Novel Integrative Methods for Sampling Environmental Contaminants

by

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ABSTRACT

Up to 25 percent of the operating budget for contaminated site restoration projects is spent on site characterization, including long-term monitoring of contaminant concentrations. The sensitivity, selectivity, and reproducibility of analytical methods have improved to the point where sampling techniques bear the primary responsibility for the accuracy and precision of the data. Most samples represent discrete concentrations in time and space; with sampling points frequently limited in both dimensions, sparse data sets are heavily extrapolated and the quality of data further limited.

Methods are presented for characterizing contaminants in water (groundwater and surface waters) and indoor air. These techniques are integrative, providing information averaged over time and/or space, as opposed to instantaneous point measurements. Contaminants are concentrated from the environment, making these methods applicable to trace contaminants. These methods have the potential to complement existing techniques, providing the practitioner with opportunities to reduce costs and improve the quality of the data used in decision making.

A conceptual model for integrative sampling of environmental waters is developed and a literature review establishes an advantage in precision for active samplers. A programmable sampler was employed to measure the concentration of chromate in a shallow aquifer exhibiting time-dependent contaminant concentrations, providing a unique data set and sustainability benefits. The analysis of heat exchanger condensate, a waste stream generated by air conditioning, is demonstrated in a non-intrusive method for indoor air quality assessment. In sum, these studies present new opportunities for effective, sustainable environmental characterization.

DEDICATION

For my mother, who has forgotten more than I’ll even know,

and my father, who taught me to keep my eyes on the ball.

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Chapter 1

INTRODUCTION AND RESEARCH OBJECTIVES

1.1 INTRODUCTION

Environmental characterization is performed for a variety of reasons: human safety in the home and workplace, detection and assessment of impacted natural systems, design of remedies, performance monitoring, and more. The United States Environmental Protection Agency (USEPA) estimates that between 2004 and 2033 up to a billion dollars will be spent annually on contaminated site characterization (USEPA, 2004), a number which is exclusive of the vast resources spent to understand workplace and home hazards, impact of human activities on natural systems, and other facets of the complex chemical environment in which we live. Further, in many cases the quality of the data generated by characterization activities will affect the downstream actions of the affected or responsible parties, who must consider the propagation of error when determining factors of safety for exposure or the design of remedies. Characterization, therefore, has a great deal of leverage on the overall cost and quality of downstream activities.

The most common methods for environmental characterization capture aliquots of the matrix of interest and return them to a laboratory for analysis. Because of the challenges involved in taking, preserving, and analyzing samples of environmental materials, the number of samples taken is typically sparse over both time (versus the time scale of temporal changes in concentration) and space (versus the scale of heterogeneity in the physical distribution of the contaminant). As a result, the reproducibility of the data suffers and extrapolation of sparse data is accepted in lieu of rich data sets. *Integrative* sampling methods—those that provide data which represents concentrations integrated over time and/or space—thus have the potential to complement the typical discrete data set by bridging transient events and spatial heterogeneity, reducing the likelihood of over- or under-representation of the contaminant concentration by discrete samples, and improving the reproducibility of sampling data in general.

1.2 RESEARCH OBJECTIVES

The research presented in this dissertation is intended to enrich the field of environmental characterization by presenting two new sampling methods and a discussion of the data quality and economic implications of using these integrative sampler designs. In doing so, this work contributes to the body of literature that enables the end users of sampling data—regulators, environmental scientists and engineers, ecotoxicologists and human health specialists—to select sampling methods that best support their missions. This work has, to date, generated two patent applications which are summarized in Appendix A.

Specifically, this dissertation provides answers to the following questions and tests the associated hypotheses.

1. How does the data quality provided by active-integrative samplers compare with that of passive-integrative samplers? Here, I hypothesize that active sampling provides greater precision than passive sampling.
2. Can an active, time-integrative sampler applying *in situ* SPE provide more utility than discrete sampling in a dynamic environment? I propose that an active

sampler can develop long time-base average data comparable to a composite of hundreds of liquid samples

3. How does *in situ* sampling with SPE impact economic and environmental sustainability? I hypothesize that scaled use of *in situ* SPE reduces waste generation, as well as the cost and carbon footprint of transportation of samples.
4. Can analysis of indoor air condensate provide a qualitative, spatially-integrated assessment of indoor air contamination? I suggest that indoor air condensate provides for detection of vapor-phase indoor air contaminants, differentiable between houses, and sensitive to introduction of new vapor sources.

1.3 DISSERTATION ORGANIZATION

The balance of this dissertation is organized into five chapters as follows:

- Chapter 2 addresses the first research question and presents a review of the factors which influence the accuracy and precision (collectively, the performance) of an integrative sampler, and provides a common set of parameters that can be used to evaluate and compare the performance of sampling systems.
- Chapter 3 addresses the second research question and presents the development and demonstration of a new apparatus for applying solid phase extraction *in situ* (the *in situ* sampler, or IS2) to generate time-integrated average samples of contaminants in environmental waters.
- Chapter 4 addresses the third research question and presents an evaluation of the costs of the IS2 and explores the implications of this system for economic and environmental sustainability.

- Chapter 5 addresses the fourth research question and presents a new method for spatially-integrated, qualitative screening of indoor air for contamination by examining the condensate generated in heat exchangers.
- Chapter 6 provides a summary of the conclusions derived from the above individual work efforts, and makes recommendations for future activities to address remaining knowledge gaps.

1.4 REFERENCES

USEPA. (2004). *Cleaning Up the Nation's Waste Sites: Markets and Technology Trends*. Washington, DC: United States Environmental Protection Agency.

Chapter 2

CRITICAL REVIEW OF FACTORS GOVERNING DATA QUALITY OF INTEGRATIVE SAMPLERS EMPLOYED IN ENVIRONMENTAL WATER MONITORING

Portions of this chapter have been prepared in an altered format for submission to *Water Research*.

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 (n = 51) 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 devices (averaging 5 – 16% relative standard deviation, RSD), active samplers effectively improve precision in sampling rate (analyte uptake), as determined for two active devices (2 – 7% average

RSD) and five passive devices (12 – 46% average RSD). In summary, major benefits of integrative sampling of environmental fluids include determination of time-integrated average concentrations, lowering of method detection limits, and notable improvements in measurement precision when using active samplers.

2.1 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 orders of magnitude 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, design 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 into the design assumptions based on those results (Barcelona et al., 1984; Liška, 2000; Maney, 2002; Pankow, 1986).

Perhaps equally important, the sampling method defines the context of the analytical data. 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 accuracy 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. Other reviews including that by Vrana et al. (2005) provide excellent overviews of the broader theory for this class of samplers, with Verreydt et al. (2010) also placing them in the context of mass flux measurement.

This work focuses on time-integrative samplers, specifically active-advective and passive-diffusive samplers, and explores the relationship between the design properties of a time-integrative sampling system and accuracy (closeness to true value) and precision (reproducibility) of the measured values it produces. A conceptual model is developed here to describe the operation of a variety of integrative samplers and the assumptions that contribute to their functionality. A discussion of the effects of these parameters on the accuracy and precision of the resulting data is presented.

2.2 THEORY AND CONCEPTUAL MODEL

2.2.1 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 2.1).

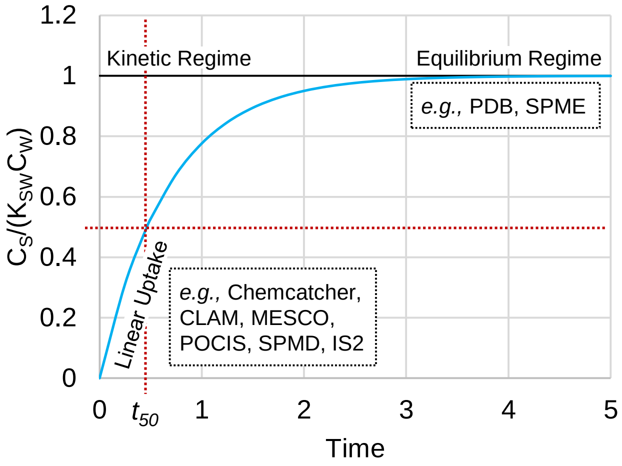

Figure 2.1. Accumulative samplers are classified according to the mass transfer regime (kinetic or equilibrium regimes) in which they operate (after Zabiegała et al., 2010). Integrative samplers [e.g., Chemcatcher, Continuous Low-Level Aquatic Monitoring (CLAM), Membrane-Enclosed Sorptive Coating (MESCO), 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.

Samplers that optimize measurement of the 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., passive diffusion bags and solid phase micro extraction) provide a time-weighted average that follows and attenuates the changes in the environmental concentration, and is biased towards the current concentration (Figure 2.2). 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).

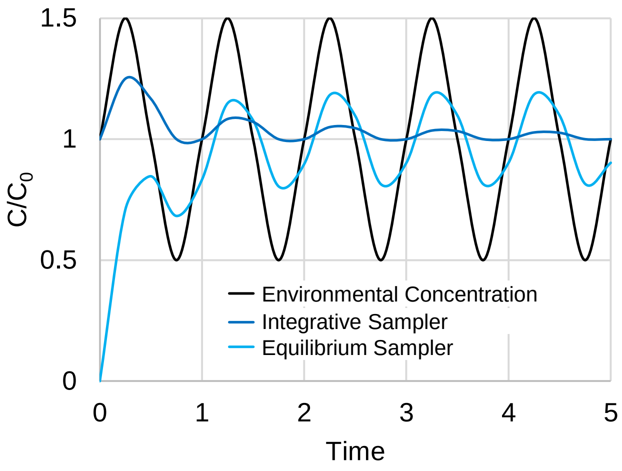

Figure 2.2. Modeled results for environmental contaminant concentration reported by integrative or equilibrium samplers. The model is based on samples obtained from an equilibrium sampler with an equilibration time of one time period (arbitrary unit) and an integrative sampler operating in an environmental 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.

2.2.2 Integrative Sampling. In contrast to equilibrium samplers, integrative samplers provide a time-integrated average concentration over the whole sampling period (Figure

2.2). 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 a long-term observation of the contaminant concentration is desired, as 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). This advantage is derived from the concentration of the analyte mass from a large volume of air or water, increasing 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).

2.2.3 Conceptual Model for Integrative Sampling. The time-integrated average concentration estimate obtained with an integrative sampler ($\overline{C_S}$) for a given analyte is proportional to the product of three parameters: its actual time-integrated average concentration in an environmental water ($\overline{C_w}$), 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 2.1):

$$\overline{C_S} = \overline{C_w}(\alpha)(\rho) \tag{2.1}$$

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).

2.3 ANALYTE UPTAKE AND RETENTION

2.3.1 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 mass (M_S) can be calculated as shown in Equation 2.2:

$$M_S = C_W V_W \tag{2.2}$$

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.

If the sampling is continuous rather than instantaneous, the analyte mass placed into contact with the sampler 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 2.2). Thus in Equation 2.3, the sample volume is described as the product of a volumetric sampling rate (R_S; [volume/time]) and time.

$$M_S(t) = \overline{C_W} R_S t \tag{2.3}$$

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 et al., 2015)].

With respect to uptake and retention, the sampling volume V_W 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 Equation 2.4:

$$F_R = \frac{C_W - LOD}{C_W} \tag{2.4}$$

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 measure contributor to the accuracy and precision of active sampling systems (Equation 2.5).

$$F_V = \frac{V_{Act}}{V_{Theo}} = \frac{(R_S t)_{Act}}{(R_S t)_{Theo}} \tag{2.5}$$

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 2.6).

$$\alpha_{active} = F_R F_V \tag{2.6}$$

72.3.2 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 samplers (chemical dosimeters) have been used for atmospheric sampling for some time (Fowler, 1982), with application to environmental waters coming more recently [e.g., Ceramic Dosimeter (Martin et al., 2001), Chemcatcher (Kingston et al., 2000), POCIS (Alvarez et al., 2004), Membrane Enclosed

Sorptive Coating (Vrana et al., 2001), and Semipermeable Polymeric Membrane Device (Huckins et al., 1990)].

Passive-diffusion samplers are designed with the critical assumption of linearity of mass transfer between the environmental fluid and the sampling phase. While more nuanced models have been developed and validated for mass transport into passive samplers (Alvarez et al., 2004; Huckins et al., 1999; Johnson, 1991), a simple one-compartment kinetic model illustrates the fundamental operation of samplers of this class (Vrana et al., 2005). In this model, the analyte concentration in the sampling phase (C_S) increases as a function of the concentration of the analyte in the environmental phases (C_W) and first-order sorption and desorption rate constants (k_1 and k_2, Equation 2.7):

$$C_S(t) = C_W \frac{k_1}{k_2}\left(1 - e^{-k_2 t}\right) \tag{2.7}$$

When a clean passive sampler is introduced to the environment, mass transfer proceeds overwhelmingly from the environment to the sampler, the concentration of the analyte in the sampling phase increases linearly or (or pseudo-linearly), and Equation 2.7 reduces to Equation 2.8.

$$C_S(t) = C_W k_1 t \tag{2.8}$$

The period of time over which the instrument can be assumed to be operating with linear accumulation is termed the '*kinetic regime*' (Figure 2.1) and is generally accepted for $t < t_{50}$, the time at which the sampler reaches 50% of its equilibrium concentration (Huckins et al., 1999; Vrana et al., 2006). While not strictly linear, the degree of non-linearity is not great enough to be distinguished from other sources of error.

The model for the accumulation in Equation 2.8 can be rearranged to match that presented in Equation 3, with M_S again representing the mass of analyte accumulated in the sampling phase as a function of time (t) and R_S the product of the sorption rate constant (k_1) and the volume of water that provides the same chemical activity as the sampling phase. In this form, R_S can be conceptually described as the volumetric rate at which the passive sampler clears analyte from the surrounding environmental fluid. Thus, the same mass uptake rate model and nomenclature (R_S) can be used to describe both active and passive samplers, and is a critical parameter for calibration of the both samplers (Fowler, 1982; Huckins et al., 1993; Huckins et al., 1999; Seethapathy et al., 2008; Stuer-Lauridsen, 2005; Vrana et al., 2001).

While active samplers regulate R_S with a mechanical pump, and thus are governed by the precision of the pump, determination of R_S for passive diffusion samplers is confounded by a number of variables, including the temperature, local advective transport and the development of a solute-depleted fluid layer around the sorbent, biofouling, capacity of the sorbent material, and other factors that can influence the uptake rate, k_1 (Alvarez et al., 2004; Llorca et al., 2009; Seethapathy et al., 2008; Vrana et al., 2005). In this case, R_S becomes a lumped parameter that accumulates error from many sources, and concentration data derived from passive samplers is only as good as the estimate for R_S derived from theoretical or empirical models. Thus for passive samplers, the uptake and retention coefficient α is defined by F_V, the ratio of the sampling rate ($R_{S\text{-}Act}$) achieved by the sampler in the field to the expected theoretical sampling rate ($R_{S\text{-}Theo}$) (Equations 2.5 and 2.9).

$$\alpha_{passive} = F_V = \frac{R_{S-Act}}{R_{S-Theo}} \tag{2.9}$$

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 $R_{S\text{-}Act}$ 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 $R_{S\text{-}Act}$. 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 2.10.

$$R_{S_{corrected}} = \left(\frac{R_{S\_standard}}{k_{e\_standard}}\right) k_{e\_in\_situ} \qquad (2.10)$$

Here $R_{S\_standard}$ and $k_{e\_standard}$ have been 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). This method improves the accuracy of R_S, but requires additional calibration studies to determine the standard elimination rate constant, and thus the constant of proportionality. As a result, the corrected R_S accumulates error from the standard laboratory determination of both rates, as well as the *in situ* determination of the emission rate constant, 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).

2.3.3 Effect of Sampler Design on Uptake Error. When α is reproducible with good precision, a model can be developed to calibrate the sampling system, compensating for systematic error and improving the accuracy of the reported concentration. Much more problematic is the introduction of random error, which can be significant. A brief 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 and 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 B.1 of Appendix B.

The observed averages and ranges for the RSD associated with sampling rate are presented in Table 2.1. 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 46% 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 and the volume of waste which it generates.

Table 2.1

Relative standard deviation (RSD) for standard sampling rate (Rs), 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 – 95 (46)	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 et al., 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.

2.4 ANALYTE RECOVERY

2.4.1 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 2.11).

$$\rho_{active} = \frac{M_{Ext}}{M_{Load}} \tag{2.11}$$

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).

2.4.2 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 brief 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 B.2 of Appendix B) and a summary presented in Table 2.2. A survey of the results suggests that the practitioner can expect RSD average values between 5 and 16% to apply to ρ, irrespective of the recovery fraction itself. 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.

Table 2.2

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 et al., 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.

2.5 CONCLUSIONS

Water sampling performed in support of the characterization, remediation, or long-term monitoring of environmental compartments of interest can provide information about the presence, fate, and transport of contaminants present. Because obtained data heavily influence downstream decisions on water uses and remediation expenditures, data users are advised to take into consideration the quality (i.e., accuracy and precision) of the information at hand. While one mission might be adequately served by data with order-of-magnitude error bars, use of the same data might waste significant resources by generating unnecessarily large engineering safety margins in the design of a remedy or put people’s health at risk from excessive, unwanted exposures. The choice and application of sampling technology must therefore be made with an appreciation for the sources of systemic and random error inherent to the situation.

The unprecedented degree of precision now provided by analytical techniques in the laboratory places increasing importance on the sampling method to define the overall data quality. As a result, the continuing development of approaches for characterizing environmental waters, including integrative samplers, has provided a spectrum of methods and instruments that improve the data quality and economy. Integrative samplers offer time-integrated averages and concentrate analytes of interest to furnish favorably low method detection limits, both of which can enrich the value of the data produced during sampling. The approach selected for integrative sampling has an impact on the accuracy and precision of the data. Though systemic error may be characterized and can be offset by calibration, random error is more likely to be a function of the fundamental design properties.

This work introduced a conceptual framework for comparing the precision and accuracy 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. Information contained in this review, can serve to inform the design of sampling equipment as well as the utility and practicality of including error information for retention, sampling rate, and recovery, thereby facilitating the development and selection of appropriate technologies for unique sampling applications by end users of active and passive sampling technologies.

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Chapter 3

APPARATUS AND METHOD FOR TIME-INTEGRATED, ACTIVE SAMPLING OF CONTAMINANTS IN ENVIRONMENTAL WATERS

Portions of this chapter have been prepared in an altered format for submission to *Science of the Total Environment* and published in *Final Report: Cost-Effective, Ultra Sensitive Groundwater Monitoring for Site Remediation and Management* (Halden & Roll 2015).

