can contain a variety of media to collect a range of less- to more-polar TOCs. Extraction events can be up to 36 h long; event duration is currently limited by the extraction disk capacity of 100 L (C.I.Agent® Storm-Water Solution Application Sheet, http://www.ciagent.com/ciagent/application_sheets/CLAM.pdf, accessed February 27, 2013) for well-retained TOCs, and by battery life. After CLAM deployment and retrieval, the extraction disk(s) is sent to a laboratory for analysis. The CLAM sampler provides an integrated sample of TOCs present in the water that accumulate over the deployment period, and that are well retained by the filtration and extraction disks, thereby increasing the probability that TOC concentrations will be above laboratory method detection limits.

CLAM sampler applications have not previously been reported in a peer-reviewed publication, and TOC detections in CLAM samples have not previously been compared to those in POCIS or discrete samples. Previous studies of POCIS have shown that the integrative nature of POCIS samplers generally results in an equal or greater number of detections of TOCs than discrete samples under field conditions (Alvarez et al., 2004; Alvarez et al., 2005; Zhang et al., 2008; Kolpin et al., 2013). The integrative capabilities of CLAM and POCIS samplers, along with planned use of the same type of extraction sorbent material in these samplers, suggest that CLAM samplers might produce results similar to those from POCIS. This study examines whether water samples collected using time-integrated CLAM and POCIS sampling methods identify a greater number of detections of TOCs than the standard discrete sampling method, which represents concentrations at one point in time.

The three sampling methods are compared in relation to TOC detections and operational dissolved-phase concentrations; possible reasons for observed differences and similarities are discussed. Quality-control (QC) samples are used to assess potential bias and variability associated with the sampling and laboratory methods, and to assess CLAM filtration and extraction disk performance. Results from each method are compared and contrasted in order to provide information for future investigators to use while selecting appropriate sampling methods for their research.

2. Methods

2.1. Field sites and deployment

The three sampling methods were tested at two sites on the Santa Cruz River in southeastern Arizona where baseflow is almost completely supported by treated effluent discharge from the Nogales International Wastewater Treatment Plant (NIWTP). The first site was located 20 m downstream of the outfall from the NIWTP (Site 1); the second site was located 16 km further downstream of the outfall (Site 2). Samples were collected at both sites over a period of 29 days, from April 9 to May 8, 2012. Eight discrete samples were collected, four from each site with a period of 7 days between samples. Two POCIS samples were collected, two from each site over a duration of 29 days. Eight CLAM samples were collected, four from each site for a duration of 19 to 23 h, with a period of 7 days between deployments. At both sites, samples were collected from consistent locations and times. Discrete samples were collected at the beginning of each CLAM deployment and at initial POCIS deployment plus 3 other times during the POCIS sampling period.

Select field QC samples were collected to assess bias and variability associated with the field methods. One discrete field blank, one CLAM field blank, and two POCIS field blanks were completed. Two field replicates were completed for the CLAM method only.

2.2. Sample collection

Discrete samples and a discrete field blank were collected following guidelines outlined in Lewis and Zaugg (2003, chap. A5). Depth-integrated water samples were collected in Teflon bottles in equal-width-increments to produce a composite sample that represents the discharge-weighted concentrations of a stream cross-section. A discrete field blank consisted of high-purity reagent water. The composite samples and the blank sample were both field filtered through 0.7-μm pore-size glass microfiber plate filters into 1-L baked amber glass bottles. All discrete samples were kept near 4 °C and arrived at the U.S. Geological Survey (USGS) National Water Quality Laboratory (NWQL) within 24 h of sample collection.

POCIS samples and POCIS field blanks were collected and extracted following guidelines outlined in Alvarez (2010). The POCIS were prepared at the USGS Columbia Environmental Research Center (CERC) and consisted of 200 mg of Oasis® HLB solid-phase sorbent (Waters Corp., Milford, MA) contained between two sheets of a 0.1-μm pore-size polyethersulfone membrane, suitable for sampling moderately polar to polar TOCs. Two POCIS were deployed mid-channel at both sites and remained submerged for the duration of the 29-day deployment period. A POCIS field blank was exposed to the atmosphere at each site during sample deployment and collection. Upon collection, all POCIS were stored, sealed and kept near 4 °C, and arrived at the USGS CERC within 24 h of sample collection.

The CLAM sampler consisted of a nylon body containing a low-flow pump, four AA batteries, and a filtration disk and two extraction disks each sealed within cartridge housings (C.I.Agent® Storm-Water Solutions; http://www.ciagent-stormwater.com). For this study, extraction disks containing a pre-filter and an Oasis® HLB solid-phase sorbent were used to collect moderately polar to polar TOCs, and to

match the sorbent used in the POCIS. Two HLB disks were installed in series within each CLAM in order to investigate the possibility of incomplete sorption of TOCs by the front disk, resulting in breakthrough to, and possibly through, the back disk. A 0.7-μm pore-size multilayer glass microfiber filtration (GFF) disk was installed prior to the HLB disks to remove suspended-sediment material. Prior to deployment, 50 mL of dichloromethane (DCM), methanol, and high-purity reagent water were pumped in series through each HLB and GFF disk at the NWQL. The wet disks were then sealed and shipped for field deployment.

The CLAMs were deployed mid-channel at both sites and remained submerged for the duration of each deployment. The volumes of samples extracted were dependent on the length of deployment and the pump rate. Total CLAM deployment times ranged from 19 to 23 h. The rate of the low-flow pump was dependent on power supply and sediment load in the water. The CLAM pump rates were measured at deployment and retrieval only; average rates (used to calculate sample volumes) ranged from 20 to 83 mL/min. Sample volumes ranged from 24 to 68 L. One CLAM field blank was collected by pumping 2 L of high-purity reagent water through a CLAM. Two CLAM field replicates were collected by deploying an additional CLAM sampler at each site for the same duration as a paired field sample. Upon collection, the GFF and HLB disks were sealed, kept near 4 °C, and arrived at the NWQL within 24 h of sample collection.

2.3. Laboratory preparation and analysis

The discrete samples and discrete field blank samples were extracted at the NWQL within 14 days of collection using and Oasis® HLB SPE cartridge as detailed in Zaugg et al. (2007a; Table 1). The sample bottle was rinsed with 15 mL of a DCM:diethyl ether mixture (80:20, v:v), which was then poured into the SPE cartridge to elute the compounds. Resultant extracts were concentrated to 400 μL final volume. Lab spike and blank samples were prepared and analyzed with each set of discrete samples to monitor method performance. Data from these set-specific QC samples were compared with performance criteria that are updated yearly using many QC samples (Maloney, 2005; Zaugg et al., 2007a,b, chap. B4).

The POCIS samples and POCIS field blank samples were eluted at CERC using a mixture of DCM:methyl-*tert*-butyl ether (80:20, v:v; Table 1). Two POCIS units per site (sampler) were eluted and combined into one extract per site during extract concentration. Concentrated extracts were sealed in 1-mL amber glass ampules, kept below 20 °C, and shipped to the NWQL for analysis. At NWQL, the extracts were transferred to receiver tubes and evaporated to 400 μL final volume. Lab blank and lab-fortified spike samples were prepared using comparable volumes of DCM and processed with the POCIS extracts.

