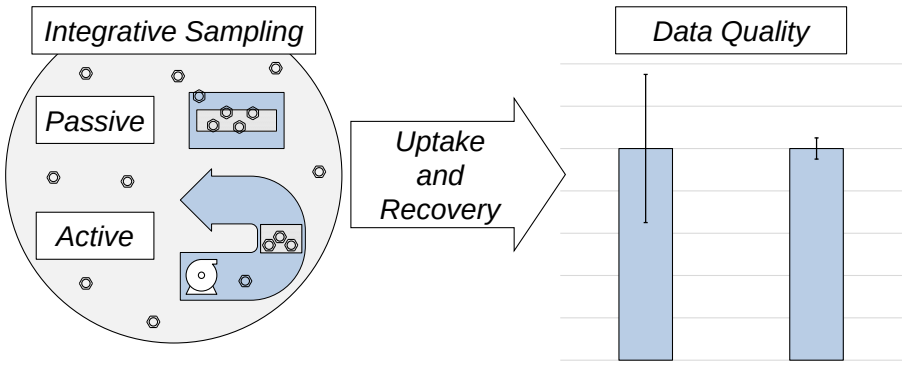
Graphical Abstract



Critical Review of Factors Governing Data Quality of Integrative Samplers Employed in Environmental Water Monitoring

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ABSTRACT

Integrative sampling enables the collection of analyte mass from environmental liquids over extended timeframes from hours to months. While the incentives to complement or replace conventional, time-discrete sampling have been widely discussed, the data quality implications of employing alternative, integrative methods have not yet been systematically studied. A critical analysis of contemporary literature reports showed the data quality of integrative samplers, whether active-advection or passive-diffusion, to be governed by uncertainty in both sampling rate and analyte recovery. Derivation of two lumped parameters, representing the coefficient of accumulation (α) of a contaminant from an environmental fluid and the coefficient of subsequent recovery (ρ) of its mass from the sampler, produced a conceptual framework for quantifying error sources in concentration data derived from accumulative samplers. Whereas the precision associated with recovery was found to be fairly consistent across eight passive-diffusion and active-advection devices (averaging 5 – 16% relative standard deviation, RSD), active-advection samplers effectively improve precision in sampling rate (analyte uptake), as determined for two active-advection devices (2 – 7% average RSD) and five passive devices (12 – 42% average RSD). In summary, an approach is presented whereby the data quality implications of integrative sampler design can be compared, which can inform the selection, optimization, and development of sampling systems to complement the state of the art.

KEYWORDS

integrative sampling; passive sampling; in situ extraction; solid phase extraction; environmental characterization; water sampling

1.0 INTRODUCTION

The typical process for characterizing the chemical milieu of an environmental compartment, such as groundwater, is to couple a sampling method in the field with an analytical method in the laboratory. Modern analytical methods have long been capable of quantifying the contaminant concentration in a sample with precision that is notably better than the inter-sample uncertainty observed in environmental fluids and process streams themselves (Green and Le Pape, 1987; Zhang and Zhang, 2012). Thus, the sampling method constitutes the primary, though often underappreciated, element for managing uncertainty in any monitoring effort, as it has the greatest potential to propagate uncertainty into the results of a monitoring scheme and ultimately into the design of remedies and other engineering works based on those results (Barcelona et al., 1984; Liška, 2000; Maney, 2002; Pankow, 1986).

Perhaps equally important, the sampling method defines the context or setting in which analytical data is understood. The choice of sampling methods determines whether resultant data represents discrete points in time and space, or an average of the concentrations present at the location under investigation during a period of time (Vrana et al., 2005). Different sampling methods may provide conceptually equivalent data, but with different degrees of error. Familiarity with the effects of various sampler designs and properties on the trueness and precision of resulting data is therefore essential for balancing project goals and data requirements with instrument cost and logistics.

One technique that has been the subject of a significant volume of literature is the development of *integrative samplers*; that is, samplers that generate time-integrated average measurements of environmental contaminant concentrations, typically by accumulation in a

sorbent. Morin et al. (2012) noted 14 reviews between 2000 and 2012 for passive samplers, and provides an extensive review for the Polar Organic Chemical Integrative Sampler (POCIS), as did Harman et al. (2012). An earlier review by Zabiegała et al. (2010) provides an indication of the growth in publications on this topic between 1999 and 2009, with a doubling in volume to more than 200 publications per year in that time. A review by Lohman et al. (2012) provides an overview of theory and examines the strength of the models which are presented in this work and statistical utility versus other contemporary monitoring methods. Other reviews including that by Vrana et al. (2005) also provide overviews of the broader theory for this class of samplers, with Verreydt et al. (2010) further placing them in the context of mass flux measurement.