ABSTRACT

Annual U.S. expenditures of $2B for site characterization invite the development of new technologies to improve data quality while reducing costs and minimizing uncertainty in groundwater monitoring. This work presents a new instrument for time-integrated sampling of environmental fluids using *in situ* solid phase extraction (SPE). The *In Situ* Sampler (IS2) is an automated submersible device capable of extracting dissolved contaminants from water (100s - 1000s mL) over extended periods (hours to weeks), retaining the analytes, and rejecting the processed fluid. A field demonstration of the IS2 revealed 28-day average concentration of hexavalent chromium in a shallow aquifer affected by tidal stresses via sampling of groundwater as both liquid and sorbed composite samples, each obtained in triplicate. In situ SPE exhibited 75 ± 6% recovery and an 8-fold improvement in reporting limit. Relative to use of conventional methods (100%), beneficial characteristics of the device and method included minimal hazardous material generation (2%), transportation cost (10%), and associated carbon footprint

(2%). Compatibility of the IS2 with an array of commercial SPE resins and standard extraction methods provides opportunities for sampling of a broad spectrum of inorganic and organic contaminants to yield time-averaged concentration data in an economical and environmentally sustainable fashion.

3.1 INTRODUCTION

The accuracy and precision of environmental monitoring methods is dictated as much by the upstream steps of sample acquisition and handling as by the downstream procedures of the analytical methods used (Green & Le Pape, 1987; Zhang & Zhang, 2012). Sources of loss and uncertainty include all of the steps (e.g., bailing, pumping, and transfer between vessels) that accompany the removal of an aliquot of liquid from the environment, and its transfer in the laboratory (Bopp et al., 2005; Parker & Britt, 2012). Furthermore, in many environments the potential exists for temporal changes in concentration as a result of natural phenomena (e.g., tidal action and storm events) or interaction with the built environment (e.g., changes associated with stream discharge, groundwater pumping, injection, and infiltration recharge systems). Capturing these phenomena with time-discrete, liquid aliquot samples requires many samples to be taken over the period of the transient condition (e.g., a day for tidal cycles). Because of the expense involved, groundwater sampling is typically sparse with respect to both frequency (e.g., quarterly) and duration (grab samples vs. time-averaged composite sampling); thus, random timing of the sampling event may either miss or coincide with extrema in the local contaminant concentration. As a result, improper conclusions may be reached regarding long term trends in concentration, compliance or non-compliance with maximum concentration level (MCL) goals, and estimations of contaminant mass flux and associated human health risks (Alvarez et al., 2004; Coes et al., 2014; Shaw & Mueller, 2009; Verreydt et al., 2014; Woodrow et al., 1986).

Integrative sampling approaches are an attractive approach to these challenges. These samplers collect the contaminant of interest from a volume of environmental water at a predictable, linear uptake rate (R_S) (ASTM, 2014). This provides a time-integrated average concentration for the contaminants of interest over the entire sampling period, which mitigates the effects of temporal changes (Bopp et al., 2005; Shaw & Mueller, 2009; Woodrow et al., 1986). Collection of the contaminant is typically performed using a sorbent media that exhibits complete or nearly complete sequestration of the contaminant targeted for capture. As a result, integrative samplers can significantly concentrate the contaminant of interest and improve overall method reporting limits (Green & Le Pape, 1987; Pankow et al., 1984; Woodrow et al., 1986).

Most contemporary integrative sampling systems are ‘passive samplers,’ designed to accumulate contaminant molecules from an external environmental phase in a separate sampling phase, with the sampling rate determined by diffusion [e.g., semipermeable polymeric membrane devices or SPMDs (Huckins et al., 1990)]. These devices are able to continuously sample groundwater over periods of several weeks (Shaw & Mueller, 2009; Vrana et al., 2001), but their use in monitoring commingled contaminants is complicated by the fact that R_S can vary by orders of magnitude for different species (Vrana et al., 2001). Calibration of R_S for even a single species carries significant uncertainty due to the influence of temperature, advective transport outside of the sampler (mixing) and boundary layer development, fouling, depletion, and other factors

(Alvarez et al., 2004; Huckins et al., 1999; Seethapathy et al., 2008; Vrana et al., 2001). 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 by taking advantage of the approximately linear relationship between the uptake and offload of the two compounds, but necessitates determination *a priori* of the correlation coefficient between the two rates (Huckins et al., 2002; Vrana et al., 2006).

One solution to sampling rate calibration is to use a mechanical pump to meter water from the environment to the sorbent media such that the value of R_S and its uncertainty are governed by the pump, rather than diffusion and environmental advection phenomena that are out of control of the analyst. While this increases the complexity of the system, ‘active samplers’ of this paradigm have been in common use for air sampling for decades, processing fluid volumes of hundreds of milliliters to several liters over as long as a day (Brown & Purnell, 1979; Ras et al., 2009; Russell, 1975). Emerging from the same paradigm, water samplers capable of rapid, large-volume extractions of tens to hundreds of liters of water *in situ* have also been developed, but also are similarly limited to taking single samples over periods of hours to a few days (Coes et al., 2014; Green et al., 1986; Stephens & Müller, 2007; Tran & Zeng, 1997).

The goal of the present work was to develop an integrative *in situ* sampler (IS2) that couples the control and reproducibility of an active sampler with the long-term, time-integrated sampling capabilities of a passive sampler, and to evaluate the tool in a real-world, groundwater monitoring situation in which fluctuations of contaminant concentrations are expected over time, taking advantage of the sampler’s integrative sampling capabilities.

3.2 EXPERIMENTAL SECTION

3.2.1 Development of the In Situ Sampler (IS2). An automated, programmable, submersible solid-phase extraction system was designed and manufactured using a combination of commercial, off-the-shelf parts and custom fabrication. Custom parts and the complete system were modeled in SolidWorks design software (Dassault Systèmes, Waltham, MA). A new multi-channel syringe pump was developed to take fluid from the screened interval of a monitoring well at very low flow rates (0.01 – 0.1 mL/min) continuously or at programmed intervals, and pass it through commercial solid phase extraction (SPE) cartridges, generating at least three simultaneous replicate samples. A software interface was developed in the Python 3.4 language (Python Software Foundation) to provide an interface for programming the syringe pump. The sampler, packaged to enable its insertion into a standard 10-cm (4-inch) inner diameter groundwater monitoring well, was outfitted for autonomous operation for periods of 28 days. The materials from which the sampler was derived were selected to be compatible for handling of a variety of chemical contaminants, and to be easily cleaned between uses to prevent cross-contamination between deployment wells.

3.2.2 Demonstration Site Description. Field demonstration data was collected in a coastal freshwater lens on Coronado Island in San Diego Bay, CA (Figure 3.1). The groundwater well selected for device deployment is situated in a parking lot near the northern end of the island, in an area of the Naval Air Station North Island that historically experienced releases of hexavalent chromium [Cr(VI)] solutions from metal plating activities. The site is underlain by sands and sandy silts and is approximately 230 m (750 ft) from the edge of a wharf. The well selected for the present study, S1-MW-09, is a 10-cm inner diameter groundwater monitoring well screened from 2.7 to 5.8 m (9 to 19 ft) below ground surface (bgs); depth to water is approximately 1.2 m (4 ft). The well is located on the dilute fringe of a Cr(VI) plume, with sampling in July 2013 reporting a concentration of 0.25 mg/L Cr(VI).

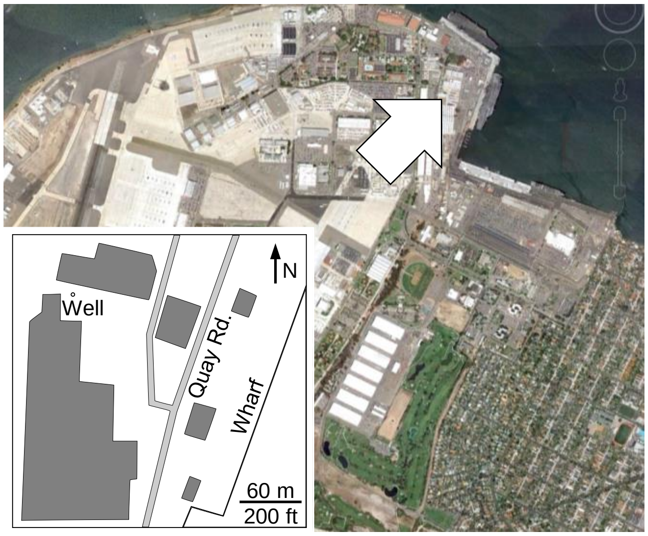

Figure 3.1. Sampling location at Naval Air Station North Island, Coronado, California.

3.2.3 Time-Discrete Sampling Series to Establish Temporal Concentration Patterns. An Isco 3700 autosampler (Teledyne Isco, Lincoln, NE) was programmed to take 12 samples of 1.0 L from the study well at 2-h intervals from a depth of 4.6 m (15 ft) bgs, which is 3.4 m or 11 ft below the water table. Sampling commenced at 1100 hours on October 4, 2014 and ended at 0900 hours on October 5, 2014. Samples were captured in open-topped high density polyethylene (HDPE) bottles (Nalgene, Thermo Fisher Scientific, Waltham, MA) and, upon sampling conclusion, were capped, and stored at 4°C until analysis for Cr(VI) by EPA Method 7196A using a Thermo Spectronic Genesys 20 spectrophotometer (Thermo Fisher Scientific, Waltham, MA). A Solinst Model 101 water level meter (Solinst Canada Ltd., Georgetown, ON) was used to record the depth to water (dtw) at four time points corresponding to predicted high and low tides. Tide height measurements for the nearby San Diego Bay (Station 9410170) were retrieved from the National Oceanic and Atmospheric Administration (NOAA) website (National Oceanic and Atmospheric Administration, 2015).

3.2.4 Time-integrated Sampling with the IS2. An IS2 device was prepared with three SPE cartridges; each cartridge comprised a 3 mL syringe barrel packed with 1.0 g of SIR-100-HP strong base anion exchange resin (ResinTech, West Berlin, NJ). Syringes and frits were obtained from Applied Separations (Allentown, PA). The sampler controller was programmed to deliver a volume of 1.25 mL of groundwater to each sampling channel every 2 h, at a rate of 0.5 mL/min, for a total of 105 mL/channel over seven days (168 h). The sampler collected three replicate sorbed samples, the liquid effluent from the sorbed samples, and three replicate liquid composite samples. Sampling commenced on November 8, 2014 and concluded on December 6, 2014. The sampler was retrieved after 7, 14, and 28 days and the liquid composite samples were collected. After 28 days, the SPE cartridges were collected and returned to the laboratory on ice, where they were stored at 4°C until elution. Cartridges were eluted twice with 50 mL of 10% w/w sodium chloride (JT Baker, Phillipsburg, NJ) solution at 0.5 mL/min. Liquid composite samples, cartridge eluate samples, and samples of the processed water captured *in situ* post-cartridge were divided into aliquots and delivered to a certified laboratory for quantification of total chromium by EPA Method 200.7. Additionally, a composite sample of crushed and homogenized SPE resin was delivered to the laboratory for acid digestion and quantification of total chromium (by EPA Methods 3050B and 6010B).

3.3 RESULTS AND DISCUSSION

In this design and validation field study, a complete system for large-volume, extended duration SPE was packaged in an autonomous, submersible instrument. The IS2 uses commercial, off-the-shelf SPE cartridges for sorbent media, metering water from the environment to the cartridges at low flow rates (e.g., 1 mL/min) continuously or at intervals (e.g., 1 mL at 1 mL/min at hourly intervals). By separating the contaminants of interest from the water *in situ*, the IS2 concentrates analyte mass over extended periods of time, thereby improving reporting limits and furnishing time-averaged concentration data, while simultaneously reducing the quantity of material required to be transported and disposed of.

To demonstrate the IS2 technology, a site was selected featuring potential shifts in analyte concentrations in groundwater over time. Before demonstration of the IS2, a series of time-discrete liquid samples was taken from a monitoring well over a 24-h period to provide baseline concentration data and to assess the degree of fluctuation of analyte concentrations over a diurnal cycle. The IS2 was subsequently deployed in the same well, to provide a 28-day time-integrated average of the contaminant concentration.

3.3.1 Embodiment of the IS2. The IS2 was sized for use in many existing conventional groundwater monitoring wells extant in the United States. The resultant device is an automated, programmable, submersible SPE system intended for use in standard 10-cm (4-inch) inner diameter monitoring wells (Figures 3.2 and 3.3).

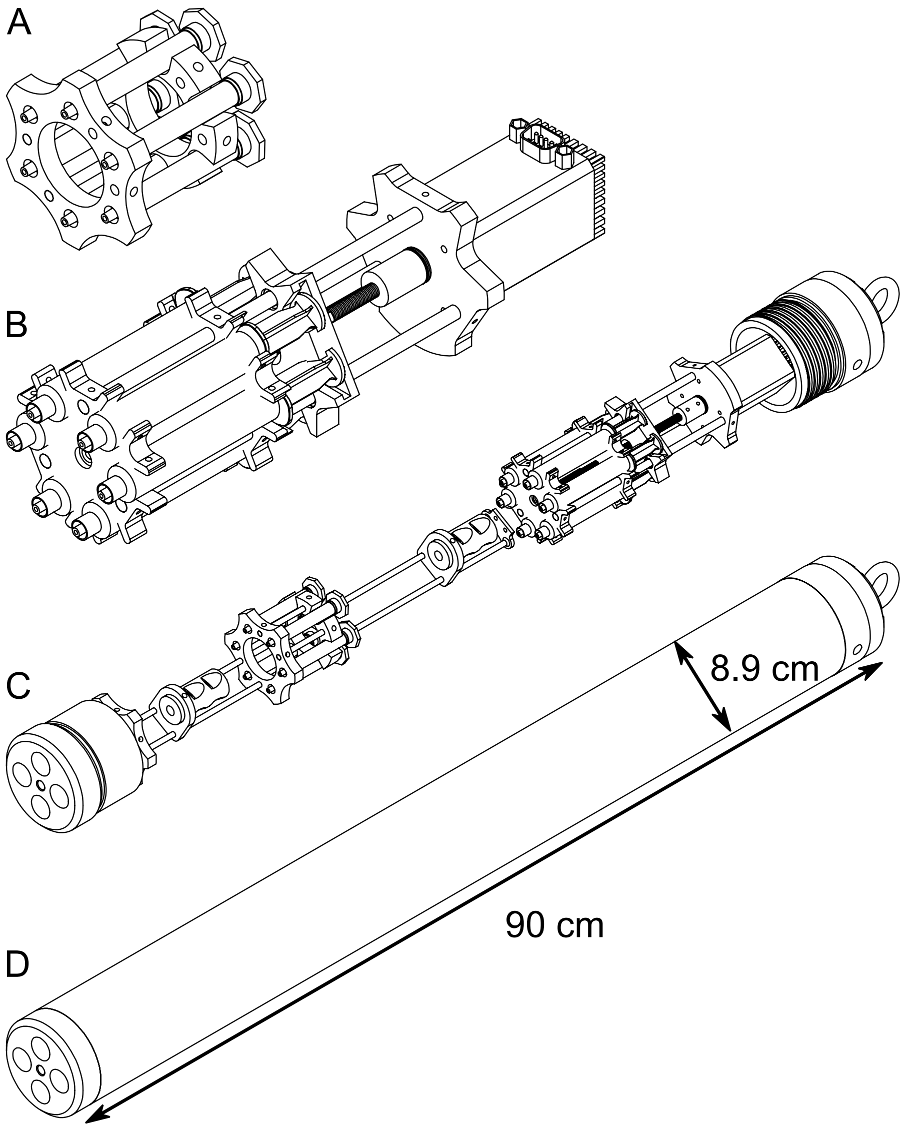

Figure 3.2. Design drawings of the embodiment of the IS2. The IS2 is an automated, submersible tool for solid phase extraction comprised of an autonomous pumping system driving fluid through an array of SPE cartridges. An assembly of up to six solid phase extraction cartridges (A) is provided for contaminant sequestration. A programmable syringe pump (B) is incorporated into an 8.9-cm (3.5-inch) diameter, 90-cm (36-inch) long submersible casing (C, D). The liquid capture system, used for validation purposes in the present study, is not shown.

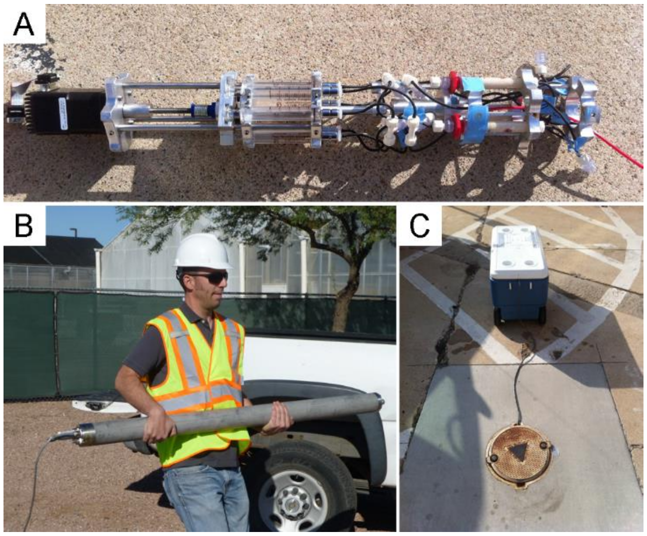

Figure 3.3. Embodiment of the IS2: (A) from left to right, the programmable syringe pump, valves, and assembly of SPE cartridge; (B) the sampler in an extended 1.4-m casing incorporating liquid capture bags; (C) the sampler installed and taking a 28-day time-integrated sample (Photographs by the author and Sara Murch).

A multi-channel, positive-displacement pump was designed and fabricated at Arizona State University. The pump utilizes a Silverpak 17C integrated motor, driver, and controller (Lin Engineering, Morgan Hill, CA), driving an assembly of up to six glass syringes capable of displacing 5 mL of liquid each (Cadence Inc., Staunton, VA). The pump program (volumetric sampling rate and duration) is communicated to the pump by a personal computer using a USB connection (Figures S1 and S2 of the Supporting Information). Power (24-V direct current) and communication to the pump are provided over a 9-channel Belden 9455 instrumentation cable (Belden, Indianapolis, IN). When submerged, the pump collects fluid from the external environment and passes it through an assembly of SPE cartridges. The fluid train within the pump is comprised of inert, fluoropolymer tubing (Cole Parmer, Vernon Hills, IL); an expanded material list is presented in Table C.1 of the Appendix C.