The GFF and HLB disks from CLAM samples, CLAM field blank, and CLAM field replicate samples were received wet at the NWQL and were dried using N_2 prior to surrogate addition directly to the cartridge bed (Table 1). The dried disks were eluted with 50 mL of DCM. Extracts were concentrated to 400 μL final volume. Laboratory blank and spike samples, consisting of either a HLB or GFF disk, were processed with each set of CLAM samples. The laboratory blank and spike samples were prepared by adding 100 μL of surrogate solution in methanol to the wet disks. The laboratory spike sample was fortified with 100 μL of solution containing the method compounds. Twenty mL of reagent-water was passed through the disks, which were then dried with N_2.

Table 1
Field and laboratory procedures used for samples collected by discrete, CLAM, and POCIS sampling methods.

	Discrete	Clam	POCIS
Sampler type	Depth–width integrated grab sample	Continuous active	Continuous passive
Samples per site per POCIS deployment period	1 per week for 4 weeks	1 per week for 4 weeks	1
Sample duration	<1 h	19–23 h	29 days
Sampled volume (L)	~1	24–68	~0.6–23[a]
Sampler components	Teflon bottle; amber glass bottle post-collection	Prefilter cartridge + 2 HLB[b] sorbent cartridges in series	Membrane encased HLB sorbent
Filtration performed	In field, post-collection	In situ	In situ
Filtration media (minimum nominal pore size; binder type)	GFF[c] (0.7-μm; none)	Graded-depth GFF cartridge (0.7-μm; acrylic binder)	Polyethersulfone membrane (0.1-μm; none)
Extraction done	At NWQL[d]	In situ	In situ
Extraction sorbent	0.5-g HLB SPE[e] column	HLB (amount per cartridge unknown)	0.2-g HLB
Transfer sorbent to SPE column	NA[f]	NA	Yes, using reagent water
Surrogate addition	Prior to SPE	After cartridge dried but before elution	Upon receipt at NWQL (see below)
Analytes fortified for QC spike sample	Prior to SPE	Prior to cartridge drying; one GFF or one HLB per set	Into simulated extract upon receipt at NWQL
Cartridge/column drying prior to analyte elution	~45 min N_2 positive pressure (~2 L/min)	6–8 h N_2 positive pressure (~2 L/min)	~15 min lab air drawn through sorbent via vacuum
Elution solvent	15-mL 20% diethylether/dichloromethane (DCM); dispensed as rinse of empty sample bottle	50-mL DCM	25-mL 20% methyl-*tert*-butyl ether/DCM
Extract concentrated by	N_2 evaporation	Micro-Kuderna-Danish distillation and N_2 evaporation	Rotary and N_2 evaporation
Extract transport to NWQL; extract to receiver, add surrogates, N_2 evaporation	NA	NA	Yes
Final extract volume[g] (μL)	400	400	400
GC/EIMS-full scan; identical conditions except number of target analytes	60 analytes (Zaugg et al., 2007a)	69 analytes (Zaugg et al., 2007b, chap. B4)	69 analytes (Zaugg et al., 2007b, chap. B4)
Theoretical concentration enrichment factor upon GC/MS injection[h]	6.25	150–425[i]	28.1[j]

[a] Volume sampled by POCIS is compound dependent and was estimated as outlined in Alvarez (2010) using either measured or calculated compound sampling rates.
[b] Oasis® HLB sorbent material.
[c] GFF, glass-fiber filter.
[d] NWQL, USGS National Water Quality Laboratory, Denver, CO.
[e] SPE, solid-phase extraction.
[f] NA, not applicable.
[g] Injection internal standards added to final extract.
[h] Theoretical enrichment does not include analyte method recovery, or analyte distribution between cartridges for CLAM samples.
[i] Based on sampled volume range.
[j] Based on an average 4.5-L sample volume.

The laboratory blank and spike disks were then eluted and processed along with CLAM field samples.

For all three sampling methods, the final extracts described above were analyzed at the NWQL by gas chromatography/mass spectrometry (GC/MS) operated in full-scan mode for up to 69 TOCs (Supplemental Table 1) following procedures in Zaugg et al. (2007a). Injection internal-standard compounds were added to all extracts prior to GC/MS for compound quantitation. In addition, surrogate compounds were added by the NWQL to every sample for all three sampling methods to evaluate gross sample processing errors and possible matrix effects, and to monitor lab performance. Uniform final extract (400 μL) and injection volumes were used for GC/MS analysis for all sample types. Differences in method reporting levels (RL) for various TOCs (Supplemental Table 2) were primarily because of differences in actual (discrete and CLAM) or estimated (POCIS) sample volumes, and secondarily by differences in analyte method recoveries.

For POCIS and CLAM samples, data were determined in compound mass per POCIS or CLAM cartridge, in part to facilitate direct comparison with blank data. Concentrations in ng/L in CLAM sampler components were derived as the compound mass on the cartridge divided by the calculated sample volume. POCIS concentrations in ng/L were estimated as outlined in Alvarez (2010) using either measured or calculated compound sampling rates.

2.4. Data analysis

For comparison of the data from the three sampling methods, only TOCs present in water in the operationally defined "dissolved phase" were considered; total TOCs were not considered. Therefore, TOC concentrations from POCIS samples and filtered discrete samples were compared with TOC concentrations from the CLAM front HLB disks. TOC concentrations from the back HLB disk were not considered in the comparative data analysis. TOC concentrations from the GFF disks and back HLB disks, however, were considered in the QC data analysis to investigate the TOC retention on the disks under field-sampling conditions.

Non-metric multi-dimensional scaling (NMS) was used to examine patterns in both TOC detections and relative concentrations between the three sampling methods at the two sites. NMS is a non-parametric multivariate ordination technique that uses ranks of the sample similarities to build a graphical representation of sample patterns in a specified number of dimensions. Unlike other ordination methods, NMS preserves relative distance in multivariate space by retaining the rank order of among-sample similarities (i.e. units are arbitrary; Clark, 1993). Interpretation of a NMS plot in two-dimensional space, therefore, is relatively straightforward; samples close in proximity are more similar than those located farther apart. The starting point for any multivariate ordination is the similarity, or distance matrix, selected to represent the sample similarity. This is computed from the correlation or resemblance between every pair of sample data (square array, with row by column) to build a relational matrix (triangular matrix). For example, the concentration of a compound collected by the CLAM is compared to the concentration of that same compound collected by the POCIS and then to the discrete sample. This sample comparison process is continued for each compound. Regardless of the method used or at what site the sample is collected, a similarity resemblance matrix is computed for all compounds providing a means to compare all samples across all methods.