The present work distinguishes itself from prior reviews by focusing on time-integrative samplers, specifically active-advective and passive-diffusive samplers, and by exploring the relationship between the design properties of a time-integrative sampling system and the quality of the data obtained with respect to trueness, i.e., closeness to true value, and precision, i.e., reproducibility of measured values). A conceptual model is developed here to describe a variety of integrative samplers and the assumptions underlying use of their data. The relevance of factors influencing data trueness and precision are discussed as well.

2.0 THEORY AND CONCEPTUAL MODEL

2.1 Accumulative Sampling. Accumulative samplers operate on the principle of mass transfer over time from an ambient fluid source (environmental phase) to an engineered sink (sampling phase) (Fowler, 1982; Woodrow et al., 1986). Mass transfer between the phases is regulated by advective and diffusive transport of the target compounds to and through the sampler. Samplers

performing mechanical work on the environment to move the contaminant-bearing phase to the sampling phase are referred to as '*active*', while those relying on diffusion or environmental advection are termed '*passive*' (Fowler, 1982; Kot et al., 2000; Vrana et al., 2001; Vrana et al., 2005). When a clean sampling phase is introduced to the environment, uptake of contaminants proceeds pseudo-linearly with time (kinetic regime), decreasing as the phase comes into thermodynamic equilibrium with the environment (equilibrium regime, Figure 1). Samplers that are intended for the determination of an environmental contaminant concentration as a function of the equilibrium concentration of the sampling phase are termed '*equilibrium samplers*' (Vrana et al., 2005). An '*integrative sampler*' is one that is designed for operation in the kinetic regime, with the environmental concentration described as a function of the uptake rate and time (ASTM, 2014).

Accumulative sampling follows a general trend in analytical chemistry towards techniques which sequester and pre-concentrate compounds of interest before analysis (Jolley, 1981; Murray, 1997) and may be contrasted with discrete (grab) sampling, which captures and removes an aliquot of the ambient fluid (Woodrow et al., 1986). Both equilibrium and integrative methods can provide pre-concentration by acting as a preferred phase for partitioning of the analyte. The key difference between the two methods lies in the dimension of time; equilibrium samplers [e.g., polyethylene diffusion bags (PDBs) and solid phase microextraction (SPME)] provide a time-weighted average that follows and attenuates the changes in the environmental concentration, and is biased towards the current concentration (Figure 2). Equilibrium samplers are typically designed for rapid equilibration (Mayer et al., 2003; Vrana et al., 2005). The degree of lag and attenuation is a function of the equilibration time of the sampler; SPME, which has a very short equilibration time (hours to days), will more closely approximate a discrete sample

(Mayer et al., 2003), while SPMDs, which have been investigated as proxies for aquatic animals, may require 10s of days or longer to reach equilibrium (Huckins et al., 1990).

2.2 Integrative Sampling. In contrast to equilibrium samplers, integrative samplers provide a time-integrated average concentration over the whole sampling period (Figure 2). This effectively manages to both capture the effect of and prevent the over- or under-representation of excursions from average concentrations of contaminants over the course of the sampling period (Alvarez et al., 2004; Bopp et al., 2005; Coes et al., 2014; Seethapathy et al., 2009; Vrana et al., 2005). This is particularly attractive in situations where the number of discrete samples required to generate equivalent data would be cost-prohibitive (Kot et al., 2000; Martin et al., 2003; Namieśnik et al., 2005; Stuer-Lauridsen, 2005; Vrana et al., 2005; Woodrow et al., 1986). Integrative samplers are frequently capable of providing lower detection limits than discrete samplers (Pankow et al., 1984; Woodrow et al., 1986; Coes et al., 2014). Lower detection limits are achieved through the concentration of the analyte mass from a large volume of air or water; this effect increases with the volume of fluid processed. Furthermore, by collecting the analyte separately from the bulk phase, integrative samplers greatly reduce the volume of material moved from the field to the laboratory, reducing waste, shipping costs, opportunities for losses, and contamination from handling steps (Green and Le Pape, 1987; Kot et al., 2000; Namieśnik et al., 2005; Pankow et al., 1984; Woodrow et al., 1986).