In a typical configuration of the tool, the pump, fluid train, and SPE cartridges are ho/used in an 8.9-cm (3.5-inch) outer diameter, 90-cm (36-inch) long stainless steel tube (Eagle Stainless, Warminster, PA). Under normal operation, the IS2 unit is designed to pass water through two SPE cartridges in series, the latter one serving as a breakthrough detection tool. Processed fluids are subsequently returned to the environment, with dilution and short-circuiting effects avoided through the judicious selection of very low-flow sampling rates, sequential intake and output followed by a waiting period, and large spatial separation of the intake and discharge tube. In the present demonstration an elongated demonstration unit enabled the onboard storage of processed liquids for post-deployment performance evaluation via chemical analysis and direct determination of fluid volumes processed. Effluent from the SPE cartridges was captured in an assembly of six 500-mL fluoropolymer bags (American Durafilm, Holliston, MA), increasing the device length to 1.4 m (54 inches).

The embodiment of the IS2 presented here was developed iteratively, with a series of earlier embodiments and experiments informing the final design. Preliminary studies that contributed to the development of the device and method are presented in Appendices D (bench studies for feasibility of *in situ* application of SPE) and E (field study of an earlier embodiment in a contaminated aquifer).

3.3.2 Baseline Field Data: Time-discrete Sampling Series. Depth to water (1.25 m or 4.1 ft) did not change appreciably in the study well over a 24-hr period; however, Cr(VI) concentrations exhibited distinctive trends (Figure 3.4). The concentration of Cr(VI) varied by 50.5% from a low of 0.99 mg/L to a high of 1.45 mg/L. The concentration thus followed the rise and fall of the tide heights for San Diego Bay, offset by a lag of approximately 2 hours. Although short-term concentration departures are not unexpected in tidal settings, they were observed and documented in this groundwater well and at this long-term remediation site for the first time.

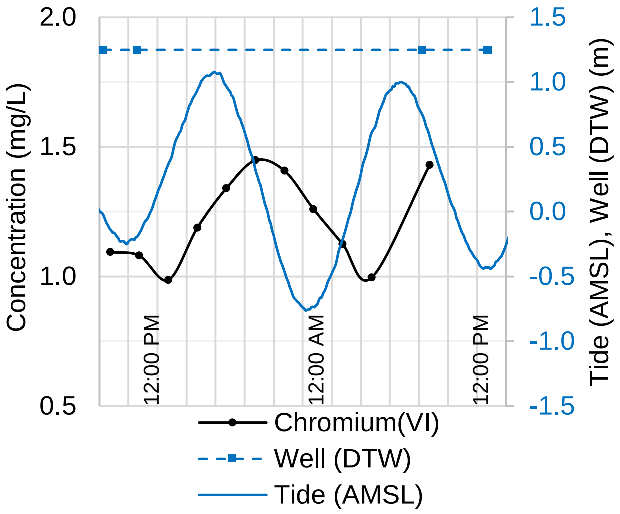

Figure 3.4. Results of 24-hr time discrete sampling at 2-hr intervals. Though the depth to water did not change appreciably, the concentration of Cr(VI) is observed to rise nearly 50% from its low value. The contaminant concentration and tide are observed to have the same period. One sample (7:00 AM, Day 2) was lost to an instrument malfunction.

The conditions that cause transient concentration changes in a contaminated aquifer may arise from any number of external stressors, including the tidal effects seen here, intermittent pumping, and recharge activities. With respect to tidal effects, a brief survey of 70 miles of San Diego County on the California coast using the GeoTracker application revealed nearly 1700 monitoring wells within 1 km of the shoreline (California Environmental Protection Agency, 2015), indicating that there may be tens to hundreds of thousands of coastal monitoring wells in the United States that exhibit similar time-dependent changes in solute concentration. However, similar to the situation at the deployment site, temporal patterns in groundwater concentration are rarely studied systematically and can remain unrecognized for years or decades.

3.3.3 Time-Integrated Data Generated with the IS2. Liquid composite samples taken at 7, 14, and 28 days from the bypass channels of the IS2 were analyzed for total chromium to assess the actual mass of contaminant that entered the sampler during deployment. The concentration was observed to decrease over the period of the study, demonstrating the utility of long time-integrated average sampling. A four-week average for the liquid samples (0.45 mg/L) and the four-week average from the sorbed samples (0.34 mg/L) were quantified (Figure 3.5). No chromium breakthrough was detected in samples of the post-cartridge effluent, confirming that the SPE resin beds selected for this study had ample capacity for the volume and flow rate selected. The recovery from the solid-phase cartridges charged in the field was 75% ± 6% of the liquid composite sample average, which agreed with recovery rates observed during method development. These values were comparable with literature reports for the collection of Cr(VI) by ion exchange SPE, where observed recoveries under various conditions were in the range of 82.1% ± 3.8% to 96.3% ± 2.4% (Wang et al., 1999) (3 mL at 30 mg/L in buffered solution), 92% ± 3% (Bowen 2014) (6.4 L at 1.4 µg/L in drinking water), and 76.8% ± 5.8% to 104% ± 5.2% (Inui et al., 2010) (500 mL at 1.0 µg/L in river, rain, spring, and tap waters).

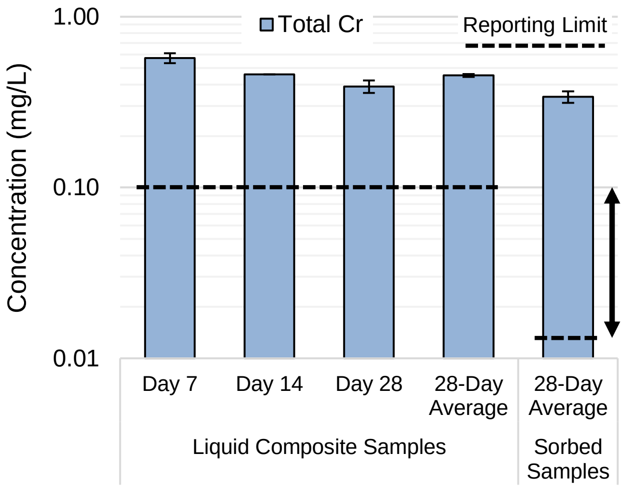

Figure 3.5. Concentration of chromium in 28-day time-integrated composite samples taken by the IS2. The sorbed samples demonstrated 75 ± 6% recovery; pre-concentration improved the reporting limit by a factor of 8.

3.3.4 Data Quality Implications. By concentrating the dissolved chromium from more than 400 mL of water into 50 mL of concentrated eluate, the IS2 effectively reduced the reporting limit for the quantification method in this study by a factor of 8 (Figure 5). This effect is even more significant if the elution step was removed, and only the resin was analyzed by acid digestion; a reporting limit of 2.0 mg-Cr per kg-resin translates into a reporting limit of 5 µg/L for a 400 mL volume processed. With stable analytes, and the capacity for larger resin bed volumes, this method could be extended to significantly larger sampling volumes and times, enabling lower reporting limits and facilitating an estimation of mass flux over many weeks. For example, concentration factors of two to three orders of magnitude are suggested by EPA Method 3535A (Solid-Phase Extraction) using commercial SPE disks and cartridges for phthalate esters, organochloride pesticides, polychlorinated biphenyls, nitroaromatics, nitramines, and explosives (USEPA, 1980).

3.3.4.1 Inter-Sample Variation. In the configuration shown in Figures 2 and 3, the IS2 device generates multiple sample replicates per sampling event, providing an estimate of the inter-sample error that is frequently missing from data obtained by discrete sampling. In the present study, the inter-sample relative standard deviation (RSD) was 7.8%, which is consistent with bench studies conducted using a pump of the same design; in the latter work, the solute concentration in the eluates of six pairs of simultaneously loaded and extracted SPE cartridges differed by an average of nearly 15% (Table S2 of the Supporting Information). Other teams investigating quantification of dissolved metals by SPE reported RSD values of 2.4 to 4.8% for chromium (Wang et al., 1999), and of 1.0 to 5.6% for manganese, iron, cobalt, nickel, copper, zinc, cadmium, and lead (Bulut et al., 2007); however, these studies were conducted using time-discrete samples, and were not subjected to the significant holding time of the present study samples.

3.3.4.2 Sampling Rate Variation. The precision of quantitative results for time-integrated sampling systems, whether passive or active, depends on to a large degree on the consistency of the sampling rate, R_S. For passive samplers, R_S is governed by a host of factors, including advective transport to and around the device and the diffusive transport of the contaminant to and into the sorbent material, the latter being a function of properties including the chemical species, ambient temperature, and length of the diffusive path. The RSD associated with R_S has been variously reported for several passive samplers for a diversity of target species and ambient conditions (Table 3.1). One study reported a range of RSD for the Membrane-Enclosed Sorptive Coating (MESCO) of 4 to 49% (Vrana et al., 2001), whereas another employing the Polar Organic Chemical Integrative Sampler (POCIS) showed values varying from 9 to 95% (Alvarez et al., 2004), and a third using the Semipermeable Polymeric Membrane Device (SPME) showed values of 1 to 33% (Huckins et al., 1999).

Table 3.1

Relative standard deviation (RSD) associated with sampling rate (R_S) for four integrative samplers.

Sampler	RSD range for R_S (%)	*n*	Citation
MESCO[a]	4 – 49	44	(Vrana et al., 2001)
POCIS[b]	9 – 95	12	(Alvarez et al., 2004)
SPMD[c]	1 – 33	37	(Huckins et al., 1999)
IS2	1 – 4	8	(This study)

Notes. (a) Membrane-Enclosed Sorptive Coating, (b) Polar Organic Chemical Integrative Sampler, (c) Semipermeable Polymeric Membrane Device.

For the IS2, the sampling rate is equivalent to the rate of fluid flow through each SPE cartridge. In the present field trial, the total average volume of water dispensed per channel (440 mL) was within 5% of the programmed volume (420 mL), with an RSD of 3.4% (Table C3 of the Supporting Information). This suggests that variance associated with R_S can be expected to be less than those associated with the extraction and quantification methods. Comparing the RSD for the sampling rate of the IS2 with that of several passive samplers, the results for the IS2 are particularly favorable, because the positive-displacement pumping system that governs R_S for the IS2 is independent of the influences of temperature, mixing, and analyte-specific chemistry that cause significant variance in R_S values of passive samplers

3.3.5 Limitations. Many of the limitations of the present sampling system are shared by contemporary alternatives. The materials present in the sampler fluid train are a particularly important design consideration, as they drive the compatibility of the instrument with the analytes to which it may be applied. As with any other sampling instrument, it is imperative that users consider material compatibility and utilize appropriate consumables. Further, while the present method is complicated by the requirement that two visits are made to the site (i.e., for instrument deployment and retrieval) versus a single visit for liquid aliquot sampling, the same requirement also applies to passive sampling systems.

3.3.6 Active Sampling Opportunities. The instrument and method presented here, collectively the IS2 technology, represent a new approach to monitoring environmental contaminants that combines the *in situ* concentration and time-averaged measurement typically achieved by passive sampling with the flexibility and reproducibility of a programmable autosampler. This instrument enables the development of large-volume extraction methods using commercial, off-the-shelf SPE media *in situ*, eliminating liquid sampling and sample handling. As a result, the instrument and method can improve reporting limits, prevent over- or under-estimation of contaminant flux by capturing transient conditions, and significantly reduce the mass of material transported from the contaminated site. These improvements in the sustainability of long-term monitoring programs may aid in attaining the objectives of recent governmental executive orders aimed to reduce energy and carbon emissions.

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Chapter 4

ECONOMIC AND ENVIRONMENTAL SUSTAINABILITY IMPLICATIONS FOR IN SITU SOLID PHASE EXTRACTION OF ENVIRONMENTAL WATER SAMPLES

Portions of this chapter have been prepared in an altered format for submission to *Science of the Total Environment*, or published in an altered format in *Final Report: Cost-Effective, Ultra Sensitive Groundwater Monitoring for Site Remediation and Management* (Halden & Roll, 2015).

4.1 INTRODUCTION

Reports by the United States Environmental Protection Agency (USEPA) and others have demonstrated that characterization and monitoring accounts for up to 25% of the $8 billion in annual expenditures for contaminated site remediation in the United States (Frost & Sullivan, 2005; USEPA, 2004). These reports indicate that the cost of sampling is a significant contributor to operating expenses. A review of the cost information for the groundwater remediation program at the United States Department of Energy (USDOE) Hanford Site agrees with the site characterization estimate, suggesting that performance monitoring (remediation system and groundwater monitoring) costs accounted for approximately 12% of the expenditures for that program in 2010, or more than 20% of the costs when capital investments are excluded (USDOE, 2011). Perhaps more significant, the resultant data inform the design, implementation, and ultimate expense of remediation for hazardous waste cleanup sites; given the leverage this information exerts on the overall management of a given remediation site, a significant impetus exists to effectively reduce costs and improve on the quality of monitoring data (ITRC, 2010; Verreydt, Bronders, & Van Keer, 2014; Zhang & Zhang, 2012). In addition, a series of governmental executive orders aimed to reduce energy and carbon emissions encourage the use of more efficient and sustainable technologies for environmental monitoring (Bush, 2007; Obama, 2009, 2015).

Figure 4.1. Characterization and monitoring as a proportion of annual site remediation expenses. These activities account for approximately 25% of yearly expenditures on contaminated site remediation, and inform the processes which determine the overall site costs (Photograph by the author).

The *in situ* sampler (IS2) described previously provides a complementary or alternative approach to contemporary methods and can improve economic and environmental sustainability of a sampling program. The IS2 sampler takes simultaneous replicate samples, passing environmental waters through commercial off-the-shelf solid phase extraction (SPE) cartridges. By collecting the analyte separately from the environmental phase, the liquid handling steps associated with discrete samples are eliminated and the overall volume of material (sample, packaging, and activity-derived waste) generated by the sampling event is reduced (Kot, Zabiegała, & Namieśnik, 2000; Namieśnik, Zabiegała, Kot-Wasik, Partyka, & Wasik, 2005; Pankow, Isabelle, Hewetson, & Cherry, 1984; Senseman, Lavy, & Mattice, 1995; Woodrow, Majewski, & Seiber, 1986). As a result, the party conducting sampling can reduce cost (e.g., transportation and hazardous waste management) and improve environmental sustainability (e.g., reduced carbon emissions and other waste).

In this chapter, the capital and operating costs for sampling with the IS2 are presented, as well as costs associated with other contemporary equipment filling similar roles. An estimate is presented for the carbon emissions reduction that can be achieved by applying *in situ* solid phase extraction, and the savings associated with sample transportation explored.

4.2 METHODS

4.2.1 Comparison of Capital Equipment Expense. Quotes were procured for three instruments that provide similar functionality to the IS2. The first was an environmental fluid autosampler (ISCO 6712; Teledyne Isco, Lincoln, NE), which is capable of generating composite liquid samples, time-sequential samples, or combinations thereof. The second was a data logger (Multi-Parameter Smart Sensor; INW, Kent, WA) capable of autonomously recording a variety of environmental water parameters (e.g. conductivity, temperature) over periods of several weeks. The third was a submersible bladder pump (Solinst 407; Solinst, Georgetown, ON) of the type commonly used to take discrete samples of groundwater under low-flow and low-purge conditions. Each of these instruments was used by the author or by technicians sampling groundwater at the IS2 demonstration sites, and so was known to be directly relevant to the present study.

An expense list was developed for the construction of an IS2 sampler of the type used in the present study. This was done by analyzing a number of quotes associated with different stages of the device development. These quotes, as well as those associated with the comparable instruments, are provided in Appendix F.

4.2.2 Estimation of Transportation Cost. Overnight shipping costs for 500 and 1500 km shipping distances were estimated from the 2015 rate tables for a major international shipping company (FedEx, 2015). Simulations for shipments assumed 1000 liquid aliquots or SPE samples, with each sample having a mass of 250 g for liquid aliquot samples or 4 g for exposed SPE cartridges. These were collected into four shipments of equal mass, conservatively rounded to 60 kg per shipment (240 kg total) for liquid samples and 1 kg per shipment (4 kg total) for SPE samples. As a conservative estimate, the mass of packaging and preservation material (e.g., ice) was not considered, but would be considerably greater for liquid samples.

4.2.3 Estimation of Carbon Impact. Carbon emissions were estimated using a method and parameters provided by the USEPA (USEPA, 2008), which is summarized here. The CO_2-equivalent emissions (E) are given in g-CO_2 per km traveled by Equation 4.1, which was adapted from the USEPA model.

$$E = 0.685 \times M[EF_{CO2} + 0.021(EF_{CH4}) + 0.310(EF_{N2O})] \qquad (4.1)$$

Here, M represents the sample mass transported in kilograms, and each EF represents the emission factor for the relevant greenhouse gas (CO_2 in kg per ton-mile, and CH_4, and N_2O in g per ton-mile). The relevant emission factors are provided in Table 4.1. The coefficients 0.685, 0.021, and 0.310 are unit conversion factors. The sample masses simulated for transport were the same as the total masses from the shipping cost estimate (240 kg for liquid samples and 4 kg for SPE samples).

Table 4.1

Emissions factors for commercial transport (USEPA, 2008).

Mode of Transportation	EF_{CO2} (kg-CO_2/ton-mile)	EF_{CH4} (g-CH_4/ton-mile)	EF_{N2O} (g-N_2O/ton-mile)
On-Road Truck	0.297	0.0035	0.0027
Aircraft	1.527	0.0417	0.0479

4.3 RESULTS AND DISCUSSION

4.3.1 Comparison of Capital Equipment Expense. A brief breakdown of the costs associated with constructing a research implementation of the IS2 sampler as embodied in the present work is provided in Table 4.2. The capital cost of an IS2 sampler is placed in context with other contemporary environmental characterization in Table 4.3.

Table 4.2

Cost of constructing the IS2 sampler (research model).

Cost Item	Expense (2015 US Dollars)
Programmable Syringe Pump	2200
Watertight Shell and End Caps	800
Internal Framework	400
Multichannel Electrical Cable (500 ft)	500
Other Hardware (Tubing, Connectors, etc.)	300
Total	*4200*

Table 4.3

Estimated capital costs for the IS2 and two contemporary groundwater sampling systems.

System	Estimated Cost (2015 US Dollars)	Source
IS2	4200	This Study
ISCO 6712 Autosampler[a]	4080	Western Environmental Equipment Company
Multi-Parameter Smart Sensor[b]	6200	INW
Solinst 407 Bladder Pump[c]	2900	EQUIPCO

Notes. (a) Components include Model 6712 Portable Sampler, 24-bottle configuration, Model 946 battery, and Model 963 battery charger; (b) Components include Product Code 2L31002 multi-parameter data logger with depth, conductivity, pH, oxidative-reductive potential, and dissolved oxygen sensors; (c) Components include Model 407 Bladder Pump, 12-V Integra Compressor, Model 464 Controller (125 psi), and SC2000 tubing reel (200 ft). Quotes and price sheets are provided in Appendix F.