A fourth-root transformation (similar to a logarithm transformation) was used to normalize the data distribution before calculating the Bray–Curtis similarity matrix. A Bray–Curtis similarity matrix is a resemblance matrix well suited for examining these data because of the flexibility to include non-detects into the matrix. A Bray–Curtis similarity matrix is most commonly used with species abundance data sets because of the frequent absence (zero count) of species between samples. Water quality is very similar to abundance data because of the frequent non-detects in samples. NMS analysis was performed on the Bray–Curtis similarity matrix and plotted in two-dimensional space to reduce misinterpretation of multivariate patterns. A measure of stress is provided from the NMS analysis as a diagnostic to determine how well the data are represented by the NMS ordination. Lower stress values are desired and stress values below 0.20 generally indicate that the NMS ordination is providing an accurate representation of the data in multivariate space.

Vector overlays were added to the NMS graphical output as an exploratory tool to visualize potential linear or monotonic relationships between influential sampling methods for each TOC and the ordination axes. Vectors with Spearman rank correlation coefficients (rho) of ± 0.70 or greater were included. The sign describes the direction and the strength is described by the magnitude, the closer a rho value is to ± 1 the stronger the correlation. The length and direction of each vector indicate the strength and sign, respectively, of the relationship between the sample and a TOC labeled (Anderson et al., 2008). It should be considered, however, that the vector overlays can over simplify the relation between individual TOCs and multivariate structure of the ordination plot.

A cluster analysis was also used to identify similar groups by evaluating minimal within-group differences and maximum differences among groups. Similar to the NMS, a Bray–Curtis similarity matrix was used in the cluster analysis. The cluster analysis used a simple agglomerative, hierarchical clustering technique with group average linkage option. A similarity profile (SIMPROF) test was used to statistically evaluate whether or not a specified set of samples, which are not a priori assigned into groups, do not differ from each other in multivariate structure (Clarke and Gorley, 2006). SIMPROF is a permutation test that statistically tests different groups ($p \leq 0.05$) by computing the likelihood that individual groups were not generated purely by chance alone.

3. Results

3.1. Analysis of quality-control data

The one discrete field blank did not contain concentrations of any TOCs greater than three times the concentration in lab blanks, the NWQL's censoring threshold (Supplemental Table 3). Over 2012, the year of this study, the NWQL completed 55 laboratory reagent-water spike samples, average mean recoveries ranged from 22 to 107% (Supplemental Table 4). Environmental concentrations for three compounds with recoveries less than 40% (BHA, tetrachloroethylene, and cotinine) were qualified as "estimated" by NWQL. During this study's time frame, the NWQL qualified the concentrations of a total of fourteen compounds as "estimated" based on laboratory method performance limitations.

The 3 POCIS blanks (1 field and 2 lab) contained detections of 16 different TOCs (Supplemental Table 3). With 3 blanks, the upper confidence limit is 91% that potential contamination is no greater than the highest blank concentration detected for any given TOC in at least 45% of the samples. Environmental concentrations for a given TOC that were less than 10 times the highest blank concentration were considered to contain some contamination and were not considered in the data analysis. Twelve of the TOCs detected in the POCIS blanks were also detected in the CLAM blanks. The recoveries in the 1 spiked POCIS extract ranged from 20% (tetrachloroethylene) to 108%. Environmental concentrations for tetrachloroethylene were qualified as "estimated"; this volatile compound also had a low average CLAM spike recovery and has a low recovery using the discrete sampling method (Zaugg et al., 2007a,b, chap. B4).

The 7 CLAM blanks (1 field and 6 lab) contained detections of 33 different TOCs (Supplemental Table 3). With 7 blanks, the upper confidence limit is 92% that potential contamination is no greater than the highest blank concentration detected for any given TOC in at least 70% of the samples. Environmental concentrations for a given TOC that were less than 10 times the highest blank concentration were

considered to contain some contamination and were not considered in the data analysis. Average recoveries in 5 CLAM lab spikes processed with the environmental samples ranged from 7 to 127%. Environmental concentrations for 5 TOCs with average spike recoveries of 25–50% were qualified as "estimated;" 4 TOCs with average spike recoveries less than 25% were omitted. The average relative percent difference (RPD) between concentrations for the 2 field replicates was calculated for each compound. Three TOCs that had average RPDs greater than 25% were qualified as "estimated."

CLAM TOC concentrations on the front HLB disk as a fraction (in percent) of the total concentration on both HLB disks provide an estimate of the retention of TOCs on the front HLB disk for the sampled water volumes. Ideally, the front HLB disk would completely retain the TOCs and no TOCs would be detected on the back HLB disk. For the CLAM samples, the average retention of the front HLB ranged from 100% (indicating excellent retention by the front HLB disk) to 0% (indicating poor retention by the HLB disk sorbent; Supplemental Tables 1 and 3). Most detected compounds had above 70% retention on the front HLB disk. Two compounds were omitted from the data analysis as breakthrough on the front HLB disk was presumed to be extensive: 5-methyl-1H-benzotriazole with an average retention of 11%, and OP1EO with an average retention of 0%.

CLAM TOC concentrations on the GFF disk as a fraction (in percent) of the total concentration on the GFF disk and the front HLB disk provide an estimate of the retention of the TOC on the GFF disk for the sampled water volumes. TOCs completely or partially retained on the GFF disk were assumed to be particle-bound and were not available for retention on the front HLB disk. The study design was to analyze the operational dissolved-phase concentrations detected by each method, and retention of particle-bound TOCs on the GFF was expected. For the CLAM samples, the average retention of the GFF disk ranged from 100% (indicating complete retention by the GFF disk) to 0% (indicating no retention by the GFF disk; Supplemental Tables 1 and 3). Twelve TOCs had GFF retention of 60% or greater. Five of these TOCs (2,6-dimethylnaphthalene, OP1EO, chlorpyrifos, fluoranthene, and benzo[a]pyrene) had CLAM GFF retentions of 100%, and were not detected in the dissolved phase