2.3 Conceptual Model for Integrative Sampling. The time-integrated average environmental concentration estimate obtained with an integrative sampler (measured value, $\overline{C_S}$) for a given analyte is proportional to the product of the actual time-integrated average concentration in an environmental water (true value, $\overline{C_W}$), a dimensionless analyte collection coefficient (α) informing on the extent of analyte uptake and retention by the collection matrix, and a

dimensionless recovery coefficient (ρ) informing on the relative success of extraction or elution of the analyte from the collection matrix (Equation 1):

$$\overline{C_S} = \overline{C_W}\alpha\rho \quad (1)$$

The design of any composite sampling system thus should take into consideration the management of uncertainty associated with these processes. This conceptualization is analogous to modeling of the efficiency of a liquid chromatography column, which likewise is governed by the coefficient of retention of an analyte on the analytical column and its coefficient of recovery (Green et al., 1986).

3.0 ANALYTE UPTAKE AND RETENTION

3.1 Active-Advection Samplers. An active, advection-regulated integrative sampler operates on the same principles as liquid chromatography and solid phase extraction. A volume of an environmental fluid (V_W) with some concentration of a dissolved contaminant (C_W) is contacted with a sampling phase or collection matrix. The total mass of the contaminant (M_S) can be calculated as shown in Eq. 2:

$$M_S = C_W V_W \quad (2)$$

Ideally, the process is fully reversible and, during subsequent extraction, the contaminant mass is removed from the sampling phase by an eluting agent (e.g., a solvent) in its totality; the sorbed mass is derived from the eluate concentration, and the environmental concentration is found by dividing the sorbed mass by the volume sampled, V_W.

A time-discrete sample may be taken by removing an aliquot of fluid from the environment "instantaneously" (e.g., by the use of a bailer or other device for separating a parcel

of fluid from the environment) and contacting the entire volume of fluid with a sorbent media. The sorbed sample thus developed represents a discrete time and space. If the process by which the sample is collected is continuous over a non-trivial time, the analyte mass placed into contact with the sorbent media is a function of both time (t) and the average concentration ($\overline{C_W}$; [mass/volume]) of the analyte in the volume of fluid sampled over time (Figure 2). Thus in Equation 3, the sample volume, V_W, is described as the product of a volumetric sampling rate (R_S; [volume/time]) and time, t.

$$M_S(t) = \overline{C_W} R_S t \quad (3)$$

This approach has long been applied to atmospheric sampling (Russell, 1975), and later for environmental waters in both discrete (e.g., Infiltrex) (Tran and Zeng, 1997) and time-integrated sampling systems [e.g., the Continuous Low-Level Aquatic Monitoring (C.L.A.M.) (Coes et al., 2014) and the *In Situ* Sampler (IS2) (Halden 2011; Halden and Roll, 2015; Roll 2015)].

With respect to uptake and retention, the sampling volume V_W (a term that by definition is inclusive of sampling time) and the column retention are the two sources of error propagated into the reported concentration. Steps taken in method development, such as selection of appropriate sorbent phases and limiting the sample volume to prevent breakthrough, can provide retention that is close enough to unity to render residual breakthrough inconsequential. Detection of considerable or unacceptable breakthrough can be accomplished by sequentially sampling the environmental water with sorbent media cartridges in series (Coes et al., 2014; Russell, 1975) or by monitoring the effluent from the sampling cartridge during method development. If the target contaminant is not detected on the second cartridge or on the effluent fluid, the limit of detection (LOD) of the analytical method provides a lower bound for the magnitude of the dimensionless cartridge retention (F_R), as shown in Eq. 4:

$$F_R = \frac{C_W - LOD}{C_W} \quad (4)$$

For active sampling methods that provide retention close to unity with good reproducibility, the sampling volume becomes the most significant source for error in the sampler's uptake process. Capture and direct measurement of the processed volume (V_W) of environmental water is impractical and frequently runs counter to advantages of *in situ* active sampling (sample size reduction, automated sample processing, large sampling volumes). Calibration of the pumps used for active sampling then becomes critical, and estimates of the error in pumping rate should be included in quality assurance processes. For active samplers, the error in sampling volume or rate is a function of a number of sources, including drift in the calibration of the pump, occlusion of the fluid train, or imprecise control of the sampling time.