While the present embodiment of the IS2 uses many commercial off-the-shelf components (motors, syringes, SPE cartridges, tubing and fasteners), the structure of the instrument and its watertight shell have to date been manufactured in small quantities by machinists. As a result, there is significant potential for cost reduction in serial production through parts substitution and economics of scale. Despite the inefficiency of prototype production, Table 4.3 indicates that the cost associated with the current embodiment of the IS2 is largely in line with other contemporary environmental characterization tools, and capital expense should not be a barrier to adoption of this technology.

4.3.2 Impact of Scaled Use on Economy. In the study presented in Chapter 3, a system was demonstrated for taking simultaneous replicate sorbed, time-integrated samples with individual masses of approximately 4 g, including the resin, syringe barrel, and small volume of encapsulated water. The processed volumes in that study represented more than 400 g of sampled water each (more than 1.2 kg total), giving an approximately 100-fold reduction in mass. Comparing these cartridges to a more conventional 250 mL (250 mg) liquid sample, sorbed samples still represent a significant mass reduction (Table 4.4). This advantage is compounded as the number of samples taken is scaled (Figure 4.2), which has significant implications for both the economic and environmental sustainability of a monitoring program.

Table 4.4

Impact of scaled use of active, in situ sampling with the IS2 versus liquid aliquot sampling on carbon footprint, hazardous material generation, and transportation costs.

	Discrete (250 ml, 250 g)	IS2 (250 ml, 4 g)	Difference (%)
Samples per kg	4	250	+ 6200
Overnight Shipping, 500 km, 1000 Samples (2015 US dollars[a])	530	53	- 90
Overnight Shipping, 1500 km, 1000 Samples (2015 US dollars[a])	1100	86	- 92
CO_2, 1000 Samples by Road (g CO_2/km)	50	1	- 98
CO_2, 1000 Samples by Air (g CO_2/km)	250	4	- 98
Hazardous Material, 1000 Samples (kg)	250	4	- 98

Notes. (a) Approximate 2015 prices using a global carrier, four shipments (one 1-kg package each) for IS2 and four shipments (two 30-kg packages each) for liquid samples.

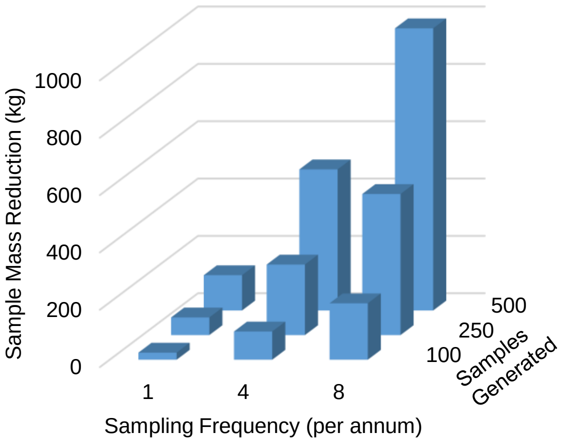

*Figure 4.2***.** Theoretical sample mass reduction based on a customary sample volume of 250 mL as a function of sampling frequency. By reducing the sample mass generated, the hazardous waste produced by the project is reduced proportionally, as well as the cost and environmental impact of transporting the samples.

By reducing the mass of samples, the expense of transporting them from the sampling site to the laboratory is reduced significantly. Using the shipping tables for an international shipping company as a benchmark, the cost to ship 1000 samples 500 km overnight was conservatively estimated to be reduced by 90%, and 92% for the same shipment to be transported 1500 km overnight (Table 4.4). The associated reduction in the mass and volume of packaging required to preserve the samples can be reasonably expected to further contribute to the economic advantage of sorbed samples.

4.3.3 Environmental Implications. With a sampling volume of 250 mL typical for metals analysis at commercial laboratories, performing the experiment Chapter 3 by sampling at two-hour intervals over 28 days would have required the transportation and disposition of as much as 84 kg of hazardous materials, or 252 kg if triplicate samples were made at each time-point. Setting aside the utility of time-integrated sampling, simple one-bottle (250 mL) quarterly sampling at this site would require the transportation and disposition of at least 1 kg of material per well annually; the same mass of IS2 samples could provide triplicate measurements in as many as eight wells. Scaling the monitoring program to 1000 samples, extracting water samples *in situ* provides a significant reduction (98%, Table 4.4) by reducing the volume and mass of hazardous waste which is generated by the sampling program. Applying the USEPA method for estimating carbon footprint, the same scaled monitoring program can reduce its greenhouse gas generation by an estimated 98%.

4.4 CONCLUSIONS

The IS2 sampler as currently embodied is a research instrument fabricated from a mixture of commercial off-the-shelf parts and parts designed in-house and fabricated by the ASU machine shop. These instruments work as intended, but are heavier, more complex, and more expensive than a commercial embodiment would be. Significant reductions in the cost and complexity of the device can be expected for an instrument that is brought to market. The expense of the research instrument supports the conclusion that a commercially available model would have capital costs comparable to contemporary environmental autosamplers and similar equipment. Thus the cost of equipment is unlikely to be a barrier to adoption of this method.

With respect to environmental sustainability, the primary benefit of the present method is to reduce the volume and mass of liquid hazardous waste removed from the contaminated site. As a result, the volume of hazardous waste disposed of decreases and the cost and carbon footprint of transportation are significantly reduced. The impact of this method on project sustainability provides a significant incentive for adoption that is aligned with current mandates for development and deployment of green technologies.

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Chapter 5

INDOOR AIR CONDENSATE AS A MONITORING POINT FOR ORGANIC CONTAMINANTS OF HUMAN HEALTH CONCERN

This chapter has been published in an altered format in the *Journal of Hazardous Materials* (Roll, Halden, & Pycke, 2015).

ABSTRACT

With the population of developed nations spending nearly 90% of their time indoors, indoor air quality (IAQ) is a critical indicator of human health risks from inhalation of airborne contaminants. We present a novel approach for qualitative monitoring of IAQ through the collection and analysis of indoor air condensate discharged from heat exchangers of heating, ventilation, and air conditioning (HVAC) systems. Condensate samples were collected from six suburban homes and one business in Maricopa County, Arizona, concentrated via solid-phase extraction, analyzed for 10 endocrine disrupting chemicals (EDCs) by liquid chromatography-tandem mass spectrometry (LC-MS/MS), and screened for additional organic compounds by gas chromatography-mass spectrometry (GC-MS). All 10 EDCs were detected in at least one of the sampled buildings. More than 100 additional compounds were detected by GC-MS, of which 40 were tentatively identified using spectral database searches. Twelve compounds listed as designated chemicals for biomonitoring by the California Environmental Contaminant Biomonitoring Program were detected. Microfiltration of condensate samples prior to extraction had no discernable effect on contaminant

concentration, suggesting that contaminants were freely dissolved or associated with inhalable, submicron particles. This study is the first to document the utility of HVAC condensate for the qualitative assessment of indoor air for pollutants.

5.1 INTRODUCTION

With Americans spending nearly 90% of their time indoors (Klepeis et al., 2001), the quality of indoor air is of significant interest in understanding human exposure to airborne contaminants and the health effects thereof (Billionnet, Gay, Kirchner, Leynaert, & Annesi-Maesano, 2011; Breysse et al., 2013). Indoor air is a dynamic matrix that carries a complex mixture of aerosols, larger suspended particles, and trace gases, all of which change over short- and long-term time scales in response to atmospheric conditions, human activities, material weathering, engineered environmental controls, regulatory changes, and other drivers (Dettmer & Engewald, 2003; LaRosa, Buckley, & Wallace, 2002). Volatile organic chemicals (VOCs) of both indoor and outdoor origin have been consistently demonstrated to be present in higher concentrations indoors than outdoors (Fuselli, De Felice, Morlino, & Turrio-Baldassarri, 2010).

Indoor air quality is a composite measure of these numerous determinants, particularly the type and condition of building materials, indoor/outdoor air exchange rates, activities of indoor space occupants, and the operation of engineered systems used for environmental control, *i.e.*, heating, ventilation, and air conditioning (HVAC) systems. The materials used to fabricate homes and consumer goods have changed significantly over recent generations, with the expected effect on the mixture of contaminants emitted into and detectable in indoor air (Seppaänen & Fisk, 2004).

Simultaneously, improvements in home energy efficiency have increased recirculation of indoor air and increasingly placed the burden of indoor-outdoor air exchange on the HVAC system (Lazzarin & Gasparella, 1998; Weschler, 2009), particularly in the developed world.

HVAC systems (which include refrigeration and heat recovery ventilation systems) are common features in new construction in developed countries, with air conditioning systems being installed in more than 90% of new construction in some regions of the United States (Weschler, 2009). The principles of operation for both refrigeration and heat recovery ventilation include a heat exchanger that removes heat from warm and humid indoor air, condensing atmospheric moisture into a stream of liquid waste, which is routed out of the building. While the condensate stream largely consists of water recovered from atmospheric moisture, human respiration, and household activities, it is also a product of interactions with a mixture of trace gases and airborne particulate matter. Fractions of this complex mixture of chemicals are expected to condense on the cooled heat exchanger or partition from the atmosphere into the liquid accumulating thereon, with the fluid stream acting as a trap for airborne contaminants. Hence, the collection of indoor air condensate allows for space and time integrated sampling of the indoor air, since the air handler of the ventilation system supplies large volumes of air from multiple rooms to the heat exchanger.

At present, indoor air chemistry is typically characterized by analysis of whole air samples, cryogenic air traps and sorptive samplers (Dettmer & Engewald, 2003; Jayanty, 1989; Ras, Borrull, & Marcé, 2009; Wang & Austin, 2006). These approaches enable detection of VOCs, semivolatile organic compounds (SVOCs), and less-volatile organic chemicals typically associated with particulate matter down to parts-per-trillion ($\text{ppt}_{w/v}$) concentrations. Such samples can be obtained either discretely in time, or over extended durations to facilitate time-integrated air quality assessments. These methods provide information that is spatially discrete within a building, and require access to the indoor environments under investigation. Analysis of dust and particulate matter (Blanchard et al., 2014; Dodson et al., 2012; Geens, Roosens, Neels, & Covaci, 2009; Huber, Haug, & Schlabach, 2011; Shoeib, Harner, Webster, Sverko, & Cheng, 2012) provides another avenue for investigating human exposure to inhalable environmental contaminants, particularly the less volatile species. These standard methods typically require access to the sampled building and are collected in discrete locations inside the building; hence, there is an opportunity to investigate the applicability of new methods that are non-intrusive and allow for time and space integrated sampling.

This work investigated a new approach to monitoring indoor air quality through the collection and analysis of condensate produced by the heat exchangers of HVAC systems. This approach enables the indirect, qualitative monitoring of air quality from buildings and living spaces at scales both large (via catchments for condensate from entire floors or buildings) and small (condensate from single family homes or apartments) without requiring access to the interior of the building. The analysis of HVAC condensate samples by liquid and gas chromatography mass spectrometry and tandem mass spectrometry demonstrated the feasibility of detecting indoor air contaminants across a generous spectrum of hydrophobicities and volatilities.

5.2 MATERIALS AND METHODS

5.2.1 Chemical Standards and Materials. A summary of commercially-sourced standards and associated vendors used for this study is provided in Table G.1 of Appendix G. Oxidized metabolites of TCC and 3,3’,4,4’-tetrachlorocarbanilide were provided by Dr. Bruce Hammock (University of California, Davis) and were manufactured as previously described (Schebb et al., 2011) and verified for purity by liquid chromatography-tandem mass spectrometry (LC-MS/MS; API 4000, AB SCIEX, Framingham, MA) upon arrival in the laboratory. Liquid chromatography-mass spectrometry (LC-MS)-grade methanol, water, and acetic acid were obtained from Fluka and LC-MS-grade acetone was obtained from Sigma-Aldrich (Sigma-Aldrich, St. Louis, MO). Individual stock solutions of the native and isotope-labeled compounds were prepared in methanol. All stock solutions were stored in glass vials with polytetrafluoroethylene septa at -20ºC. All glass bottles were washed with detergent, rinsed three times with 18 MΩ·cm (ultrapure) water, and then baked (decontaminated) at 500ºC for 5 hours.

5.2.2 Sampling Sites and Participants. Samples were collected from six residences and one business in Maricopa County, Arizona during August and September of 2013. Participants were recruited from the staff and acquaintances of the author. All seven buildings have central air conditioning with condensate drains installed in easily accessed locations; a schematic representation of the air conditioning systems is presented in Figure G.1 of Appendix G. These buildings were constructed between 1960 and 2012, and were distributed over an area of more than 1000 km^2 (Figure 3.1). Participants were provided instructions for sampling and sample handling. Participants were also provided with new, unused dust filters to install in their air handlers, to ensure proper air flow through the heat exchanger, and to reduce any effect of accumulated particulate contamination on the condensate contaminant mix. However, the installation of clean filters was not mandatory or recorded.

Condensate samples were collected to provide information about the unique chemistry of individual buildings (7 locations, Figure 3.1), changes in the mixture of indoor air contaminants detected over the course of several days (typically three sampling dates per location), and the effects of occupancies and human activities in the home on the chemical composition of collected condensate (one location per parameter). De-identified information on approximate location and specific processing steps and analyses is provided in the Table G.2 of Appendix G.

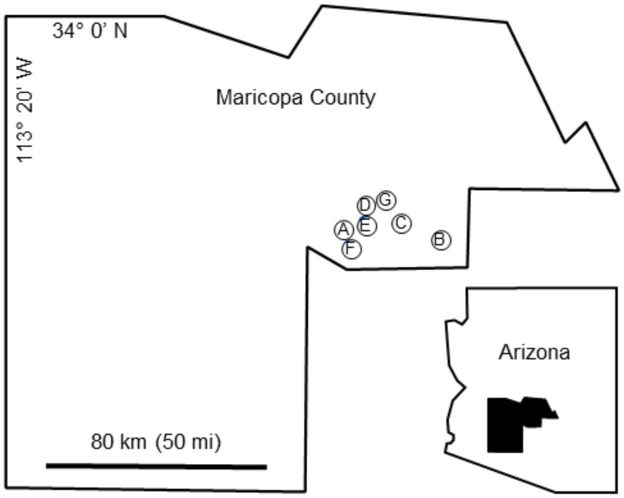

Figure 5.1. Approximate locations of condensate sample collection sites in Maricopa County, Arizona.

The research and the survey were approved by the Arizona State University Office of Knowledge Enterprise Development Institutional Review Board (IRB) and are considered to be exempt pursuant to Federal regulations, 45 CFR 46.101(b)(2). All participants provided signed informed consent forms informing them of the aims of the study and their rights according to IRB guidelines. All participants were provided with the option to be informed of the results from their samples accompanied by supporting information relating to their origin and significance for environmental health.

5.2.3 Sampling Procedure. Decontaminated 1.0-gallon (3.8-liter) glass bottles were placed beneath outdoor HVAC condensate drain spouts such that the condensate dripped directly into the bottle with no physical contact between the spout and the bottle. The volume of condensate recovered in the sampling period varied from 600 to 3800 mL. The production of HVAC condensate was greater on days with higher atmospheric humidity, but did not explore this relationship quantitatively due to the number of variables (e.g., HVAC operation and capacity, time and duration of sampling).

The bottle, and the interface between the opening of the bottle and the spout were covered with decontaminated (muffle furnace-baked) aluminum foil to protect the sample from sunlight, mitigate sample evaporation, prevent sample contamination due to atmospheric deposition of particulates, and to exclude natural outdoor condensation (e.g., rain and dew) from the sample. If rain was documented during the sampling period, the sample was discarded.

The samples from homes were typically collected overnight to maximize the number of inhabitants and minimize indoor/outdoor air exchanges through doors and windows; the sample from a business was collected during peak operating hours. Upon cessation of sampling, the bottle was capped, immediately refrigerated with ice packs and shipped to the laboratory for storage at 4ºC, and subsequent processing (*i.e.,* aliquoting, weighing, filtering, and extraction) within 24 hours.

A field blank study was conducted at two homes. Field blanks consisting of 1.0-liter glass bottles of ultrapure water were exposed to the indoor and outdoor atmosphere for 12 hours via brass swan-neck tubes, permitting interaction of the bottle headspace with the atmosphere while mitigating the intrusion of suspended aerosols and particulates. At each home, one field blank was located adjacent to the exterior HVAC condensate spout and another placed near the air handler intake within the building. Trip blanks of identical volume accompanied the field blanks but were not exposed to the atmosphere at the sampling sites.

Within one day of sampling, all samples were homogenized by rotary shaking and split in two equal-volume subsamples based on gravimetric analysis. One volume was extracted as collected ("unfiltered"), and the other ("filtered") represented processed condensate, filtered using a decontaminated vacuum filtration assembly (Sigma-Aldrich) with 47 mm GF/F 0.6 - 0.8 μm, borosilicate glass fiber filters (Whatman). Filters were replaced at intervals of approximately 250 mL of concentrate to ensure rapid flow of all samples and to minimize losses of volatile contaminants during vacuum filtration. After filtration, both filtered and unfiltered condensate subsamples were transferred to decontaminated glass receptacles and immediately extracted.

5.2.4 Solid-Phase Extraction. All samples were extracted using an automated offline solid-phase extraction (SPE) apparatus (Dionex Autotrace 280, Thermo Fisher Scientific Inc., Sunnyvale, CA) using Strata C18-E SPE cartridges (Phenomenex, Torrance, CA) with 500 mg sorbent. Aliquots of up to 1000 mL of condensate were automatically loaded onto the cartridge, which was then eluted with 5 mL of MS-grade methanol.

5.2.5 Analysis by LC-MS/MS. Sixteen samples from seven buildings were analyzed on a liquid chromatograph (LC; Prominence, Shimadzu Corp., Kyoto, Japan) with autosampler coupled to a tandem mass spectrometer (MS/MS) with electrospray ionization (API 4000, AB SCIEX, Framingham, MA). The analytes of interest were separated on a 4.6 × 150-mm C_8 column (X-Bridge, Waters, Milford, MA) with 3.5-µm particle size preceded by an equivalent guard column. The MS/MS was programmed to perform multiple reaction monitoring of a suite of ten anthropogenic compounds relevant to human biomonitoring studies (Butt & Stapleton, 2013; Buttke, Sircar, & Martin, 2012; Darbre & Harvey, 2008; Tang, Amin Usmani, Hodgson, & Rose, 2004; Tarnow, Tralau, Hunecke, & Luch, 2013), a manufacturing impurity and two human metabolites associated with one of the compounds, four carbon-13 labeled surrogates, and a laboratory control compound. The control compound, 4-methylumbelliferone (MUF), had been used extensively in this laboratory as a component of other LC-MS/MS studies, and would provide an indication of cross-contamination from preparatory surfaces and instruments. The instrument parameters for the LC-MS/MS method and tables of the compounds and their primary and secondary ions (Table G.3) and of the limits of detection and quantification (Table G.4) are provided in Appendix G.