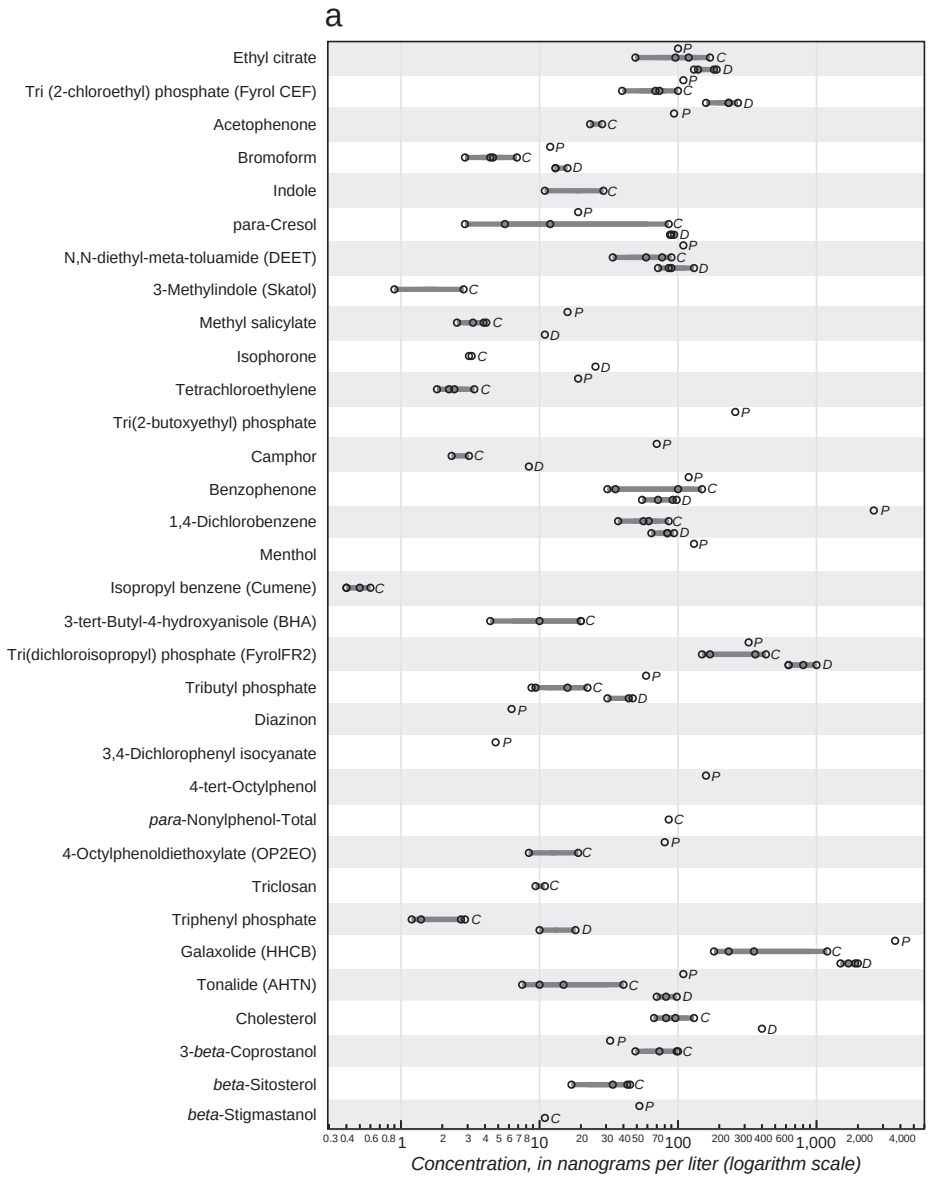

Fig. 1. (a) Boxplot of wastewater compounds detected at Site 1 by collection method (P = POCIS, C = CLAM, D = discrete sample). Compounds not detected by any method are not included. (b) Boxplot of wastewater compounds detected at Site 2 by collection method (P = POCIS, C = CLAM, D = discrete sample). Compounds not detected by any method are not included.

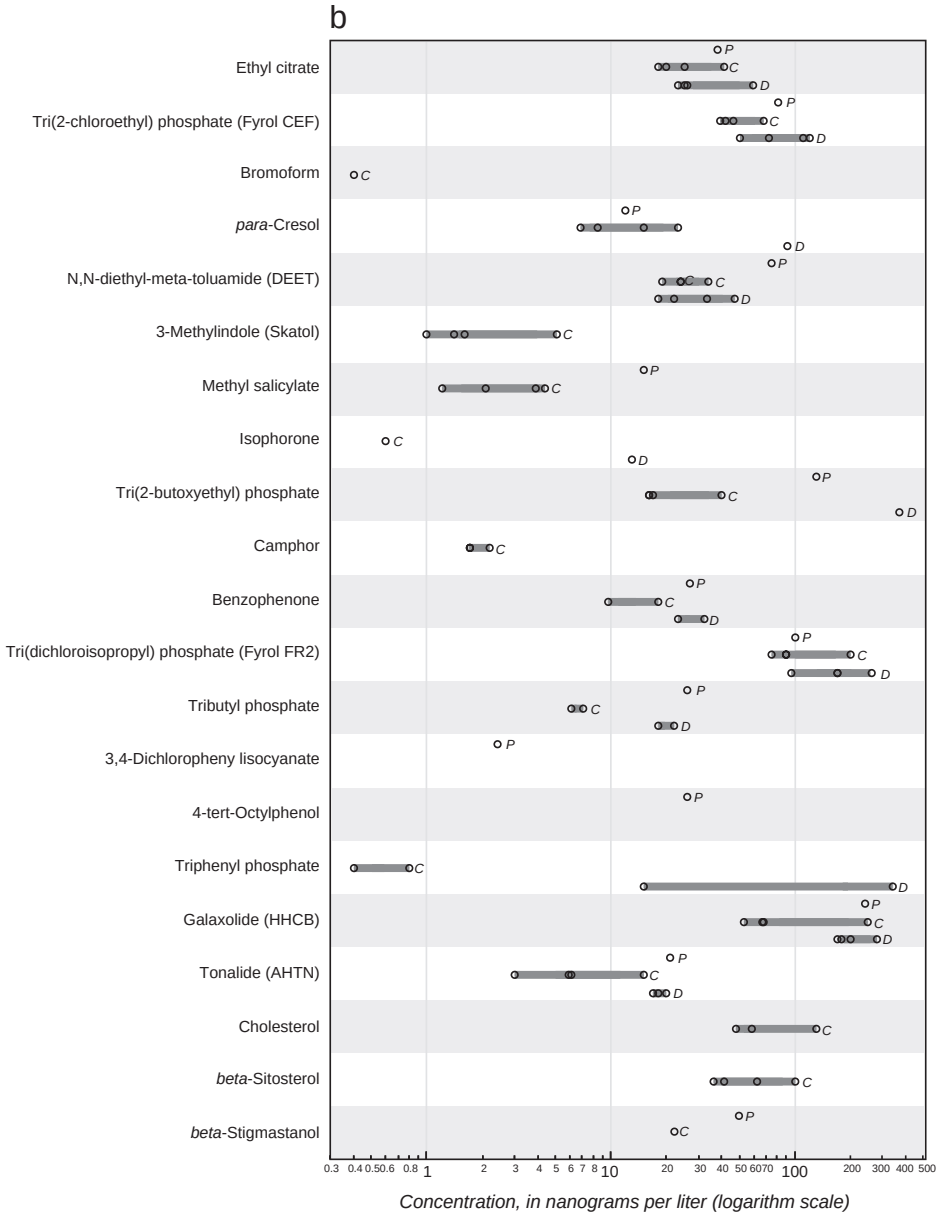

Fig. 1 (*continued.*)

by any of the three methods; these TOCs are all less polar and are expected to be mostly particle-bound. One TOC (3,4-dichlorophenyl isocyante) had a CLAM GFF retention of 100%, but was detected by the POCIS; this TOC is moderately polar. Six TOCs (AHTN, HHCB, 3-*beta*-coprostanol, chlolesterol, *beta*-sitosterol, and *beta*-stigmastanol) had CLAM GFF retentions of 60%–86%. These TOCs were some of the least polar TOCs sampled, and the TOCs would be expected to be mostly particle-bound. Each of these TOCs was detected, however, in the operational dissolved-phase by one or more of the three sampling methods.