Thus the ratio (F_V) of the volume of environmental water that actually passes through the sorbent bed (V_{Act}) to the theoretical or programmed volume (V_{Theo}) becomes an important contributor to the trueness and precision of active sampling systems (Equation 5).

$$F_V = \frac{V_{Act}}{V_{Theo}} = \frac{(R_S t)_{Act}}{(R_S t)_{Theo}} \quad (5)$$

For an active sampler, the dimensionless uptake coefficient (α) is the product of the dimensionless relative retention (F_R) and the dimensionless sampling volume ratio (F_V), both of which ideally approach unity with good precision (Equation 6).

$$\alpha_{active} = F_R F_V \quad (6)$$

3.2 Passive-Diffusion Samplers. Passive-diffusion samplers expose the sampling phase directly to the environment, often incorporating a housing and aperture that acts to limit natural advective flow of the sampled fluid to the locale and interface where mass transfer and analyte collection take place. Like the active-advection samplers described previously, passive-diffusion

197 samplers (chemical dosimeters) have been used for atmospheric sampling for some time (Fowler,
198 1982), with application to environmental waters coming more recently [e.g., Ceramic Dosimeter
199 (Martin et al., 2001), Chemcatcher (Kingston et al., 2000), POCIS (Alvarez et al., 2004),
200 Membrane Enclosed Sorptive Coating (Vrana et al., 2001), and Semipermeable Polymeric
201 Membrane Device (Huckins et al., 1990)].

202 Passive-diffusion samplers are designed with the assumption of linearity of mass transfer
203 between the environmental fluid and the sampling phase. While more nuanced models have been
204 developed and validated for mass transport into passive samplers (Alvarez et al., 2004; Huckins
205 et al., 1999; Johnson, 1991), a simple one-compartment kinetic model illustrates the fundamental
206 operation of passive-diffusion samplers (Vrana et al., 2005). In this model, the analyte
207 concentration in the sampling phase (C_S) increases as a function of the concentration of the
208 analyte in the environmental phases (C_W) and first-order sorption and desorption rate constants
209 (k_1 and k_2, Equation 7):

210 $$C_S(t) = C_W \frac{k_1}{k_2}(1 - e^{-k_2 t}) \quad (7)$$

211 When a clean passive sampler is introduced to the environment, mass transfer proceeds
212 overwhelmingly from the environment to the sampler, the concentration of the analyte in the
213 sampling phase increases linearly or (or pseudo-linearly), and Equation 7 reduces to Equation 8.

214 $$C_S(t) = C_W k_1 t \quad (8)$$

215 The period of time over which the instrument can be assumed to be operating with linear
216 accumulation is termed the '*kinetic regime*' (Figure 1) and is generally accepted for $t < t_{50}$, the
217 time at which the sampler reaches 50% of its equilibrium concentration (Huckins et al., 1999;
218 Vrana et al., 2006). While not strictly linear, the degree of non-linearity is not great enough to be
219 distinguished from other sources of error.

220 The model for the accumulation in Equation 8 can be rearranged to match that presented
221 in Equation 3, with M_S again representing the mass of analyte accumulated in the sampling phase
222 as a function of time (t), and R_S substituted for the product of the sorption rate constant (k_1) and
223 the volume of water that provides the same chemical activity as the sampling phase. In this form,
224 R_S can be conceptually described as the volumetric rate at which the passive sampler clears
225 analyte from the surrounding environmental fluid. Thus, the same mass uptake rate model and
226 nomenclature (R_S) can be used to describe both active and passive samplers, and is a critical
227 parameter for calibration of the both samplers (Fowler, 1982; Huckins et al., 1993; Huckins et
228 al., 1999; Seethapathy et al., 2008; Stuer-Lauridsen, 2005; Vrana et al., 2001), though it should
229 be noted that passive samplers typically sample the dissolved contaminant fraction, while active
230 samplers may sample two compartments, dissolved and particle bound (Coes, et al. 2014), and
231 that temperature can affect both the rate of diffusion and the extent of sorption of analytes to
232 colletion media.
233 While active samplers regulate R_S with a mechanical pump, and thus are governed by the
234 precision of the pump, determination of R_S for passive diffusion samplers is confounded by a
235 number of variables, including the temperature, local advective transport and the development of
236 a solute-depleted fluid layer around the sorbent, biofouling, capacity of the sorbent material, and
237 other factors, k_1 (Alvarez et al., 2004; Llorca et al., 2009; Seethapathy et al., 2008; Vrana et al.,
238 2005). In this case, R_S becomes a lumped parameter that accumulates error from many sources,
239 and concentration data derived from passive samplers is only as good as the estimate for R_S
240 derived from theoretical or empirical models. Thus for passive samplers, the uptake and retention
241 coefficient α is defined by F_V, the ratio of the sampling rate (R_{S_Act}) achieved by the sampler in
242 the field to the expected theoretical sampling rate (R_{S_Theo}) (Equations 5 and 9).