5.2.6 Analysis by GC-MS. The same sixteen samples, and an additional two that were prepared subsequent to LC-MS/MS analysis, were analyzed on a gas chromatograph (GC; Model 7890, Agilent Technologies, Santa Clara, CA) equipped with an autosampler (MPS, GERSTEL GmbH & Co. KG, Mülheim an der Ruhr, Germany) coupled to a tandem mass spectrometer (MS/MS; Model 7000, Agilent Technologies, Santa Clara, CA). A DB-5MS column (30-m long x 0.250-mm inner diameter x 25-µm film thickness;

Agilent Technologies, Santa Clara, CA) was used with helium carrier gas. The MS was operated in scan mode over an *m/z* range of 50 to 300 with a dwell time of 500 ms. The National Institutes of Standards and Technology (NIST) Mass Spectral Search Program (Version 2.0f) with the NIST/EPA/NIH Mass Spectral Library (NIST 08) was used to identify the result, and descriptors of the most likely candidate compound (including percent match, CAS number, and retention time) were recorded as a database entry. The instrument parameters for the GC-MS method are provided in Table G.5 of Appendix G.

5.3 RESULTS AND DISCUSSION

5.3.1 Quality Control. Trip blanks and indoor and outdoor field blanks were provided for two of the locations sampled during the study, and showed no contamination during LC-MS/MS or GC-MS analysis. Extractions of unadulterated ultrapure water were performed with each batch of samples. None of these reagent blank samples (*i.e.*, procedural blanks) showed contamination during LC-MS/MS or GC-MS analysis (Figure 3.2), and the signal/noise ratios never exceeded 3

for the 16 specific mass transitions included in the LC-MS/MS program. The laboratory contamination control compound MUF was not detected in any samples analyzed by the LC-MS/MS, indicating that contamination from laboratory instruments or surfaces was unlikely.

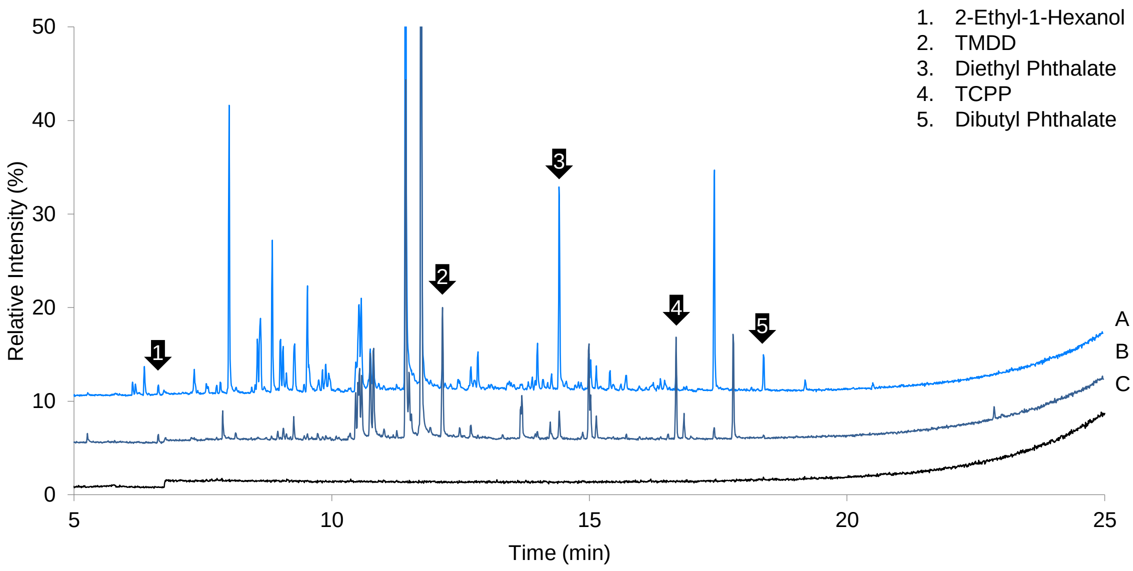

Figure 5.2. Gas chromatograms representing samples derived from (A) House A, (B) House B, and (C) a reagent blank. Traces from the two houses (of seven structures studied) illustrate the shared and the unique chemistry of the HVAC condensate produced. Five contaminant compounds which have been confirmed with authentic standards are indicated. The relative intensity has been scaled to half of the most abundant peak to show finer detail, and the chromatograms for Houses A and B have been offset by +10 and +5%, respectively for clarity.

5.3.2 Targeted Survey of Endocrine Disrupting Compounds. Analysis by LC-MS/MS demonstrated the presence of all ten targeted endocrine disrupting compounds (EDCs) in at least one of the 16 HVAC condensate samples (Table 3.1). The insecticide fipronil and antimicrobial triclosan (TCS) were detected in all samples (100%). Five parabens (methyl-, ethyl-, propyl-, butyl-, and benzyl-) commonly used as preservatives in personal care and food products were detected in 14 to 16 samples (88% to 100%), with propylparaben and butylparaben being ubiquitous (100%). Triclocarban (TCC), which is a compound commonly used in antimicrobial soaps, and its tetrachlorinated manufacturing impurity 3'-Cl-TCC were detected (and co-occurred) in half (8 of 16, 50%) of the samples analyzed. The brominated flame retardant tetrabromobisphenol-A (TBBPA) was detected in nearly half (7 of 16, or 44%) of the samples, whereas its nonbrominated congener, bisphenol-A (BPA), which is a common component of polycarbonate plastics, was detected in only two samples (13%).

Table 5.1

Suite of compounds targeted for detection by LC-MS/MS in submicron-filtered HVAC condensate, sorted by molecular weight.

Compound	Source	MW[a]	BP (°C)[b]	log K_{OW}[c]	No. Detected (Percentage)
Paraben, methyl-	Preservative	152	266	1.9	14 (88%)
Paraben, ethyl-	Preservative	166	297	2.4	15 (94%)
Paraben, propyl-	Preservative	193	329	2.8	16 (100%)
Paraben, butyl-	Preservative	194	309	3.5	16 (100%)
BPA	Plastic monomer	228	401	3.4	2 (13%)
Paraben, benzyl-	Preservative	228	390	3.6	15 (94%)
TCS	Antimicrobial	290	345	5.2	16 (100 %)
TCC	Antimicrobial	316	344	5.7	13 (81%)
Fipronil	Insecticide	437	510	4.8	16 (100%)
TBBPA	Flame retardant	544	418	7.3	7 (44%)

[a]Molecular Weight, [b]Boiling Point at 1.0 atm predicted by ACD/Labs, [c]Octanol-Water Partitioning Coefficient predicted by ACD/Labs. BPA is bisphenol A, TCS is triclosan, TCC is triclocarban, and TBBPA is tetrabromobisphenol A.

Two additional human metabolites of TCC, 2'-hydroxytriclocarban (2'-OH-TCC) and 3'-hydroxytriclocarban (3'-OH-TCC) were screened for but never detected in condensate extracts (IDLs of 9 and 10 ng/L, respectively). Lack of detection of these human metabolites of the antimicrobials was expected, as these compounds are excreted in the urine and stool, whereas the TCC detected in the condensate samples would be expected to be a product of the storage and topical application of TCC-containing products.

5.3.3 Non-Targeted Survey of Organic Contaminants. Eighteen samples were analyzed by GC-MS in full scan mode (*m/z* 50-300). Seventeen samples (16 previously analyzed by LC-MS/MS and one subsequently prepared) were used for a non-targeted survey of organic contaminants; the eighteenth was prepared specifically to investigate the effect of the introduction of a new household chemical (Section 3.3.4), and was excluded from the non-targeted survey. The survey samples ($n = 17$) yielded an average of 33 chromatographic peaks at a total of 112 unique retention times. Approximately 85% of these peaks were tentatively identified by their corresponding mass spectra. A subset of samples was analyzed in scan mode over an *m/z* range of 50-600, but as it did not yield additional peaks, the more sensitive *m/z* 50-300 data was used for all subsequent analysis. A robust subset of the data was selected by retaining components that (i) were detected at unique retention times, (ii) occurred in multiple samples, and (iii) corresponded to compounds for which standards were commercially available. A total of 40 unique, tentatively identified compounds remained (Table G.5 of Appendix G). To evaluate the quality of the tentative identifications, a randomized analysis of 25% of these signal-producing entities was performed by comparing their retention times and mass spectra to those of commercial, authentic standards. Among the 10 randomly selected compounds detected in condensate, the identity of nine (90%) was confirmed unambiguously using this approach (Table 3.2). Positively identified compounds included common fragrances, solvents, and the chlorinated organophosphate flame retardant TCPP.

Table 5.2

Anthropogenic compounds detected and confirmed by GC-MS in HVAC condensate, sorted by molecular weight.

Compound	Source	MW[a]	BP (°C)[b]	log K_{OW}[c]	No. Detected (Percentage)
Propylene glycol butyl ether	Solvent (Dowanol)	132	171	1.1	9 (50%)
2-Ethyl-1-hexanol	Solvent	130	185	2.8	12 (67%)
p,α,α-Trimethyl-benzyl alcohol	Fragrance (Cherry)	150	205	2.2	4 (22%)
TMDD	Surfactant (Surfynol)	226	253	3.1	16 (83%)
γ-Undecalactone	Fragrance (Peach)	184	286	2.9	8 (44%)
Diethyl phthalate	Solvent, Plasticizer	222	294	2.7	17 (94%)
Methyl dihydrojasmonate	Fragrance (Jasmine)	226	308	2.5	16 (89%)
Dibutyl phthalate	Solvent, Plasticizer	278	337	4.8	9 (50%)
TCPP	Flame Retardant	328	358	2.5	11 (61%)

[a]Molecular Weight, [b]Boiling Point at 1.0 atm predicted by ACD/Labs, [c]Octanol-Water Partitioning Coefficient predicted by ACD/Labs. TMDD is 2,4,7,9-tetramethyl-5-decin-4,7-diol, and TCPP is tris(chloropropyl)phosphate.

5.3.4 Contaminant Mixtures Detectable in Condensate as a Function of Sampling Location and Human Activity. A comparison of chromatograms of contaminant mixtures present in condensate from different homes readily revealed some marked differences as well as similarities between buildings (Figure 4.2). These may be partly ascribed to the manner of operation of the HVAC system (*e.g.*, duration of use) and the physical layout of the building. The single sample taken from a commercial structure, for example, exhibited the fewest detectable contaminants (11 peaks recorded) when analyzed by GC-MS. This is suspected to be an effect of dilution of the liquid stream due to higher condensate production, resulting from the larger capacity of the system, larger enclosed space, and different ventilation requirements of a commercial system.

In addition, the present study demonstrates that condensate chemistry is directly impacted by human activities in the buildings. Repeated sampling of the same buildings on different dates demonstrated that the mixture of contaminants detected in each building (*i.e.*, the indoor contaminant fingerprint) was largely consistent over time (Figure 3.3A). Yet, the introduction of new household activities was immediately apparent in GC-MS chromatograms when the occupants of one home were asked to burn a scented candle at least 20 feet away from the HVAC intake vent (Figure 3.3B). These participants were known to not have used such products, and the additional activity produced new, easily discernable peaks when comparing chromatograms from before and after the requested activity.

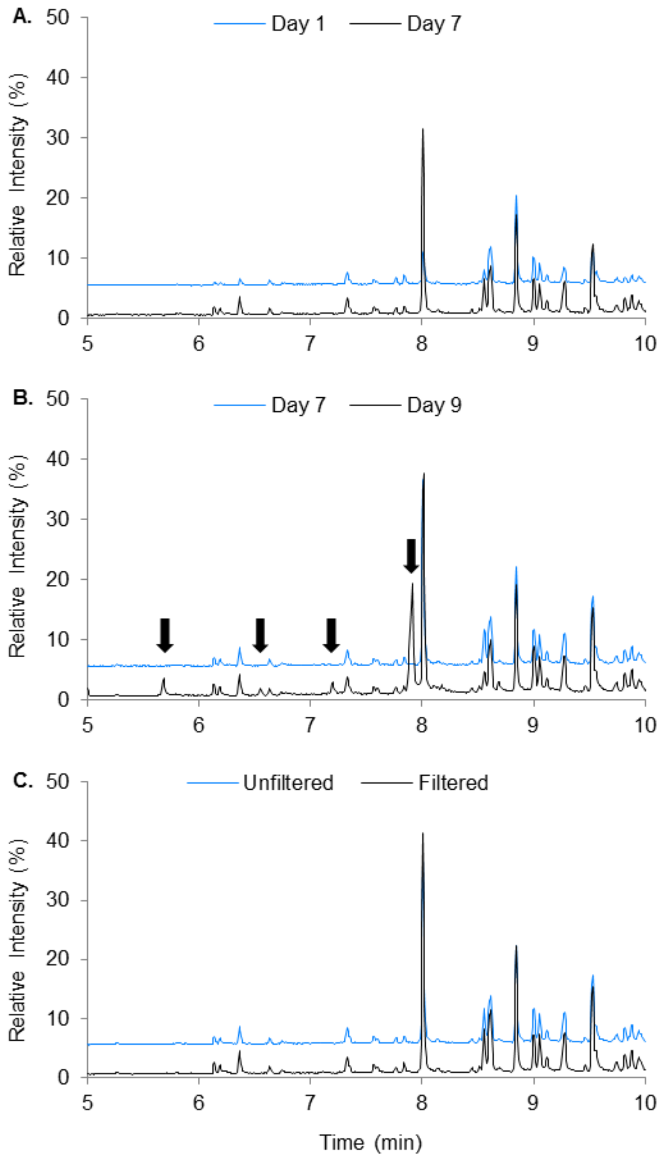

Figure 5.3. Gas chromatograms for condensate samples. (A) Samples taken at different dates from House A showed consistency in the chemical mixtures present and revealed differences in the strength of detected signals. (B) Controlled introduction of a new household product (in this case, burning of a scented candle) generated new, easily discerned peaks (indicated by vertical arrows) when comparing chromatograms taken from condensate samples before and after the product was used. (C) Example GC-MS chromatograms resulting from the analysis of unfiltered and filtered condensate from one of the study locations. The relative intensities have been scaled to half of the most abundant peak (not shown) to show finer detail and one chromatogram offset +5% for clarity.

5.3.5 Results Not Affected by Submicron Filtration. One of the critical questions when assessing the relevance of HVAC condensate for monitoring indoor air quality and the associated human exposures is the transport mechanism by which contaminants enter the liquid stream. To address this question, extracts were prepared with and without submicron filtration of the condensate sample prior to SPE. For unfiltered samples, contaminant mass associated with particulate matter would be physically retained on the SPE cartridge, and expected to be eluted by the organic solvents used during solid phase extraction, leading to the appearance or magnification of peaks for contaminants that did not previously partition effectively from the particulate matter into the condensate. The flame retardant TCPP, detected here in condensate and previously in both particle and vapor phases (Salamova, Ma, Venier, & Hites, 2013), would be expected to demonstrate this effect if it occurs. However, the comparison of chromatograms of all filtered and unfiltered samples consistently failed to demonstrate such an artifact (Figure 3.3C), suggesting that the contaminant contribution from particles greater than approximately 0.7 μm was negligible for the contaminants detected in this study.

While TCC, TCS, and most of the parabens have boiling points that suggest low volatility, they nevertheless were detectable in the condensate samples. All of these compounds are common components of personal care products. Their detection in condensate may be facilitated by volatilization or aerosolization (*e.g.*, during showering). Typically, TCS, BPA, and TBBPA exist in household dust at ng- and μg-per-g concentrations (Huber et al., 2011). Yet, the ubiquitous detection of TCS in this study is noteworthy given its low volatility and the fact that (i) sampling occurred downstream of the air filtration unit of the HVAC systems, (ii) many samples were collected after installation of clean air filters, (iii) none of the participants reported showering during the sampling period, and (iv) the condensate samples were filtered prior to extraction.

Furthermore, the ubiquitous detection of TCS occurred without regard to the age of construction of the monitored buildings, which were constructed over a five decades between 1960 and 2012. This is noteworthy as the age of construction impacts both the type of building material used (including the introduction of antimicrobial building materials (Microban International, 2014) and the accumulation of dust and contaminants in the air handling system. Thus, multiple lines of evidence point to gas phase and fine (submicron) aerosols as the source of the analytes detected; yet, future studies should substantiate the extent to which these chemicals occur as volatiles or associated with submicron aerosols to assess the relevance for human exposures of this plausibly inhalable fraction.

5.3.6 Hydrophobicity and Volatility Range of Analytes. The thermodynamic properties of indoor air contaminants would be expected to drive the mixture found in condensate, with boiling point and octanol-water partitioning coefficients being chief among them. To better understand the effect of these physical properties, predicted values were tabulated (Table 3.1 and Table G.5 of Appendix G) and plotted for all of the compounds targeted by LC-MS/MS and those tentatively or positively identified by GC-MS/MS (Figure 3.4). For data consistency, chemical-physical data for chemicals were taken from the ACD/Labs suite of chemical property predictive software. For the compounds reported in this study, predicted boiling points ranged from less than 150°C to more than 500°C suggesting that the spectrum of air pollutants suitable for monitoring in condensate may extend far beyond the limited range of volatile compounds featuring boiling points at or below ambient air temperature. Similarly, the compounds investigated in this study covered a significant spectrum of hydrophobicity, indicated by predicted log K_{OW} values ranging from -2 to nearly 8.

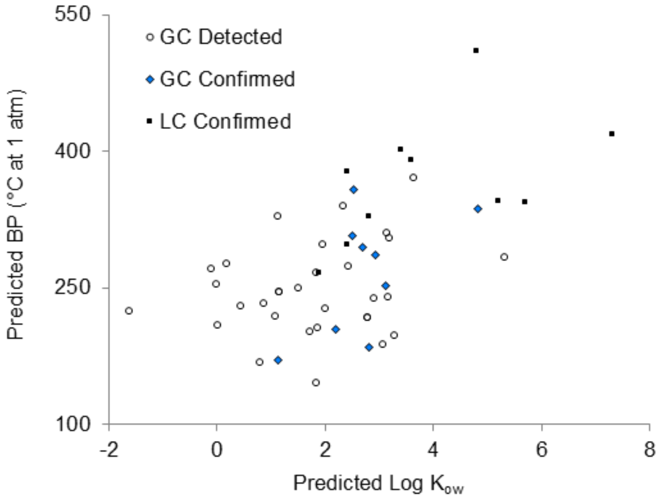

Figure 5.4. Range of volatilities (expressed as Boiling Point, BP) and hydrophobicities (as Octanol-Water Partitioning Coefficient, log K_{OW}) of compounds identified in HVAC condensate.