3.2. Analysis of environmental data

Thirty-four unique TOCs were detected by one or more methods at one or both of the sites (Fig. 1; Supplemental Table 1). All three methods detected a greater number of TOCs, and generally higher concentrations, at upstream Site 1 just below the NIWTP outfall than at Site 2. At both sites, a greater number of TOCs were detected in the CLAM samples than in the discrete or POCIS samples. This is attributed in large part to differences in RLs for the 3 sampling methods (Supplemental Table 2). The number of TOC detections at Site 1 was 16 for discrete, 23 for POCIS, and 29 for CLAM; the number of TOC detections at Site 2 was 12 for discrete, and 14 for POCIS, and 19 for CLAM. At both sites, for TOCs detected in the CLAM samples and by at least one other sampling method, the concentrations in the CLAM samples were significantly lower than the concentrations in the discrete (Wilcoxon rank sums; both Site 1 and Site 2, $p < 0.0001$) and (or) the POCIS (Wilcoxon rank sums; Site 1, $p < 0.0008$; Site 2, $p = 0.032$) samples. For many TOCs, the lower concentrations detected by the CLAM are most likely related to partial TOC non-retention by the front CLAM HLB disk (Supplemental Table 3), including those TOCs with higher K_{ow}s that are associated with (partition into) dissolved organic matter, which itself is not well retained by the HLB sorbent material (Mackintosh et al., 2006; Zarnadze and Rodenburg, 2008; Cornelissen et al., 2010). For the less polar TOCs, lower CLAM concentrations may also be related to the sorbing of dissolved-phase TOCs onto particle material as material accumulates on the GFF over the sampling period, a sorption process well documented in sampling semivolatile organics from air and that can be enhanced by filters containing binders (Arp et al., 2007). The CLAM GFFs used in this

study contained an organic acrylic binder (Brent Hepner, C.I.Agent® Storm-Water Solutions, written communication, 2013).

At both sampling locations, nine TOCs were detected by all three methods: ethyl citrate, galaxolide (HHCB), tonalide (AHTN), benzophenone, *N*,*N*-diethyl-meta-toluamide (DEET), *para*-cresol, tri(dichloroisopropyl) phosphate, tributyl phosphate, and tri(2-chloroethyl) phosphate. Bromoform, camphor, 1,4-dichlorobenzene, and methyl salicylate were detected by all three methods at Site 1 only. HHCB had the highest concentration detected for all three methods at Site 1, concentrations decreased an order of magnitude at the downstream Site 2. *Beta*-sitosterol, *para*-nonylphenol-total, triclosan, cumene, 3-*tert*-butyl-4-hydroxyanisole (BHA), skatol, and indole were only detected by CLAM samplers. 4-*Tert*-octylphenol, 3,4-dichlorophenyl isocyanate, diazinon, and menthol were only detected by POCIS samplers. There were no TOCs only detected by discrete samples.

Flow variability at Site 1 had a consistent diurnal pattern (around a 400 to 600 L/s change; Fig. 2a). The number of CLAM detections at Site 1 remained relatively consistent over the 4 sampling periods at 21 to 24 detections, which was similar to the integrated POCIS sample (23 detections). The concentrations in the CLAM samples, however, were somewhat variable. The discrete samples at Site 1 had 10 to 11 detections over the first three samples, but increased to 16 during the last sampling event. The variability of the CLAM concentrations and the discrete detections suggests that the variability of TOCs in the samples from Site 1 may have been affected by factors other than stream discharge. The most likely cause is changes in the discharge from the wastewater treatment plant. Seasonal changes in wastewater constituent composition with seasonal local population shifts have previously been documented (Walker et al., 2009).

The NMS ordination of samples collected at Site 1 indicated that the number and concentrations of TOCs were very different between the three sampling methods (Fig. 3a). Multivariate dispersion, or spread, between the four temporal samples was greater with the CLAM than with the discrete method. The plotted positions of the CLAM samples in the NMS ordination are associated (i.e., a TOC concentration increases in the direction of the arrow and samples along the same trajectory will have greater concentrations of the TOC represented by the arrow) with detections of the less polar (K_{ow} >3) compounds *beta*-sitosterol, triclosan, cumene, 3-*beta*-coprostanol, and 3-*tert*-butyl-4-hydroxyanisole (BHA), and the more polar (K_{ow} <3) compound skatol. The plotted positions of the discrete samples in the ordination are associated with the relatively higher concentrations of the less polar compound tri(dichloroisopropyl) phosphate and the more polar compound tri(2-chloroethyl) phosphate. The plotted position of the time-integrated POCIS sample in the ordination is controlled by the detection of TOCs not collected (or not determined) by the other two methods (Fig. 1a), specifically: the less polar compounds 4-*tert*-octylphenol and 3,4-dichlorophenyl isocyanate (CLAM results censored for both of these TOCs based on QC data), diazinon, menthol, and tri(2-butoxyethyl) phosphate. Both CLAM and POCIS samples were associated with the less polar compounds *beta*-stigmastanol and tetrachloroethylene, and the more polar compound acetophenone. Both discrete and POCIS samples were associated with the less polar compounds tonalide (AHTN) and galaxolide (HHCB).