$$\alpha_{passive} = F_V = \frac{R_{S\_Act}}{R_{S\_Theo}} \quad (9)$$

The inclusion of performance reference compounds (PRCs; e.g., perdeuterated analogs for the analytes of interest) has been studied as a means by which to assess R_{S_Act} on a per-sample basis (Belles et al., 2014; Booij et al., 1998; Huckins et al., 2002). This method takes advantage of the approximately linear relationship between the uptake and offload of the two compounds, and accounts for the various factors (e.g., temperature and turbulence) that typically affect estimates of R_{S_Act}. By quantifying the mass of PRC remaining on the sampler after environmental exposure, the *in situ* offload or elimination rate constant (k_e) can be calculated, and used to correct R_S as shown in Equation 10.

$$R_{S\_corrected} = \left(\frac{R_{S\_Theo}}{k_{e\_Theo}}\right) k_{e\_Act} \quad (10)$$

In practice, R_{S_Theo} and k_{e_Theo} are determined in calibration studies and their ratio is a constant of proportionality between the uptake and offload rates (Belles et al., 2014). Alternatively, the ratio between the standard and *in situ* elimination rate constants may be described as an exposure adjustment factor, EAF (Huckins et al., 2002). The inclusion of PRCs improves the trueness of R_S, but requires additional calibration studies to determine the standard elimination rate constant. As a result, $R_{S\_corrected}$ accumulates error from the standard laboratory determination of R_{S_Theo} and k_{e_Theo}, as well as the *in situ* determination of the elimination rate constant k_{e_Act}, with one study estimating the cumulative RSD for this process at ±35% (Huckins et al., 2002). Additionally, when screening for a variety of compounds, it may not be feasible to include analogs for all of the compounds of interest; as such, the accurate determination of the constant of proportionality is critical and the most important source of error in R_S (Huckins et al., 2002; Vrana et al., 2006).

3.3 Effect of Sampler Design on Uptake Error. When α is reproducible with good precision, a constant of proportionality between C_S and C_W can be developed to calibrate the sampling system, compensating for systematic error and improving the trueness of the reported concentration. Much more problematic is the introduction of random error, which can be significant, as explored hereafter and documented in Table 1 and Table S1 of the Supplementary Material. A review of the literature was conducted and is presented in the following to provide some context for the range in magnitude of the uncertainties practitioner can expect to encounter when applying integrative sampling systems. Because retention (F_R) for active samplers can be largely controlled with judicious selection of column volumes, sampling rate, sampling volume, and column affinities, the sampling rate (R_s) can be used as a proxy for α, and the performance of active and passive samplers broadly compared. Field or bench observations of sampling rate which included uncertainty, expressed as Relative Standard Deviation (RSD), for eight devices were tabulated and converted as necessary and are available in Table S1 of the Supplementary Material.

The observed averages and ranges for the RSD associated with sampling rate are presented in Table 1. The sensitivity of the sampling rate of passive integrative methods to ambient conditions (mixing, temperature, etc.) and differences in the uptake kinetics between chemical species of interest can introduce considerable uncertainty in the sampling rate (average RSD of 12 to 42% for five passive devices). This may be contrasted with active samplers (2.2 and 7.0% for two devices), in which mechanical metering of the flow rate and total capture of the analyte mass provide greater precision for R_S, while reducing or rendering inconsequential any effects of ambient conditions. This suggests that active-advective samplers have the potential to reduce error in R_S, by applying high-precision mechanical pumps to regulate the delivery of the

sample stream to the sorbent, at the expense of some increase in cost and complexity. The introduction of fluid flow meters could further reduce this uncertainty (with the governing parameter than being the precision of the flow meter as opposed of the precision of the pump), while capture of the entire volume of processed fluid can eliminate it for all practical purposes. The latter option may be unattractive, however, as it greatly increases the size of the device.