Non-targeted condensate surveys, such as the one presented here, will be biased towards an optimal hydrophobicity and boiling point associated with the specific sample collection, extraction, and analysis methods (Figure 3.5). For the GC-MS data presented (n = 40), a central tendency for predicted boiling point is demonstrated around a mean of 252 ºC with a standard deviation of 54ºC, and similarly for predicted log K_{OW} around a mean of 2.0 with a standard deviation of 1.4. Available data suggest that more hydrophobic or acidic contaminants were not a substantial component of the collected condensate samples, since non-targeted GC-MS analysis of subsequent toluene elution of the C_{18} cartridges and acidification of the condensate sample prior to SPE, respectively, did not yield additional chromatographic peaks in the GC-MS (results not shown). The spectrum of indoor air pollutants to be monitored using condensate may potentially be expanded, however, by modifying the protocol to include refrigeration of sampling containers, the use of different stationary extraction phases, elution with different solvents, and analysis by employing alternative or additional methods such as liquid chromatography-high resolution mass spectrometry (LC-HRMS).

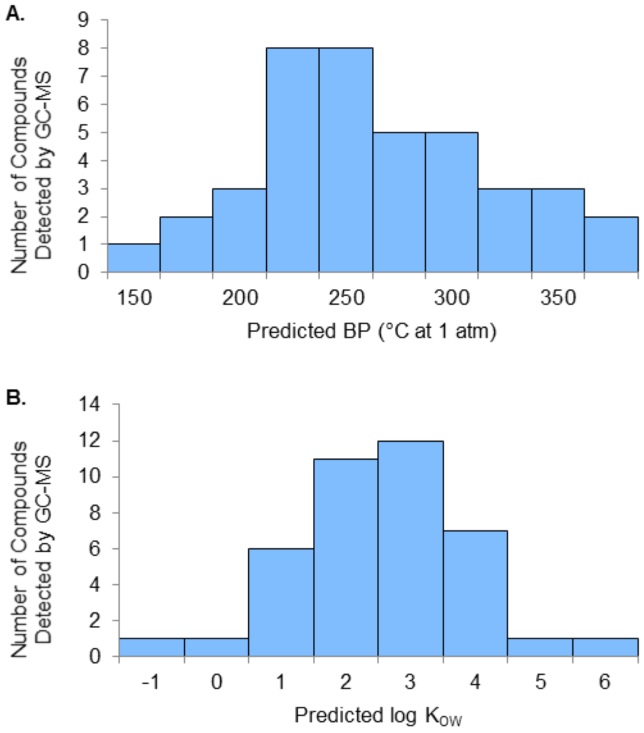

Figure 5.5. Histograms illustrating the number of compounds detected within a given range of (A) boiling points and (B) log KOW values. Boiling Point (BP) and Octanol-Water Partitioning Coefficient (log KOW) predicted by ACD/Labs.

5.3.7 Quantification Remains a Challenge. The most significant difference between the data provided by conventional air sampling techniques and the condensate sampling technique presented here is the ability to predict concentrations in the bulk indoor air. At this time, no conclusions can be drawn about the abundances of contaminants in the air itself, as there is currently no model to predict the relationship between contaminant abundances in condensate and the air from which it was derived. Such a model may be difficult to develop due to the many variables contributing to the contaminant concentration in the condensate, including the variability in the volume of condensate generated by the HVAC, the indoor air temperature requested by the inhabitants, the cooling efficiency of the system, and the relative humidity of the indoor air, all of which would be expected to affect the abundances in the condensate.

5.3.8 Implications for Future Environmental Exposure Studies. The California Environmental Contaminant Biomonitoring Program maintains a list of designated chemicals from the United States Centers for Disease Prevention biomonitoring studies and the recommendations of its own Scientific Guidance Panel from which is used to determine targets for human biomonitoring studies (California Environmental Contaminant Biomonitoring Program, 2014a, 2014b). Taking together the targeted LC-MS/MS and non-targeted GC-MS data from indoor air condensate analyses, the present study identified 12 compounds from the February 2014 Designated Chemicals list, 9 by LC-MS/MS (BPA, fipronil, parabens [methyl-, ethyl-, propyl-, and butyl-], TBBPA, TCC, and TCS) and 3 by GC-MS (dibutyl phthalate, diethyl phthalate, and TCPP). These data illustrate that condensate analysis is a promising technique for non-invasive, qualitative screening of living spaces for chemicals of concern. Detection of harmful substances may then warrant follow-up studies, possibly involving conventional air sampling and biomonitoring studies of occupants, as indoor air condensate analysis is currently limited in its ability to provide a quantitative assessment of indoor air quality.

5.4 CONCLUSIONS

This work presents a new, economical and promising approach to characterizing indoor air contaminant mixtures by sampling condensate from HVAC systems. This approach is spatially integrated over the whole accessible living space, and does not require access to the interior of the home. A wide range of volatile, semivolatile, and low-volatility anthropogenic substances was demonstrated to be detectable in indoor air with this approach. In this work, the mixture of contaminants detected was not influenced by the filterable fraction of particulate matter in air; rather, it was the product of gas phase and submicron (*i.e.*, inhalable) contaminants that are readily available through the inhalation route to building occupants. Detected mixtures were largely consistent over short time spans for individual buildings, identifiably different between buildings, and sensitive to the introduction of consumer products to the living space. Potential exists for this approach to be used in the screening of living spaces for contaminants of concern, for surveys of large numbers of living spaces, and for monitoring the changes in indoor air quality associated with aging of construction materials.

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Chapter 6

CONCLUSION AND RECOMMENDATIONS

The subject of this dissertation has been integrative methods for sampling contaminants in environmental compartments. Two methods were presented, *in situ* solid phase extraction (SPE) with a programmable sampler (IS2), and collection and analysis of indoor air condensate. In this chapter, the research questions and hypotheses from the introduction are revisited, and recommendations for relevant future work explored.

6.1 RESEARCH QUESTIONS REVISITED

6.1.1 Data Quality. The second chapter addressed the data quality implications of active versus passive integrative sampler designs, and presented a conceptual and mathematical model that provides a framework for characterizing sources of error. I hypothesized that active sampling provides greater precision than passive sampling. In both sampler designs, the sources of systematic and random error in the contaminant concentration derived from a sample (C_S) could be broadly categorized grouped into two terms, the uptake and recovery coefficients (α and ρ, Equation 6.1) applied to the true environmental concentration (C_W).

$$C_S = C_w(\alpha)(\rho) \tag{6.1}$$

Because of a paucity of error data for active samplers, there are not enough observations for a rigorous statistical comparison, but the available data strongly support the hypothesis: active samplers—by managing error in the sampling rate (R_S) mechanically—provide an opportunity to improve the precision of integrative sampler data.

6.1.2 Utility of In Situ SPE. The third chapter presented the development and demonstration of a programmable, submersible sampler that applies SPE *in situ*, the *In Situ* Sampler (IS2). I hypothesized that an active sampler can develop long time-base average data comparable to a composite of hundreds of liquid samples. In the subsequent demonstration, a 12-sample time series generated on 2-hr intervals over the course of a day showed that the concentration of the principal contaminant (Chromium-VI) varied cyclically by more than 50%. A series of liquid composite and SPE composite samples obtained in 2-hr intervals over 28-days then demonstrated that sorbed samples from the IS2 provided results comparable to those of the liquid composite samples, but with enhanced detection limits, supporting the original hypothesis.

6.1.3 Impact on Sustainability. The fourth chapter of this work explores the economic and environmental implications of substitution of *in situ* SPE for conventional liquid samples. In the introduction, I hypothesized that scaled use of *in situ* SPE reduces waste generation, as well as the cost and carbon footprint of transportation of samples. The study presented in the third chapter supports the first part of the hypothesis, by showing that sorbed samples provide comparable data to liquid samples while significantly reducing the volume of contaminated material removed from the site. The fourth chapter extrapolated from this study to show how this reduction of mass affects cost and carbon footprint generated by sample transportation (reduced in both cases by more than 90%), further supporting the hypothesis.

6.1.4 Utility of Condensate Analysis. The fifth chapter presented a new method for qualitative analysis of indoor air quality through detection of contaminants in the condensate produced by heat exchangers. I hypothesized that indoor air condensate could be a matrix for detection of vapor-phase indoor air contaminants, differentiable between houses, and sensitive to introduction of new vapor sources. In this work, I demonstrated the detection and preliminary identification of a spectrum of semi-volatile contaminants, and confirmed the identity of 90% of a random sample of the contaminants with standards. The study further demonstrated that mixtures of contaminants present in different structures had both shared and unique components, and that the introduction of a new contaminant source was readily discernable.

6.2 RECOMMENDATIONS FOR FURTHER DEVELOPMENT OF THE IS2

The feasibility of the IS2 method and instrument has been established in this work, leaving two principal challenges for future development. The first challenge is to move the design of the hardware forward, from research instrument to a form that can be commercialized. The second is to identify and execute applications that demonstrate the unique utility of the IS2, in order to provide a body of literature that informs the relevant user communities.

6.2.1 Further Development of IS2 Instrument. The instrument presented in the third chapter was the product of more than four years of iterative design, incorporating parts manufactured by the Arizona State University Instrument and Prototype Shop as well as commercial off-the-shelf (COTS) parts. This instrument has reached a point in development at which a commercialized model can reasonably be expected to largely share the same layout and functions. However, as an evolving research instrument, the present embodiment is a study in compromise between form and function, with many artifacts of the design process that, if addressed, should yield an instrument even more attractive for commercial use. These include:

6.2.1.1 Inert Polymer Casing. The steel casing used to date has proven robust, but was inherited from a much larger instrument requiring significantly greater structural strength. A COTS steel tubing in the desired dimensions was readily available while a comparable polymer casing has not yet been identified. To reduce the weight of the instrument, the casing of the IS2 should be manufactured from an inert polymer compatible with the material with which the instrument can be expected to be in contact. This would greatly improve the usability of the device, particularly when employed by a single technician.

6.2.1.2 Load-Bearing Multi-Conductor Cable. As with the steel casing, the present independent load-bearing and instrumentation cables were inherited from the design of a larger instrument and are over-engineered for this application. For shallow deployments (e.g., 40 ft), they are of limited usability concern; however, as deployment depth below ground surface increases, the weight of the two cables becomes a significant barrier to the unassisted deployment of the sampler. There are COTS load-bearing instrument cables available (e.g., PN 801140, Load Bearing Data Cable, Sea-Bird Electronics, Bellevue, WA, USA); the substitution of an appropriately specified cable of this type should be a priority to reduce the weight and improve the usability of the instrument.

6.2.1.3 Purpose-Built Fluid Train. The present fluid train is assembled from COTS medical-grade fluidics parts and flexible tubing. While these parts greatly facilitated the rapid reconfiguration of the instrument, they pose chemical compatibility limitations for certain analytes and represent established points of occasional failure during use. Fittings in particular (e.g., check valves) were frequently unavailable in materials with desired chemical compatibilities, and the instability of the design made the third-party manufacture of custom parts unattractive. With the design of the instrument now largely frozen, exclusive use of rigid fluoropolymer tubing is recommended over existing materials with compatible fittings designed to specification and manufactured by an established third party (e.g., Halkey Roberts Corporation, St. Petersburg, FL, USA).

6.2.2 Further Development of IS2 Applications. The IS2 has the capability to provide both unique data (time-integrated average concentrations) and unique data quality (intersample variance with simultaneous replicates; improved precision with active sampling). Two kinds of application demonstrations are recommended for the future in order to advance the wider application of this method and instrument: unique application studies that generate incomparable data and direct comparison studies that demonstrate improved utility.

6.2.2.1 Unique Application: Long Time-Base Sampling. Passive samplers operate in an integrative mode for a limited time during which contaminant uptake is a linear; the IS2 should be applied to generate time-integrated average samples of a contaminant over a time period that is significantly longer than that for which established COTS passive samplers are capable. The Chemcatcher, for example, is typically exposed for 14 days (Vrana et al., 2006), so the employment of the IS2 to reproduce a relevant Chemcatcher study at 28 or 56 days would effectively demonstrate the long time-base capabilities of the instrument.

6.2.2.2 Unique Application and Direct Comparison: Low-Affinity Contaminants. Both passive and active samplers rely on partitioning kinetics to capture the contaminant of interest; for passive samplers, this can create a significant limitation in the case of contaminants for which high-affinity sorbent materials are not available. These contaminants are treated as having very low sampling rates (R_S); while this increases the time over which time-integrated sampling may take place, the mass of contaminant returned for quantification may be prohibitively low. An active sampler, in contrast, regulates R_S mechanically and can compensate for low sorbent affinity with a longer contact time and greater contact surface area (e.g., by increasing the length of a column of packed sorbent beads). Thus, an active sampler such as the IS2 should be readily configurable to provide a significant improvement to such compounds, and should be applied to demonstrate such. A recent study using the Polar Organic Chemical Integrative Sampler (POCIS) with 200 mg of Oasis HLB sorbent to detect a suite of 21 contaminants (Belles et al., 2014) could be replicated with the IS2 under identical conditions.

6.2.2.3 Direct Comparison: High-Precision Time-Integrated Sampling. One of the limitations of the present study is the lack of direct comparison between the IS2 and passive samplers, with directly comparable data sets. This should be addressed by performing an identical data collection experiment for the same suite of contaminants using the IS2 and a COTS passive sampler, preferably one that uses a packed granular sorbent, for total compatibility of the methods. This application would provide further support for the comparability of IS2 data with contemporary methods, and should demonstrate the improved precision of IS2 data versus passive sampling, which has to date only been supported by literature analysis of dissimilar studies. With Semipermeable Polymeric Membrane Devices (SPMEs) being well-established and commercially available, there is an opportunity to provide a dataset taken under identical conditions with an SPME and the IS2.

6.3 RECOMMENDATIONS FOR FURTHER DEVELOPMENT OF INDOOR AIR CONDENSATE MONITORING.

Having established that indoor air condensate carries information about the airborne contaminants present in the associated living spaces, there are two principal efforts that should be made to further develop this method. The first is to conduct a parallel study with a conventional air sampling system, and the second is to demonstrate the unique applicability of condensate sampling to specialized environments.

6.3.1 Parallel Sampling Studies. While indoor air condensate analysis is unlikely to yield quantitative results for homes and other structures, the sensitivity of the method to a suite of common contaminants should be established with simultaneous sampling using a conventional whole-air sampler or sorbent sampler. Such a study would further provide the opportunity to determine whether or not significant magnification of the study contaminants occurs in the condensate, which may result in greater sensitivity for the indoor air condensate method.

6.3.2 Sampling in Specialized Environments. For structures, there are a number of confounding factors that relating indoor air condensate contaminant concentrations to those in the air itself nearly impossible. These include unknown degrees of air exchange between the indoor and outdoor environment, variable humidity, and significant differences in efficiency and operating program between air conditioning systems in different buildings. All of these confounding factors are, however, highly controlled in aircraft. A significant step in the development of the air condensate monitoring method would be to monitor the composition of air from the heat exchanger in an aircraft ventilation system. By simultaneously logging parameters such as humidity and the air exchange rate, and measuring the volumetric flow rate of the system, it should be possible to develop a model to relate condensate contaminant concentrations with air contaminant concentrations. Further, if a time-series of condensate samples are taken, it should be possible to establish the lag-time between the introduction of new contaminants and their detection in condensate. As a spatially-integrative monitoring method, condensate monitoring has the potential to provide a unique access point to the air quality in highly controlled spaces such as aircraft and may provide information that is complementary to or inaccessible to existing methods.

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APPENDIX A

PATENT APPLICATIONS

A.1 PATENT APPLICATION FOR IN SITU SAMPLER FOR BIOAVAILABILITY

Title: Devices and Methods for Determination of Bioavailability of Pollutants

Inventors: Rolf U. Halden and Isaac B. Roll.

Assignee: Arizona Board of Regents

Publication Number: US 2014/0102182

Abstract: Contaminant mass collection in saturated sedimentary environments for bioavailability determination. A casing includes a screen between the environment that is subject to sampling, such as a saturated sediment and the device itself. The casing includes a water intake zone, a pump, and sorptive media. The water intake zone, the pump, the screen and the sorptive media, are all operably linked in sequence. The screened casing is secured to form an in situ device; the screen is in fluid communication with the water intake zone and excludes endemic sediments and aquatic life. The in situ device is deployed in the saturated sedimentary environment. The pump operates to concentrate analytes from the selected environment in the sorptive media, where the concentrated analytes include the analyte mass of time-weighted fluid samples.

A.2 DISCLOSURE OF METHOD FOR CONDENSATE MONITORING

Title: Method and System for Monitoring Airborne Contaminants

Inventors: Benny F. G. Pycke, Rolf U. Halden, and Isaac B. Roll

Assignee: Arizona Board of Regents

Publication Number: Pending (Arizona Technology Enterprises Case # M14-109L)

Abstract: Indoor air pollution has been identified as being among the top five environmental health risks. Air contaminants stem from both the components of the building itself and human activities and natural conditions in and around the building. There are a multitude of indoor environments that require air pollution monitoring – ranging from aircrafts and submarines to commercial buildings and storage units. Current methods to sample and monitor air contaminants are expensive, difficult to use for those not trained in the field, and intrusive to the area they monitor.

Researchers at Arizona State University have developed a novel system that can easily, economically, remotely, and rapidly monitor the air quality of closed or semi-closed environments. This system can qualitatively and quantitatively assess the air quality in all buildings or environments, particularly those with HVAC duct work or an air recirculation system. The process is cost effective and sampling and monitoring can be performed by non-technical personnel as the system does not require specials skills or training. Moreover, real-time sensors can be utilized to enable early warning/immediate response mechanisms.

This technology represents a novel and viable process that can effectively capture indoor air pollution in an effort to monitor contaminants where air quality may be of concern.

APPENDIX B

SUPPLEMENTARY MATERIAL FOR CHAPTER 2

Table B.1

Collected sampling rate and standard deviation data for five integrative samplers.