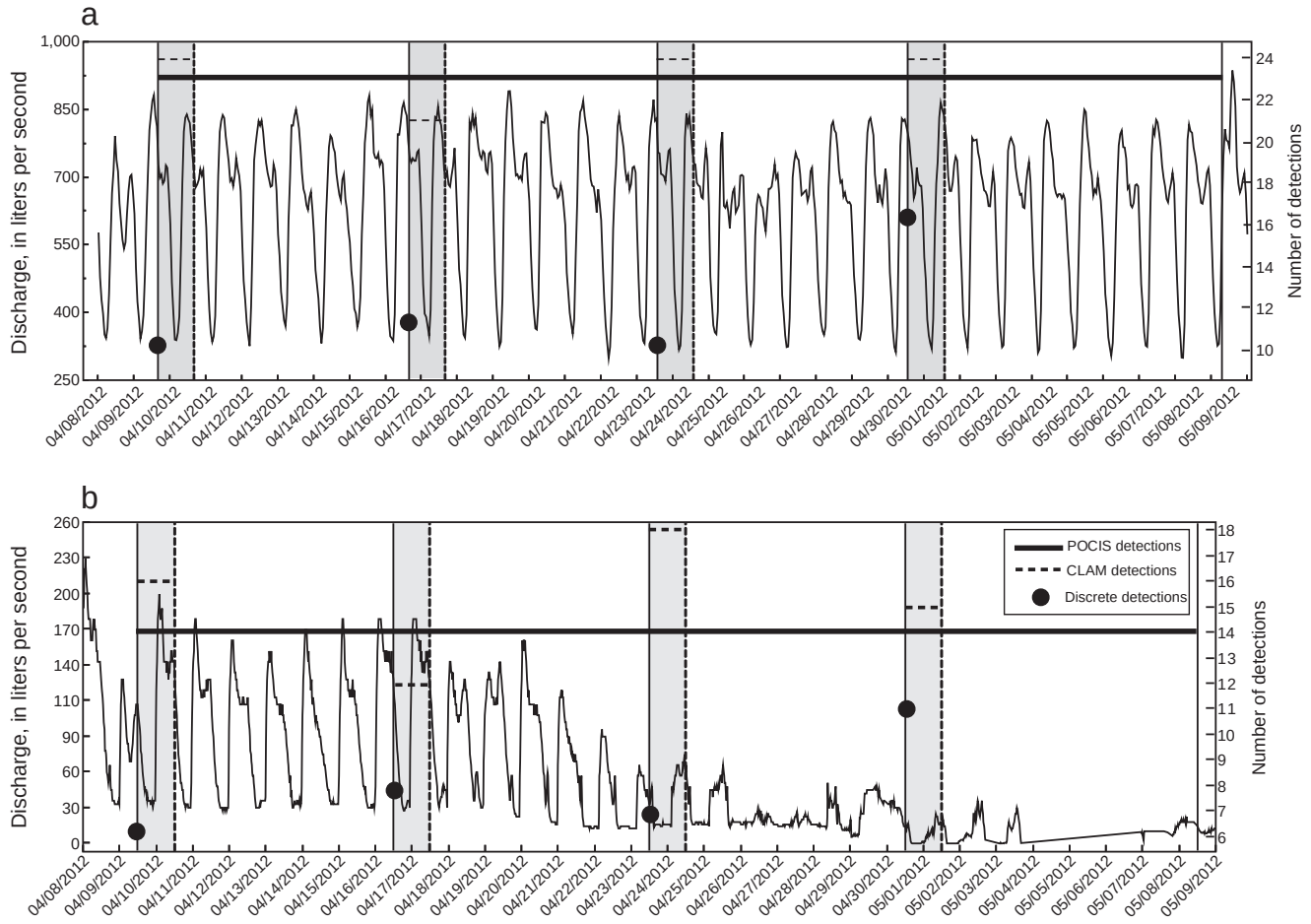

Fig. 2. (a) Nogales International Wastewater Treatment Plant discharge hydrograph at Site 1. (b) USGS stream gaging station Santa Cruz River at Tubac, AZ (09481740) discharge hydrograph, downstream of Site 2.

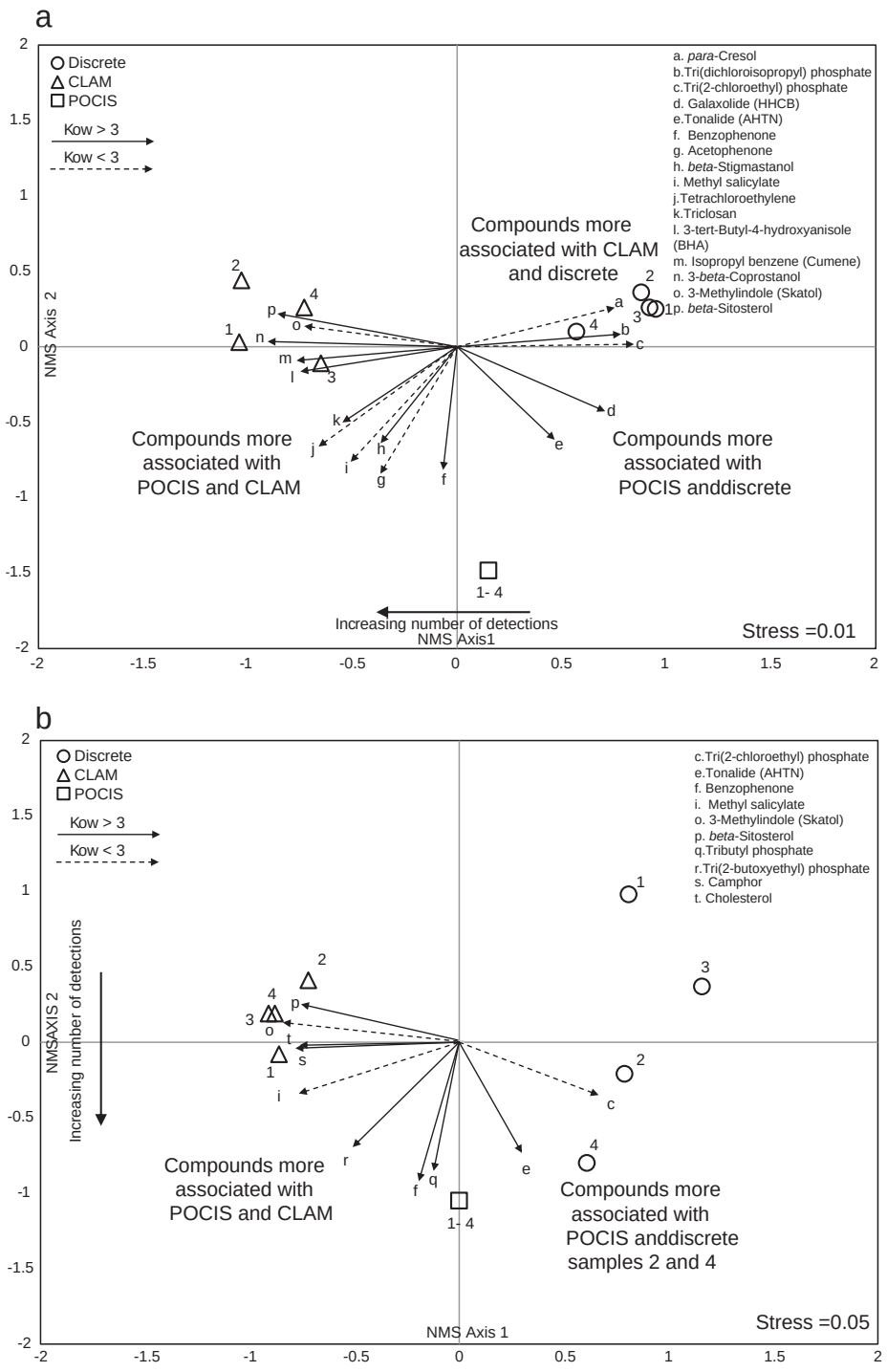

Fig. 3. Non-metric multidimensional scaling ordination for the three collection methods; discrete water sample, CLAM, and POCIS for (a) Site 1 and (b) Site 2. Sampling events numbered 1, 2, 3, and 4 for discrete and CLAM samples, and 1–4 for POCIS sampling interval. Spearman rank correlation vectors for each compound with a Rho greater than 0.7 are shown with arrows. Direction and length signify compound–axis association and Rho magnitude, respectively.