4.0 ANALYTE RECOVERY

4.1 Determination of Recovery. The dimensionless coefficient of recovery (ρ) represents the fraction of the captured mass detected after extraction of the loaded sorbent material; it is a lumped parameter determined empirically for both active-advection and passive-diffusion samplers. For an active-advection sampler, relative recovery is defined as ratio between the mass of analyte extracted (M_{Ext}) from the sampling phase and the mass applied (M_{Load}), assuming that the retention was unity (Equation 11).

$$\rho_{active} = \frac{M_{Ext}}{M_{Load}} \quad (11)$$

In bench experiments, recovery for samplers operating by passive diffusion or active advection in a controlled volume of contaminated fluid can be established by performing a mass balance on the initial and final concentrations of the analytes in the fluid and the mass recovered from the sampler (Martin et al., 2003). Alternatively, exposed samplers can be spiked with a known mass of labeled surrogate standards, which, when extracted along with the analytes of interest, can provide a means to estimate recovery and to correct direct measurements of the analytes (Shaw and Mueller, 2009). Both methods are equally applicable to passive and active samplers.

A number of factors contribute to the recovery coefficient for any integrative method that relies on sequestration of the analyte of interest in a sorbent. A fraction of the mass collected by the sampling phase may be irreversibly bound, reducing the mass recoverable by elution. For example, with silica-based, siloxane-bonded sorbents, compounds with an anionic moiety may be retained through both sorption to the siloxane-bonded phase and ion-exchange with the silica substrate; elution with a non-polar solvent will fail to recover the ion-exchange fraction (Poole, 2003).

In general, losses of the target analyte are a function of the properties of the analyte and the chemical environment with which it interacts, and of the processing steps taken to recover and quantify it. The latter processes (e.g., solvent extraction or washing, solvent exchange or blowdown, thermal desorption, etc.), which are sources of systematic error, must be quantified and controlled through regular quality control efforts in the laboratory. Processes related to the chemical properties of the analyte and the environment (e.g., volatility, reactivity and susceptibility oxidation, photodegradation, hydrolysis, biodegradation, etc.) are a critical consideration when liquid aliquot samples of environmental fluids are taken, as these samples may exhibit considerable losses without preservation or observation of maximum holding times. Field extraction of samples (e.g., by *in situ* solid phase extraction) has been shown to be effective in reducing these losses by stabilizing a variety of organic analytes (Barceló et al., 1994; Green and Le Pape, 1987; Hennion, 1999; Liška, 2000; Senseman et al., 1995).

4.2 Effect of Sampler Design on Coefficient of Variance of Recovery. Recovery is a critical aspect of an environmental sampling method, and unlike uptake and retention, it is conceptually similar across the spectrum of sorbent-based integrative samplers. As a result, the sampling

method and instrument can be expected to have less of an effect on recovery than the underlying physical and chemical processes taking place (i.e., sorption, elution, degradation), and the random error introduced by recovery steps should thus be largely similar across methods.

A review of literature for field or bench observations of analyte recovery and recovery-associated RSD from active-advective and passive-diffusive samplers supports this proposition. Records of results obtained by eight devices were tabulated (Table S2 of the Supplementary Material) and a summary presented in Table 2. A survey of the results suggests that the practitioner can expect the coefficient of recovery, ρ, to exhibit average RSD values between 5 and 16%, irrespective of magnitude of the coefficient. This appears to be consistent across the range of devices and without respect to the uptake strategy (active or passive), for which two active samplers and four passive samplers are included. All of the devices surveyed sequester the analytes of interest through non-polar sorption or ion exchange, methods which have been developed on the bench for efficiency and reproducibility. Thus it may be concluded, particularly for the case of passive samplers, that greater gains in reproducibility (i.e., precision) may be gained by refining the uptake process rather than the recovery procedure.

5.0 LIMITATIONS AND FUTURE WORK

This work suggests that the literature and practice can benefit from the systematic description of the trueness and precision of the uptake and recovery processes independently, so that their individual contributions to the method trueness and precision can be understood. While a large body of literature has developed with respect to the design and application of integrative samplers, there is a paucity of studies that provide information beyond the method recovery. For

passive samplers, where calibration of R_S is a critical design factor, this information is more commonly reported, but for active samplers the trueness and precision of the pump are rarely broken out. As a result, while the results of this study suggest that active samplers have an advantage in managing error, a larger body of work is needed in order to confirm this relationship. For active samplers, in particular, an examination of the effect of pre-filtration of particulate matter on data quality may prove timely and useful. Additionally, while statistically robust numbers of sample replicates may be included in studies that establish method trueness and precision in literature, in practice field replicates may be limited. Future work to explore the effect of the number of field replicates on data quality for environmental sampling, including cost/benefit analysis, could be of significant interest to the practice.