Instrument (Citation)	Parameters	Compound	R_S (mL/d)	Std. Dev. (mL/d)	RSD (%)
IS2 (Roll et al., 2015)					
	28 days	Chromium-VI	16	0.54	3.4
	18 hrs	n/a*	533	13.56	3.5
	18 hrs	n/a*	533	8.72	2.3
	18 hrs	n/a*	533	4.77	1.3
	18 hrs	n/a*	533	7.52	1.9
	4 hrs	n/a*	2400	13.97	3.5
	4 hrs	n/a*	2400	3.39	0.8
	2 hrs	n/a*	4800	2.73	0.7
				Range:	1 - 4
				Average:	2.2
				Std. Dev.	1.1
				n:	8
		*bench testing of pump			
IS2B (Supowit et al., 2015)					
		all	102	7	6.8
POCIS (Alvarez et al., 2004)					
	quiescent	Diuron	5	2	40
	turbulent	Diuron	45	16	36
	quiescent	Isoproturon	15	3	20
	turbulent	Isoproturon	86	8	9
	quiescent	Azithromycin	21	6	29
	turbulent	Azithromycin	120	75	63
	quiescent	Fluoxetine	12	7	58
	turbulent	Fluoxetine	86	23	27
	quiescent	Levothyroxine	9	8	89
	turbulent	Levothyroxine	53	28	53
	quiescent	Omeprazole	7	4	95
	turbulent	Omeprazole	30	8	27
				Range:	9 - 95
				Average:	46
				Std Dev:	26
				n:	12

SPMD (Huckins et al., 1999)

10 °C	napthalene	1900	1.5
10 °C	acenaphthylene	2300	8
18 °C	acenaphthylene	1400	3
26 °C	acenaphthylene	1700	4
10 °C	acenapthene	2700	5
18 °C	acenapthene	2300	5
26 °C	acenaphthene	2400	7
10 °C	fluorene	3000	5
18 °C	fluorene	1700	6
26 °C	fluorene	2800	1
10 °C	phenanthrene	3800	9
18 °C	phenanthrene	3600	14
26 °C	phenanthrene	5000	12
10 °C	anthracene	2900	9
18 °C	anthracene	3600	17
26 °C	anthracene	4600	31
10 °C	pyrene	4500	15
18 °C	pyrene	5200	10
26 °C	pyrene	7600	12
10 °C	benz[a]anthracene	3200	14
18 °C	benz[a]anthracene	3200	18
26 °C	benz[a]anthracene	4700	17
10 °C	chrysene	3700	18
18 °C	chrysene	4800	11
26 °C	chrysene	7600	10
10 °C	benzo[b]fluoranthene	2800	16
18 °C	benzo[b]fluoranthene	3000	20
26 °C	benzo[b]fluoranthene	3300	33
10 °C	benzo[k]fluoranthene	2900	18
18 °C	benzo[k]fluoranthene	3900	13
26 °C	benzo[k]fluoranthene	5500	19
10 °C	benzo[a]pyrene	3200	3
18 °C	benzo[a]pyrene	3700	26
26 °C	benzo[a]pyrene	5400	10
10 °C	ideno[I,2,3-cd]pyrene	3000	5
18 °C	ideno[I,2,3-cd]pyrene	3800	20
26 °C	ideno[I,2,3-cd]pyrene	4700	8
		Range:	1 - 33
		Average:	12
		Std Dev:	8

		n:	37

MESCO (Vrana et al., 2001)

19 °C	HCB	2.7	7
14 °C	HCP	1.1	50
19 °C	γ-HCB	8.1	41
14 °C	γ-HCB	4.5	47
19 °C	p,p-DDE	7.3	7
14 °C	p,p-DDE	3.4	28
19 °C	PCB28	8.1	49
14 °C	PCB28	11.9	57
19 °C	PCB52	6.6	32
14 °C	PCB52	9.5	40
19 °C	PCB101	5.4	13
14 °C	PCB101	6.4	28
19 °C	PCB138	5.4	6
14 °C	PCB138	6.5	29
19 °C	PCB153	4.5	7
14 °C	PCB153	5.5	30
19 °C	PCB180	2.6	8
14 °C	PCB180	2.7	33
19 °C	acenapthylene	11.6	7
14 °C	acenapthylene	16.8	16
19 °C	acenapthene	6.7	8
14 °C	acenapthene	5.7	14
19 °C	fluorene	9.4	7
14 °C	fluorene	11.6	16
19 °C	anthracene	11.1	15
14 °C	anthracene	13.0	21
19 °C	phenanthrene	7.7	10
14 °C	phenanthrene	6.1	17
19 °C	fluoranthene	9.3	11
14 °C	fluoranthene	5.2	31
19 °C	pyrene	12.2	15
14 °C	pyrene	6.5	30
19 °C	benzo[a]anthracene	14.3	4
14 °C	benzo[a]anthracene	5.1	33
19 °C	chrysene	15.4	8
14 °C	chrysene	5.2	32
19 °C	benzo[b]fluoranthene	10.9	5
14 °C	benzo[b]fluoranthene	5.6	26
19 °C	benzo[k]fluoranthene	11.9	8

14 °C	benzo[k]fluoranthene	5.1		28
19 °C	benzo[a]pyrene	9.3		7
14 °C	benzo[a]pyrene	7.2		18
19 °C	indeno[1,2,3-cd]pyrene	7.1		5
19 °C	benzo[ghi]perylene	5.7		9
			Range:	4 - 49
			Average:	21
			Std Dev:	14
			n:	44
POCIS (Belles et al., 2014)				
	1,2,4 DCPU	290	20	7
	1,3,4 DCPU	280	30	11
	1,3,4,3 DCPMU	290	40	14
	Atrazine	370	50	14
	Chlortoluron	400	30	8
	Chlorsulfuron	160	30	19
	Cyanazine	310	20	6
	DEA	250	10	4
	DIA	230	30	13
	Diuron	280	40	14
	Irgarol	410	20	5
	Isoproturon	460	30	7
	Linuron	200	70	35
	Metoxuron	410	80	20
	Nicosulfuron	160	40	25
	Prometryn	420	10	2
	Propazine	390	50	13
	Pymetrozine	280	100	36
	Simazine	390	70	18
	Terbutryn	500	20	4
	Terbuthylazine	360	50	14
			Range:	2 - 36
			Average:	14
			Std Dev:	9
			n:	21
Chemcatcher (Vrana et al., 2006)				
6 °C	Acenaphthene	65		47
0 RPM	Fluorene	72		41
	Phenanthrene	65		38
	Anthracene	81		42

	Fluoranthene	55	36
	Pyrene	50	38
	Benz[a]anthracene	36	33
	Chrysene	26	25
	Benzo(b)fluoranthene	13	44
	Benzo(k)fluoranthene	14	33
	Pentachlorobenzene	77	62
	Hexachlorobenzene	46	60
	Lindane	9	46
	Endosulfan I	27	35
	Dieldrin	52	43
6 °C	Acenaphthene	103	14
40 RPM	Fluorene	126	11
	Phenanthrene	143	16
	Anthracene	97	19
	Fluoranthene	48	28
	Pyrene	40	28
	Benz[a]anthracene	13	59
	Chrysene	14	45
	Benzo(b)fluoranthene	10	23
	Benzo(k)fluoranthene	10	24
	Benzo(a)pyrene	9	27
	Hexachlorobenzene	24	23
	Endosulfan I	10	27
	Dieldrin	14	15
6 °C	Acenaphthene	137	19
70 RPM	Fluorene	225	16
	Phenanthrene	323	17
	Anthracene	324	19
	Fluoranthene	298	23
	Pyrene	291	24
	Benz[a]anthracene	108	27
	Chrysene	98	27
	Benzo(b)fluoranthene	25	26
	Benzo(k)fluoranthene	24	22
	Benzo(a)pyrene	14	29
	Pentachlorobenzene	65	24
	Hexachlorobenzene	63	25
	Lindane	17	28
	Endosulfan I	32	20
	Dieldrin	43	21
11 °C	Acenaphthene	139	25

0 RPM	Fluorene	150	20
	Phenanthrene	191	28
	Anthracene	187	27
	Fluoranthene	145	27
	Pyrene	100	25
	Benz[a]anthracene	43	25
	Chrysene	42	23
	Benzo(b)fluoranthene	17	32
	Benzo(k)fluoranthene	13	27
	Benzo(a)pyrene	14	31
	Pentachlorobenzene	112	25
	Hexachlorobenzene	45	24
	Lindane	30	21
	Endosulfan I	54	20
	Dieldrin	73	20
11 °C	Acenaphthene	263	22
40 RPM	Fluorene	371	18
	Phenanthrene	657	38
	Anthracene	376	21
	Fluoranthene	514	27
	Pyrene	335	20
	Benz[a]anthracene	153	25
	Chrysene	152	25
	Benzo(b)fluoranthene	43	30
	Benzo(k)fluoranthene	35	30
	Benzo(a)pyrene	27	35
	Pentachlorobenzene	295	29
	Hexachlorobenzene	137	30
	Lindane	45	32
	Endosulfan I	88	27
	Dieldrin	129	26
11 °C	Acenaphthene	381	30
70 RPM	Fluorene	43	26
	Phenanthrene	733	29
	Anthracene	452	60
	Fluoranthene	74	22
	Pyrene	586	25
	Benz[a]anthracene	385	24
	Chrysene	339	23
	Benzo(b)fluoranthene	152	28
	Benzo(k)fluoranthene	113	25
	Benzo(a)pyrene	127	21

	Indeno[1,2,3-cd]pyrene	38	39
	Dibenz[a,h]anthracene	52	31
	Benzo[g,h,i]perylene	42	26
	Pentachlorobenzene	432	40
	Hexachlorobenzene	254	23
	Lindane	50	40
	Endosulfan I	142	19
	Dieldrin	207	23
18 °C	Acenaphthene	87	24
0 RPM	Fluorene	82	24
	Phenanthrene	112	29
	Anthracene	46	25
	Fluoranthene	68	27
	Pyrene	33	23
	Benz[a]anthracene	8	40
18 °C	Acenaphthene	31	48
40 RPM	Fluorene	515	46
	Phenanthrene	724	34
	Anthracene	582	34
	Fluoranthene	1379	54
	Pyrene	1260	59
	Benz[a]anthracene	470	32
	Chrysene	484	46
	Benzo(b)fluoranthene	319	71
	Benzo(k)fluoranthene	92	34
	Benzo(a)pyrene	50	32
	Dibenz[a,h]anthracene	13	53
	Benzo[g,h,i]perylene	16	47
	Hexachlorobenzene	849	73
	Lindane	45	20
	Endosulfan I	150	25
	Dieldrin	323	31
18 °C	Acenaphthene	314	33
70 RPM	Fluorene	476	22
	Phenanthrene	597	28
	Anthracene	510	17
	Fluoranthene	1113	45
	Pyrene	1079	27
	Benz[a]anthracene	524	27
	Chrysene	495	27
	Benzo(b)fluoranthene	315	74
	Benzo(k)fluoranthene	81	44

	Benzo(a)pyrene	64		46
	Hexachlorobenzene	609		36
	Endosulfan I	144		23
	Dieldrin	273		25
			Range:	11- 74
			Average:	31
			Std Dev:	12
			n:	134

Chemcatcher (Aguilar-Martinez et al., 2008)

4°C SL2	tributyltin	42	11	26
4°C SL3	tributyltin	174	36	21
11°C SL1	tributyltin	29	12	41
11°C SL2	tributyltin	117	27	23
11°C SL1	tributyltin	201	21	10
18°C SL1	tributyltin	56	17	30
18°C SL2	tributyltin	106	25	24
18°C SL3	tributyltin	202	28	14
4°C SL2	dibutyltin	45	8	18
4°C SL3	dibutyltin	129	22	17
11°C SL1	dibutyltin	41	25	61
11°C SL2	dibutyltin	137	34	25
11°C SL1	dibutyltin	189	32	17
18°C SL1	dibutyltin	48	14	29
18°C SL2	dibutyltin	141	36	26
18°C SL3	dibutyltin	204	28	14
4°C SL2	monobutyltin	3	1	33
4°C SL3	monobutyltin	23	7	30
11°C SL1	monobutyltin	6	2	33
11°C SL2	monobutyltin	18	5	28
11°C SL1	monobutyltin	22	5	23
18°C SL1	monobutyltin	4	1	25
18°C SL2	monobutyltin	11	3	27
18°C SL3	monobutyltin	18	7	39
4°C SL2	triphenyltin	32	8	25
4°C SL3	triphenyltin	160	33	21
11°C SL1	triphenyltin	26	9	35
11°C SL2	triphenyltin	60	15	25
11°C SL1	triphenyltin	191	29	15
18°C SL1	triphenyltin	38	12	32
18°C SL2	triphenyltin	59	19	32
18°C SL3	triphenyltin	173	28	16

Range:	10-61
Average:	26
Std Dev:	10
n:	32

Table B.2

Collected recovery and standard deviation data for six integrative samplers.

Instrument (Citation)	Compound	Recovery	CV (%)
IS2 (Roll et al., 2015)			
	Chromium-VI	75	5.9
IS2B (Supowit et al., 2015)			
	Fipronil	92	24
	-sulfide	9	22
	-sulfone	86	9
	-amide	77	12
	-desulfinyl	95	13
		Range:	9 - 24
		Average:	16
		Std Dev:	6
		n:	5
POCIS (Alvarez et al., 2004)			
	Atrazine	88	1
	Diazinon	98	1.8
	Diuron	92	11
	17α-Ethynylestradiol	97	3
	Isoproturon	99	12
	Azithromycin	110	28
	Fluoxetine	95	19
	Levothyroxine	86	26
	Omeprazole	95	16
		Range:	1 - 28
		Average:	13
		Std Dev:	10
		n:	9
Ceramic Dosimeter (Martin et al., 2003)			
	benzene	93	4.7
	toluene	93	5.5
	ethylbenzene	89	6.2
	m- and p-xylene	93	3.3
	o-xylene	91	9.2
	1,3,4-trimethylbenzene	87	4.4
	naphthalene	89	9.9
	2-methylnaphthalene	100	9.2

	1-methylnaphthalene	95	7.9
	TCE	101	13
	PCE	90	6.4
		Range:	3.3- 9.9
		Average:	7
		Std Dev:	3
		n:	11
Chemcatcher (Shaw et al., 2009)			
	6 various	83	10
SPMD (Huckins et al., 1999)			
	16 PAHs	21 - 109	<20%
SPMD (Huckins et al., 1990)			
	2,2',5,5'-TCB	95	6
	3,3',4,4'-TCB	82	3
	Mirex	78	2
	Fenvalerate	90	7
		Range:	2 - 7
		Average:	5
		Std Dev:	2
		n:	4
POCIS (Belles et al., 2014)			
	1,2,4 DCPU	102	12
	1,3,4 DCPU	109	9
	1,3,4,3 DCPMU	117	19
	Atrazine	91	13
	Chlortoluron	98	20
	Chlorsulfuron	95	19
	Cyanazine	81	13
	DEA	98	18
	DIA	115	19
	Diuron	100	14
	Irgarol	95	15
	Isoproturon	100	21
	Linuron	75	24
	Metoxuron	106	20
	Nicosulfuron	69	13
	Prometryn	100	7
	Propazine	87	10

	Pymetrozine	84	45
	Simazine	91	13
	Terbutryn	87	6
	Terbuthylazine	89	12
		Range:	6 - 45
		Average:	16
		Std Dev:	8
		n:	21
Infiltrex (Tran & Zeng)			
	Naphthalene	59	2.0
	2-Methylnaphthalene	57.8	3.6
	1-Methylnaphthalene	58.4	4.2
	Biphenyl	56.8	1.5
	2,6-Dimethylnaphthalene	58.1	1.7
	Acenaphthylene	55.3	4.5
	Acenaphthene	55.7	4.3
	2,3,6-Trimethylnaphthalene	58.2	7.2
	Fluorene	55.5	7.3
	Phenanthrene	89.6	27.8
	Anthracene	84.4	23.6
	2-Methylphenanthrene	77.6	15.2
	1-Methylphenanthrene	91	20.2
	3,6-Dimethylphenanthrene	87.6	14.5
	Fluoranthene	84.2	7.1
	Pyrene	89.7	5.9
	2,3-Benzofluorene	81	3.5
	Benzo[a]anthracene	95.3	9.8
	Chrysene	92.9	11.6
	Benzo[b]fluoranthene	96.9	23.5
	Benzo[k]fluoranthene	88.3	20.3
	Benzo[e]pyrene	98.8	32.2
	Benzo[a]pyrene	100.3	28.5
	Perylene	102.3	32.0
	Naphthalene-d8	54.4	1.0
	Acenaphthene-d10	58.1	5.9
	Phenanthrene-d10	85.7	16.6
	Chrysene-d12	90.5	8.2
	Perylene-d12	92.7	27.3
	g-BHC	81.5	8.9
	Heptachlor	91.7	5.8
	Aldrin	76.5	5.6

Heptachlor epoxide	89.8	7.5
o,p’-DDE	92.8	1.2
a-Chlordane	85.5	8.4
trans-Nonachlor	84.8	8.1
p,p’-DDE	81.5	4.7
Dieldrin	40.1	3.6
o,p’-DDD	38.6	2.8
Endrin	71.5	1.4
p,p’-DDD	61.1	1.3
o,p’-DDT	46.1	1.0
p,p’-DDT	60.9	3.6
Mirex	39.7	1.8
PCB 65	95.2	2.1
PCB 189	56.2	5.0
PCB 8	107.9	18.3
PCB 18	107.1	6.1
PCB 29	112.5	17.5
PCB 50	108.1	15.5
PCB 28	92.5	18.1
PCB 52	82.7	9.5
PCB 104	99.9	13.2
PCB 44	99.4	12.8
PCB 66	103.1	7.6
PCB 101	102.3	11.8
PCB 87	104.1	7.1
PCB 77,154	101.3	9.6
PCB 118	99.6	12.3
PCB 188	107.5	11.1
PCB 153	104.8	11.6
PCB 126	103.8	13.6
PCB 187	106.4	10.6
PCB 128	101.1	10.0
PCB 200	109.2	7.9
PCB 180	103	10.3
PCB 170	98.7	9.5
PCB 195	97.6	9.3
PCB 206	94.4	8.9
PCB 209	92.3	7.5
PCB 65	87.2	10.1
PCB 189	87.5	7.0
	Range	1.0 - 32.2
	Average:	10