The number of TOCs detected by all methods at Site 2 was lower than at Site 1, and TOC concentrations were generally an order of magnitude lower at Site 2 than at Site 1 (Fig. 1b). Flow variability at Site 2 had a diurnal pattern similar to Site 1, but the overall flow at Site 2 decreased over the sampling period (Fig. 2b). The USGS stream gaging station Santa Cruz at Tubac, AZ (09481740), located approximately 5.6-km downstream of Site 2, recorded an order of magnitude decrease (183 to 17 L/s) in mean daily flow over the sampling period. The first two discrete sampling events and CLAM deployments were during higher flows when compared to the lower flows of the third and fourth sampling events. The number of CLAM detections at Site 2 remained relatively consistent over the 4 sampling periods at 12 to 18 detections, which was similar to the integrated POCIS sample (14 detections). The discrete samples at Site 2 had 6 to 8 detections over the first three samples, but increased to 11 during the last sampling event. The fourth discrete sample also had overall greater TOC concentrations relative to the preceding discrete samples. This variability might be related in part to the decreasing mean daily discharge of the stream. Factors

such as temperature, water evaporation, bank storage, and microbial degradation were most likely also changing during this time, and probably contributed to fluctuations in TOC concentrations at Site 2.

Similar to Site 1, Site 2 samples grouped in the NMS ordination based on method type (Fig. 3b). The plotted positions of the CLAM samples are associated with detections of the less polar (K_{ow} >3) compounds *beta*-sitosterol and cholesterol, and the more polar (K_{ow} <3) compounds skatol and camphor. The plotted position of the time-integrated POCIS sample in the ordination is controlled by the detection of the less polar compounds 4-*tert*-octylphenol and 3,4-dichlorophenyl isocyanate (Fig. 1b); the CLAM data was censored for both of these TOCs based on the QC data. The CLAM samples and the POCIS samples were associated with the less polar compound methyl salicylate. Both discrete and POCIS sample were associated with the less polar compound tonalide (AHTN) and the more polar compound tri(2-chloroethyl) phosphate. The discrete samples at Site 2 had considerably more multivariate dispersion between the 4 sampling events than at Site 1. This variability in the discrete samples was partially related to the TOCs tributyl phosphate and benzophenone, which were only detected in discrete samples 2 and 4, but were detected in all CLAM and POCIS samples. In addition, the TOCs isophorone and tri(2-butoxyethyl) phosphate were only detected by the discrete method in sample 4.

Constituent loading may contribute to the difference in the variability between the three methods at Sites 1 and 2. At Site 1, where constituent loading is high because of the site's proximal location to the outfall of the NIWTP, the dissimilarity of the POCIS sampling method from the discrete sampling method can be attributed to the POCIS sample containing the highest concentrations of several TOCs. At downstream Site 2, where constituent loading is relatively less because of, in part, dilution, degradation, and adsorption, POCIS and discrete sampling methods were generally more similar in number and concentration of TOCs detected than at Site 1.

The NMS and cluster analysis of sampling methods on the basis of only TOC concentrations indicate that the site from which a sample was collected was most significant (Fig. 4a). Samples were divided into two groups based on sampling site (groups a and b). After the site from which the sample was collected, the sample collection method was next in significance (groups c, d, e, f; Fig. 4a).

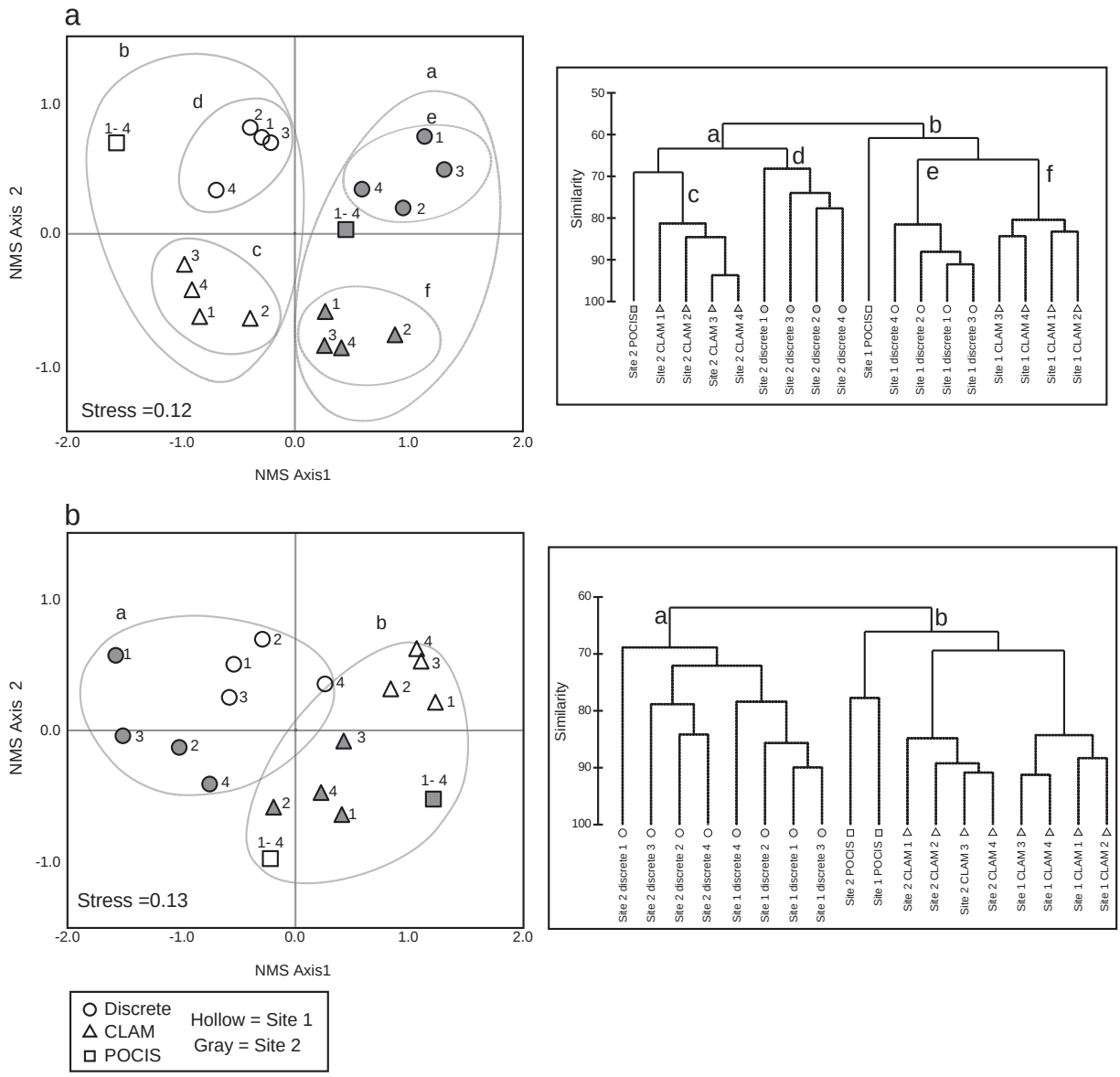

Fig. 4. A non-metric multidimensional scaling (NMS) ordination for discrete, CLAM, and POCIS sampling methods for (a) compound concentrations and (b) presence/absence of compounds. Sampling events are numbered 1, 2, 3, and 4 for discrete and CLAM sampling events, and 1–4 for POCIS integrated sampling interval. Cluster analysis dendograms are shown to identify groupings in the NMS analysis.