The selection of sampling strategies for monitoring of environmental fluids will always be influenced in part by consideration of costs. Whereas a detailed analysis of cost data on different sampling strategies was beyond the scope of this paper, it is safe to say that a major advantage of passive samplers over active samplers is a relatively lower cost. This likely holds true even for low-capital cost active sampling equipment after repeated use, due to the added expense associated with maintenance and replacement of moving parts as well as the cost embedded in powering the device.

The typically much lower cost for a passive sampler may enable users to increase the number of replicates and to increase spatial coverage, which is an important dimension of environmental monitoring that can be mentioned here in passing only. Active samplers may provide multiple replicates via use of a multi-channel design but outfitting a single device with multiple intakes to increase spatial coverage is more challenging, yet technically feasible for special applications (Supowit et al., 2016).

Whereas this article mainly focused on data quality aspects linked to sampling strategy, it can make only a brief reference here to the important fact that passive and active samplers monitor distinct phases of environmental fluids. Diffusive processes leveraged in passive samplers enable the capture of freely dissolved contaminants only whereas active samplers capture freely-dissolved compounds as well as sorbed analytes, with a potential opportunity to distinguish among the latter between filterable, particulate associated and non-filterable, e.g., colloid-associated analyte mass.

The above aspects suggest that use of a combination of active and passive sampling devices simultaneously may potentially enhance the overall information garnered in a sampling campaign by seeking to optimize spatial coverage through use of passive samplers and by collecting potentially valuable information on the relative importance of sorption processes through the use of active sampling devices. Whereas comparisons of different samplers of similar design exist (Allan et al., 2009) and some studies targeted hundreds of analytes at a time (Moschet et al., 2005), there is a noted paucity of studies having used both passive and active advective sampling devices simultaneously; this represents both a current limitation and an area for promising research to be conducted in the future.

6.0 CONCLUSIONS

This work introduced a conceptual framework for comparing the precision and trueness of passive and active samplers by introducing two dimensionless lumped parameters, the coefficient of uptake (α) and the coefficient of analyte recovery (ρ) that approach unity in optimal conditions. Factors influencing the two are commonly investigated in the development

and validation of sampling systems. The mathematical framework provided here can be used to organize and conceptualize major sources of error in sampling applications. A compilation of literature values on error sources influencing data quality suggests that active and passive integrative sampling systems are subject to similar random error in analyte recovery, while active samplers provide greater precision with respect to uptake. The present framework can be used for both active and passive sampling strategies to quantitatively assess data quality parameters of existing tools and to inform the design of next-generation equipment. Assessments of data quality in this manner can provide an additional point of reference for sampler selection when weighed against cost and other programmatic requirements. This work demonstrates the utility provided by the inclusion of data on the precision of the individual processes of retention, sampling rate, and recovery, which facilitate the development and selection of appropriate technologies for unique sampling applications by end users of active and passive sampling technologies. Active and passive samplers provide similar but non-identical information, suggesting that judicious selection of sampling strategies and the possible use of approaches combining both techniques may yield a maximum amount of useful, high quality information.

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Table 1. Relative standard deviation (RSD) for standard sampling rate (R_S), uncorrected by performance reference compounds, as reported for seven integrative samplers.

Sampler	Range of RSD (average), %	n^a	Citation
Passive Samplers			
Chemcatcher	11 – 74 (31)	134	(Vrana et al. 2006)
	10 – 61 (26)	32	(Aguilar-Martinez et al., 2008)
CSS[b]	4 – 29 (15)	18	(Llorca et al., 2009)
MESCO[c]	4 – 49 (21)	44	(Vrana et al., 2001)
POCIS[d]	9 – 89 (42)	12	(Alvarez et al., 2004)
	2 – 36 (14)	21	(Belles et al., 2014)
SPMD[e]	1 – 33 (12)	37	(Huckins et al., 1999)
SPMD with PRCs[f]	35	estimated	(Huckins et al., 2002)
Active Samplers			
IS2[g]	0.7 – 3.5 (2.2)	8	(Roll 2015)
IS2B[h]	(6.8)	1	(Supowit 2015)

Notes: (a) *n* is the number of RSD values reported by each study, (b) Continuously Stirred Sorbent, (c) Membrane Enclosed Sorptive Coating, (d) Polar Organic Chemical Integrative Sampler (e) Semipermeable Polymeric Membrane Device, (f) Performance Reference Compound, (g) In Situ Sampler, and (h) In Situ Sampler for Bioavailability. The sampling rate R_S is calculated on a per-compound basis for passive samplers, often under multiple conditions (e.g., temperature, stirring) per compound, while for active samplers it is equal for all study compounds.