The NMS and cluster analysis of sampling methods on the basis of only TOC detection (presence/absence), regardless of concentration, indicate that the sampling method was most significant (Fig. 4b). Samples were divided into two groups based on sampling method (groups a and b). This indicates that samples from the same collection method are more similar to one another, regardless of the TOC concentration or the site where the samples were collected. On the basis of TOC detections, discrete samples were significantly different than CLAM or POCIS samples (group a), while CLAM and POCIS samples were more similar to one another than to discrete samples (group b). This is not unexpected based on the higher RLs for the discrete method compared to POCIS and CLAM methods.

4. Discussion

Several factors need to be taken into account while discussing the results of this study. First, and foremost, this study compares and contrasts the operational dissolved-phase concentrations of samples collected using three different sampling methods, with particular focus on the CLAM sampling method. It was not expected that the three different sampling methods would necessarily produce the same results, but rather that the results would illuminate the strengths and limitations of each field sampling method and help guide future investigators in selecting which sampling method is most appropriate for their research. The sampling methods differ in several ways, most notably by time, volume, and filter pore size. By maintaining consistent sampling sites, field personnel, handling procedures, and laboratory procedures, however, variability between the results from each sampling method ideally will be related largely to the sampling methods themselves. Second, the sampling method differences of time, volume, and filter pore size influenced the analytical RLs for each method, and the RL for each TOC was not consistent between the three sampling methods (Supplemental Table 2). Third, a wastewater-dominated stream was chosen for this study with the goal of having sufficient stream concentrations to obtain detections of multiple TOCs by all three methods. Applying this type of study to a much less anthropogenically-affected stream would likely yield fewer detections by all three sampling methods. Finally, field and lab quality-control data must be given careful consideration when using any of these methods for TOC analysis. Bias, variability, and HLB disk breakthrough affected 54% of the TOCs sampled by the CLAM method, while 20% of the TOCs sampled by the POCIS and the discrete methods were affected by bias and (or) variability. Seven percent of the TOCs sampled by the CLAM samplers were omitted due to unacceptably poor QC data (Supplemental Table 3).

Future investigators need to carefully consider many factors when selecting a sampling method for determining TOCs in natural waters. This study concluded that CLAM, POCIS, and discrete sampling methods differ greatly in both the number of TOCs detected, and the concentrations of the TOCs detected. When comparing only the number of TOCs detected, regardless of concentration of the TOCs, the sampling method was found to be more significant than sampling site or sampling event. The low laboratory RLs for TOCs sampled with the CLAM sampling method resulted in the CLAM method detecting more TOCs than the POCIS or discrete sampling methods. Concentrations of TOCs detected by the CLAM sampling method, however, were significantly lower than concentrations of the same TOCs detected by the POCIS and discrete sampling methods. This is most likely a result of partial TOC non-retention by the HLB disk and (or), for less polar TOCs, sorption of TOCs on to particle material accumulated on the GFF. The time-integrative nature of the CLAM method minimized the effect of surface-water flow variability on TOC detections, unlike the discrete method. The CLAM and POCIS sampling methods were generally able to detect a range of K_{ow} TOCs, including several of the more polar detergent metabolites and less polar sterols, that were not detected in the discrete samples. While the CLAM and POCIS sampling methods detected a range of TOCs with different K_{ow}s, the CLAM sampling method had a greater positive association with more of the less polar compounds over the four sampling events than the POCIS and discrete sampling methods. Overall, the effect of the K_{ow} on the types of TOCs detected by each of the sampling methods was inconclusive; TOC detections were observed for each method across the range of the TOCs' K_{ow}s, and a trend was not apparent.

Each sampling method has its own logistical advantages and disadvantages. The discrete sampling method has a well-tested and well-documented collection method, and simple interpretation of observed TOC concentrations. The collection of a discrete sample requires only one visit to a site, but the time required at the site is generally several hours to allow for sample collection and processing. A discrete sample only represents a single point in time; intermittent pulses of TOCs, common in wastewater effluent-dominated streams, can be missed. In addition, the relatively small sample volumes of discrete samples can result in TOC RLs higher than environmental concentrations. A sample collected with either the CLAM or POCIS methods represents a time-integrated sample, and the relatively larger sample volumes of POCIS and CLAM samples are more likely to result in TOC RLs lower than environmental concentrations. POCIS and CLAM sampling methods require two visits to a site to allow for deployment and retrieval, but the time required at the site is much shorter than the discrete sampling method. Both POCIS and CLAM samplers are required to be fixed to the streambed for a period of weeks to months (POCIS) or hours to days (CLAM), and both POCIS and CLAMs are susceptible to loss or damage during their deployment time. The POCIS is also susceptible to biofouling and the CLAM is susceptible to clogging of the GFF and is limited by battery life. The CLAM also requires a pump rate measurement upon deployment and retrieval (and ideally over the entire sampling period). The measured flow rate of the CLAM allows the user to determine concentrations based on an actual volume of water filtered, whereas the POCIS relies on theoretical uptake models to determine concentrations.

5. Conclusions

Trace organic compound concentrations in water collected with CLAM samplers were compared to those collected with POCIS samplers and those collected with discrete methods. The CLAM sampler is a submersible, low flow-rate sampler, that continuously draws water through solid-phase extraction media. CLAM samplers were deployed at two wastewater-dominated stream field sites in conjunction with the deployment of POCIS samplers and the collection of discrete water samples. All samples were analyzed for a suite of 69 TOCs. The CLAM and POCIS samples represent time-integrated samples that accumulate the TOC present in the water over the deployment period (19–23 h for CLAM and 29 days for POCIS); the discrete samples represent only the TOCs present in the water at the time and place of sampling. Non-metric multi-dimensional scaling and cluster analysis were used to examine patterns in both TOC detections and relative concentrations between the three sampling methods.

The comparison of the TOC results from the CLAM, POCIS, and discrete sampling methods provides information for future investigators to use while selecting appropriate sampling methods for their research. This study concluded that when comparing only the number of TOCs detected, regardless of concentration of the TOCs, the sampling method was more significant than sampling site or sampling event. Overall, the larger sample volumes of the CLAMs led to a greater number of TOCs detected in the CLAM samples than in the discrete or POCIS samplers. For TOCs detected by the CLAM samplers and at least one other method, the concentrations in the CLAM samples were generally lower than the concentrations in the discrete and (or) the POCIS samples, most likely because of partial TOC non-retention by the front CLAM HLB disk. All three methods detected TOCs across a wide polarity range, but the CLAMs did have a greater positive associated with more of the less polar compounds than the other two methods.

The CLAM, POCIS, and discrete sampling methods differ in several ways, most notably by time, volume, and filter pore size; these differences influence the analytical RLs for each method, and the RL for each TOC was not consistent between the three sampling methods. The variability in the results between the three methods was also influenced by variability in stream discharge and possibly constituent loading. In addition, TOC detections and concentrations were affected by the bias, recovery, and performance of each method. The effects of these factors should be taken into consideration when choosing the appropriate sampling method for a study.

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.scitotenv.2013.12.082.

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Disclosure statement

Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

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