Table 2. Relative standard deviation (RSD) for analyte recovery as reported for eight integrative samplers.

Sampler	Range of RSD (average), %	n^a	Citation
Passive Samplers			
Ceramic Dosimeter	3.3 – 9.9 (7.2)	11	(Martin et al., 2003)
Chemcatcher	(10)	6	(Shaw et al., 2009)
POCIS[b]	1 – 28 (13)	9	(Alvarez et al., 2004)
	6 – 45 (16)	21	(Belles et al. 2014)
SPMD[c]	2 – 7 (5)	4	(Huckins et al., 1990)
Active Samplers			
Seastar	2.1 – 19 (7.8)	9	(Green et al., 1986)
Infiltrex	1.0 – 32 (10)	72	(Tran & Zeng, 1997)
IS2[d]	6	1	(Roll 2015)
IS2B[e]	9 – 24 (16)	5	(Supowit 2015)

Notes: (a) *n* is the number of RSD values reported by each study, (b) Polar Organic Chemical Integrative Sampler, (c) Semi-Permeable Membrane Device (d) In Situ Sampler, (e) In Situ Sampler for Bioavailability.

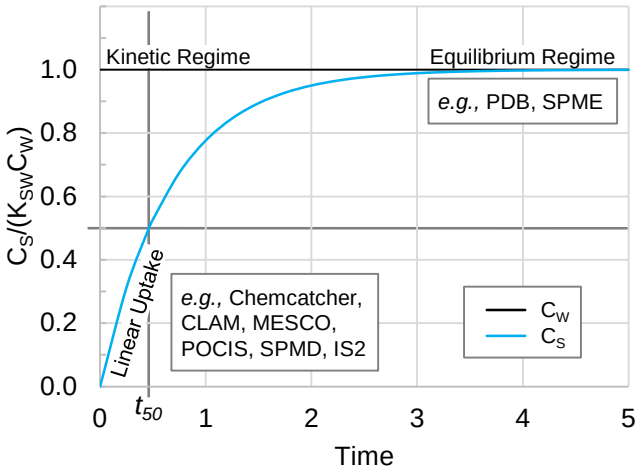

Figure 1. Accumulative samplers are classified according to the mass transfer regime (kinetic or equilibrium regimes) in which they operate (after Zabiegała et al., 2010). Integrative samplers [e.g., Chemcatcher, Continuous Low-Level Aquatic Monitoring (CLAM), Membrane-Enclosed Sorptive Coating (MESCO), Polar Organic Chemical Integrative Sampler (POCIS), Semipermeable Polymeric Membrane Device (SPMD) and *In Situ* Sampler (IS2)] are designed to operate in the kinetic regime, while equilibrium samplers [e.g., Polyethylene Diffusion Bag (PDB) and Solid Phase Microextraction (SPME)] operate in the equilibrium regime. C_S is the contaminant concentration in the sampling phase, C_W is the contaminant concentration in the environmental phase, and K_{SW} is the partitioning constant between the phases.

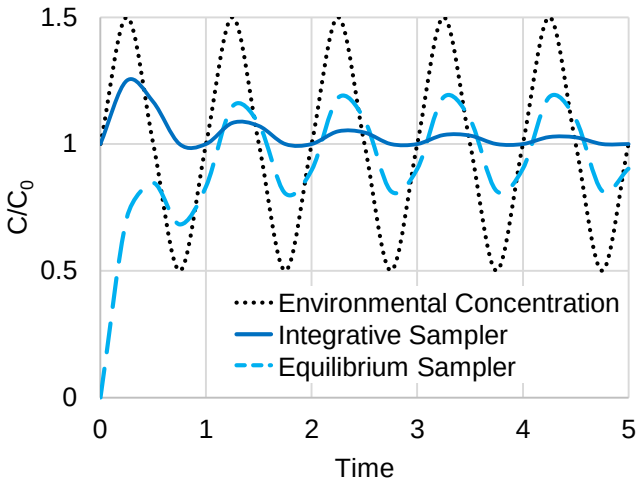

Figure 2. Hypothetical results for environmental contaminant concentration based on samples obtained from an equilibrium sampler with an equilibration time of one time period (arbitrary unit) and an integrative sampler operating in an environmental fluid where the contaminant concentration varies between 50 and 150% of the initial (and average) value. The equilibrium sampler provides a time-weighted average concentration, which attenuates and lags the environmental concentration. The integrative sampler provides an average concentration reflecting the entire duration of the sampling period.