	Std Dev:	8
	n:	72

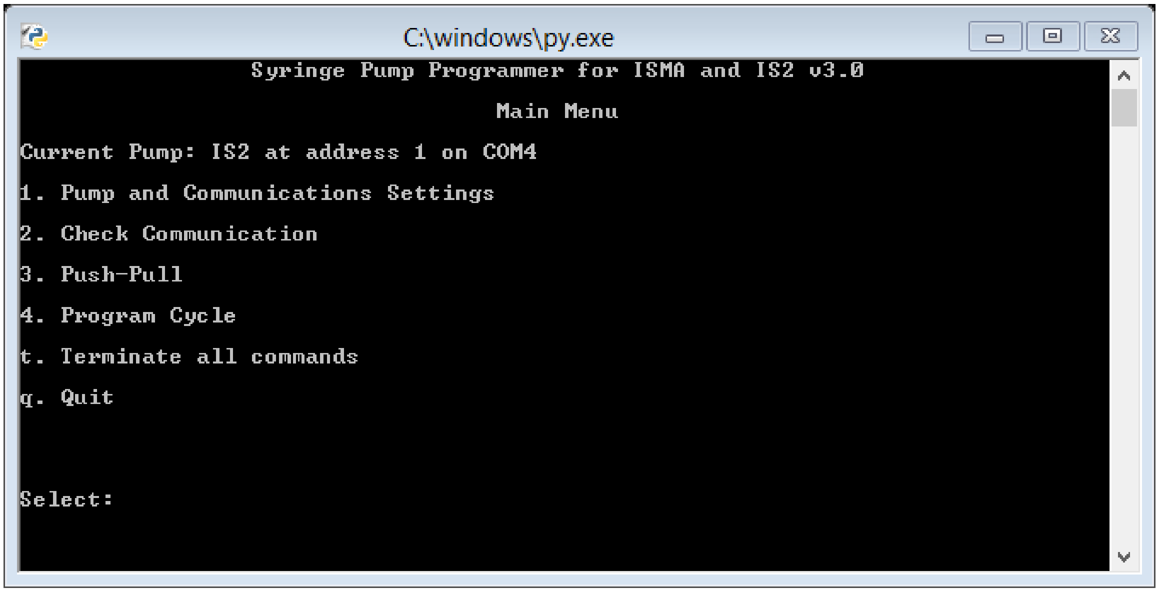
APPENDIX C

SUPPLEMENTARY MATERIAL FOR CHAPTER 3

C.1 SOURCE CODE FOR PUMP PROGRAM

A program to control the syringe pump was developed for the Python 3.4 environment and is usable from both Microsoft Windows and common UNIX (e.g., Apple MacOS X and various Linux) operating systems. The program provides an interface for creating and saving instructions for the programmable syringe pump in the IS2, communicating these instructions, and terminating programs already in progress. The programmable syringe pump targeted here is based on a Lin Engineering SilverPak 17C Integrated Motor/Driver/Controller. The program takes user parameters for the syringe pump (stroke length, speed, and time between strokes) and writes a machine-formatted command string to the submersible onboard controller. This program provides an interface only; it is not resident in the submersible and the interfacing computer can be disconnected from the submersible while the program is being executed.

The program is available for download at http://iroll.sdf.org/PUBS/pumper.py



```
                 Syringe Pump Programmer for ISMA and IS2 v3.0
                                    Main Menu
Current Pump: IS2 at address 1 on COM4
1. Pump and Communications Settings
2. Check Communication
3. Push-Pull
4. Program Cycle
t. Terminate all commands
q. Quit


Select:
```

Figure C.1. Screenshot of pump interface software developed for long time-base, low-flow sampling.

Figure C.2. Surface package providing power and communication channels to the submersible sampler. A weather-tight case houses a 24-V battery pack, a USB interface for communication, and spool of 9-channel cable driving the submersible unit (Photograph by the author).

Table C.1

List of materials in the in situ sampler (IS2) fluid train as used in the present study. Materials are listed in order of fluid contact.

Component	Material	Supplier
Tubing, 1.6 mm ID, 3.2 mm OD	PTFE[a]	Cole Parmer, Vernon Hills, IL
Union, 3.2 mm OD tubing	PTFE	Swagelok, Solon, OH
Union, 3.2 mm OD to 0.5 inch NPT	PTFE	Swagelok, Solon, OH
6-channel fluid splitter	PTFE	In House
Female luer to 10/32 NPT	Nylon	Cole Parmer, Vernon Hills, IL
Luer check valve, female-male	SAN[b], silicone	Nordson Corp., Westlake, OH
Female luer tee	Nylon	Cole Parmer, Vernon Hills, IL
Tubing, 0.89 mm ID	Viton	Cole Parmer, Vernon Hills, IL
Syringe, 5 mL, barrel and piston	Glass	Cadence Inc., Staunton, VA
SPE Cartridge, syringe barrel	Polypropylene	App. Separations, Allentown, PA
Liquid storage bag (optional)	Fluoropolymer	Am. Durafilm, Holliston, MA

Notes. (a) Polytetrafluoroethylene, (b) Styrene-acrylonitrile resin

Table C.2

Concentration of chromium (total) derived from six pairs simultaneously loaded and eluted solid phase extraction cartridges (1.0 g SIR-100 resin loaded with 400 mL of 1.1 mg/L Cr solution at 1 mL/min).

Sample	Chromium (total, mg/L)	Difference (%)
1A	8.5	--
1B[a]	5.1	40
2A	7.7	--
2B	7.8	(1.2)
3A	8.6	--
3B	8.8	(2.3)
4A	7.1	--
4B	8.0	(13)
5A	7.7	--
5B	5.1	34
6A	4.7	--
6B	4.8	(2.1)
	AVERAGE	15

Notes. (a) Sample loading was noted to be interrupted.

Table C.3

Sampling rates and volumes determined for six channels of the IS2 during field study at Naval Air Station North Island.

Channel	Sampling Rate, R_S (mL/day)	Total Volume (mL)
1	14.8	415
2	15.4	430
3	16.0	447
4	16.6	464
5	15.8	444
6	15.6	437
AVERAGE	15.7	440
STANDARD DEVIATION	0.545	15.0
RSD	3.41	3.41

APPENDIX D

PRELIMINARY STUDIES: FEASIBILITY OF IN SITU SOLID PHASE EXTRACTION

The work in this appendix has been published in an altered format in *Final Report: Cost-Effective, Ultra Sensitive Groundwater Monitoring for Site Remediation and Management* (Halden & Roll 2015).

D.1 INTRODUCTION

Laboratory studies were performed to demonstrate the feasibility of the method, and in anticipation of any field studies. This was typically accomplished by replicating aspects of field studies on the bench with groundwater sourced from relevant sites, with the site contaminants intact or spiked with a simulated contaminant mixture. In addition to bench studies before any field demonstration, there were a series of early field deployments of the *in situ* sampler (IS2) to test the mechanism and develop the standard operating procedure for field work.

D.2 FEASIBILITY STUDY: CARTRIDGE OBSTRUCTION OR FOULING

An early concern expressed by project reviewers was the potential for the available solid phase extraction (SPE) cartridges to become obstructed by sediments accumulated during large-volume extractions.

D.2.1 Methods and Materials. A common SPE cartridge (Strata C-18; Phenomenex, Torrance, California, USA) was loaded with large volumes of groundwater over a period of three weeks. Three cartridges were loaded with unfiltered groundwater, while an additional three cartridges received water filtered by glass fiber filters (Acrodisk AP-4523T; Pall GmbH, Dreieich, DE).

A peristaltic pump of the type used in early embodiments of the IS2 was programmed to deliver groundwater at 5 ml/hr to the cartridges. The groundwater samples used for the test were taken from perchlorate-contaminated aquifer to which the author had access, and which were known to contain significant amounts of salts (Table D.1).

Table D.1.

Example anion concentrations in groundwater used for feasibility studies.

Anion	Concentration (mg/L)
Chloride	210 ± 4
Sulfate	45 ± 1
Nitrate	7.9 ± 0.3

D.2.2 Results. Over 23 days, the average flow rate decreased by approximately 20% in all cartridges (Figure D.1). This was not a significant impediment, and much of this decrease can also be attributed to wearing of the peristaltic pump tubing. Measurements of the pressure at the entrance to each cartridge were also taken (Figure D.2), and it was noted that the filters appeared to be accumulating enough particulate matter to influence the pressure in the cartridges, the absolute difference between the two groups was not very large.

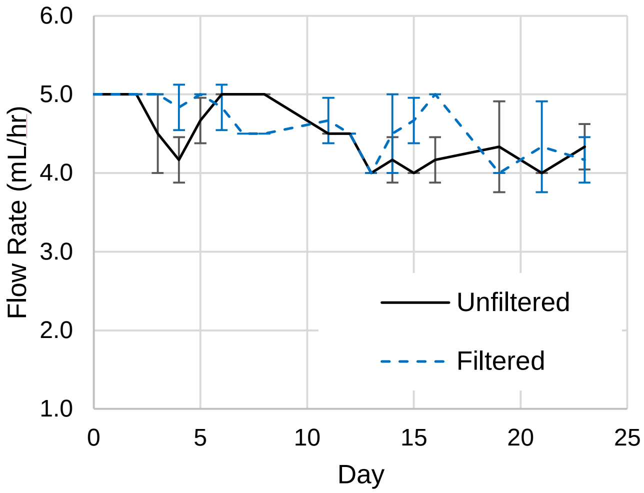


Figure D.1. Flow characteristics through C-18 SPE cartridges over several weeks.

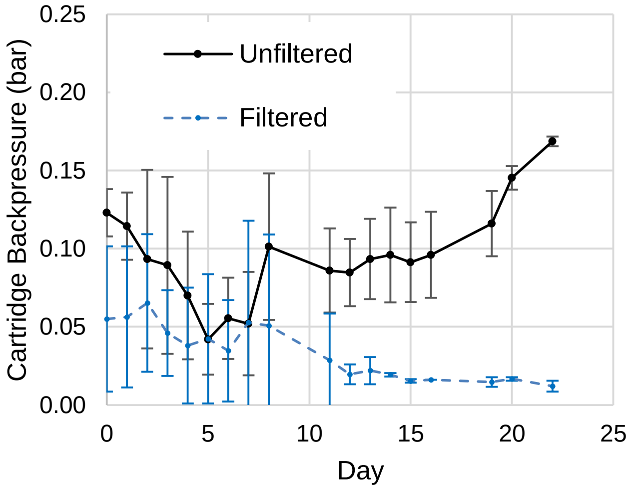


Figure D.2. Pressure observed upstream of C-18 cartridges over several weeks.

While groundwater is not typically turbid, surface waters contain significantly greater quantities of particulate matter, particularly suspended organic matter. Visible accumulation of suspended organic matter upon the entrance frit of SPE cartridges (Figure D.3) has been noted in high-turbidity waters, but there is no evidence that this accumulation restricted flow through the cartridge appreciably.

Figure D.3. Accumulation of surface water sediments upon the frit of an SPE cartridge (Photograph by Samuel Supowit).

D.3 FEASIBILITY STUDY: CONTAMINANT APPLICABILITY

A number of compounds were screened for applicability to the IS2 method from either contaminated site samples or from groundwater spiked to environmentally relevant contaminant concentrations. Contaminants that were screened in the laboratory include those listed in Table D.2.

Table D.2.

Compounds screened in the laboratory for IS2 sampling.

Chemical Name	CAS No.	Typical Uses	Relevant Properties
Perchlorate ion	14797-73-0	Oxidizer	Anion
Chromate ion	11104-59-9	Metal Plating	Anion
Benzene	71-43-2	Fuel Component	Aromatic
Toluene	108-88-3	Fuel Component	Aromatic
Ethylbenzene	100-41-4	Fuel Component	Aromatic
Isopropylbenzene	98-82-8	Fuel Component	Aromatic
Parabens (methyl-, ethyl-, propyl-, butyl-, benzyl-)	Multiple	Antimicrobial	Aromatic (Benzoates)
Naphthalene	91-20-3	Fuel Component	Polycyclic Aromatic
Dibenzofuran	132-64-9	Insecticide	Polycyclic Aromatic
Fipronil	120068-37-3	Insecticide	Polycyclic Aromatic
Triclosan	3380-34-5	Antimicrobial	Polycyclic Aromatic
Triclocarban	101-20-2	Antimicrobial	Polycyclic Aromatic
Bisphenol-A	80-05-7	Plastic Monomer	Polycyclic Aromatic
Tetrabromobisphenol-A	79-94-7	Flame Retardant	Polycyclic Aromatic
N-Nitrosamines	Multiple	Disinfection Byproducts	Nitrosamine

D.4 FEASIBILITY STUDY: PERCHLORATE

The perchlorate anion is an emerging contaminant frequently associated with spent munitions. A preliminary study targeting perchlorate was conducted using groundwater samples acquired from an impacted aquifer in the Salt River Valley near Mesa, Arizona. The site is characterized by good hydraulic conductivity with water at 187 ft bgs in fluvial material consisting of silty sands and gravels, poorly and well-graded sands, clayey sands, and clayey gravels. Access to the aquifer was provided by a four-inch monitoring well screened from 109 to 259 ft bgs.

D.4.1 Methods and Materials. Groundwater samples were recovered from the well for characterization and bench development of the IS2 sampler using a bailer or Hydrasleeve (GeoInsight, Las Cruces, New Mexico), transferred to 1-liter HDPE sample bottles, and refrigerated at 4 °C until used. Aliquots of the groundwater samples were filtered and characterized for a suite of anions by ion chromatography; the most significant components are presented in Table D.1.

Perchlorate can be effectively removed from aqueous solution by applying ion exchange SPE (Medina, Larson, Extine, & Bednar, 2005). Interference is a challenge when perchlorate exists as a minor co-contaminate in solution with other anions at concentrations 3 to 5 orders of magnitude greater, as the weakly-charged perchlorate ion often exhibits lower affinity for the ion exchange media. For this trial, Strata X-AW 3 mL/500 mg (Phenomenex, Torrence, California) weak anion exchange cartridges were selected. Bench trials showed that when presented with high ionic-strength solutions, this resin exhibited relatively low capacity before breakthrough (less than 10 mL at the salt concentrations noted in Table D.1) but also offered favorable selectivity and recovery for perchlorate. Quantification was performed on an ion chromatograph (IC) with a conductivity detector. This method is described in detail by EPA Method 314.0, “Determination of Perchlorate in Drinking Water Using Ion Chromatography.”

To simulate a sampling event with the IS2, a bench model of the unit was prepared with three sampling channels (for replicate samples), each with three SPE cartridges in series (increasing sorbent volume to offset the low specific capacity of the sorbent). A fourth channel (bypass) was prepared to collect a composite sample of the same groundwater without solid phase extraction. The bench unit was programmed to deliver 50 mL of groundwater to each channel. The volumes of water actually delivered per channel were recorded, and the liquid composite sample from the bypass was directly characterized for perchlorate. The concentration detected in the bypass sample and the volumes delivered to the sorbent channels were used to estimate the mass delivered to the sorbent channels, and subsequently to estimate the recovery for perchlorate in this experiment.

D.4.2 Results. A mass balance for the collection of perchlorate is presented in Table D.3. The average recovery was determined to be 77%.

Table D.3.

Mass balance data for feasibility experiments with perchlorate.

Sample	Processed Volume (mL)	Groundwater Perchlorate Concentration (µg/L)	Recovery (%)
Unprocessed Groundwater	49.7	30.2	-
SPE Eluate	47.2 (±3.3)	23.2 (±0.7)[a]	77 (±2)

Notes. (a) Calculated from eluate concentration and processed volume.

In the field, the IS2 sampler is configured either to capture the processed water post-processing or to discharge it back into the well. While the bench trial captured effluent, the programmed dispensation volume values (which differed from the actual values by a few percent) could be used to determine the concentration values that a user of the device would have reported had the device been configured for effluent discharge. A comparison of the data which was generated in each mode is presented in Figure D.4, illustrating the propagation of the error in the dispense volume values. Though the uncertainty increases, the results are not significantly different.

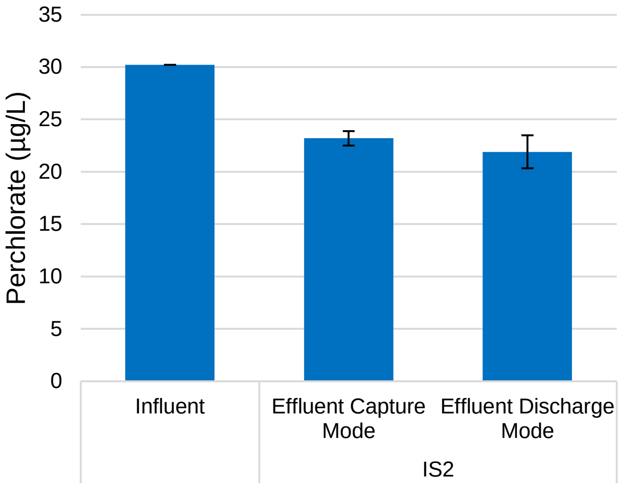


Figure D.4. Comparison perchlorate concentration data quality observed during preliminary study using effluent capture or effluent discharge mode.

Due to the relatively large sorbent bed volumes required to effectively process such a low volume of groundwater, the present method was determined to be a poor match for an IS2 demonstration. As the purpose of this project was to demonstrate the application of standard methods in the field, further development of an applicable perchlorate method was determined to be outside of the project scope.

D.5 FEASIBILITY STUDY: INSTRUMENT DEPLOYMENT

Though the perchlorate extraction chemistry demonstrated here was not efficient enough for field use, the site presented an opportunity to test the mechanical operation of the IS2 sampler *in situ* and to develop the deployment procedures. The sampler was deployed twice to a depth of 190 ft bgs. This experience informed the standard operating procedure; most importantly, that while the device as currently embodied can be manually inserted to significant depths, an experienced well support crew with a boom truck (crane) should be employed for depths greater than 60 ft. This experience also lead to the development of the cable management system and significant changes to the internal layout of the device, making it more robust.

D.6 REFERENCES

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APPENDIX E

PRELIMINARY STUDY: IN SITU SOLID-PHASE EXTRACTION OF JET PROPELLANT COMPONENTS IN GROUNDWATER

The work in this appendix has been published in an altered format in *Final Report: Cost-Effective, Ultra Sensitive Groundwater Monitoring for Site Remediation and Management* (Halden & Roll 2015).

E.1 INTRODUCTION

Petroleum fuels are complex mixtures of compounds featuring a wide range of vapor pressures and solubilities in water. Analysis of groundwater samples with, for example, headspace techniques, provides high resolution, time-discrete information about dissolved contamination. However, these techniques are vulnerable to variability introduced by sample handling, for example, the method by which samples are originally decanted, or the storage of filled sample vials with headspace (Parker & Britt, 2012). Additionally, temporal variations as a result of well pumping or tidal effects might lead discrete sampling to miss transient concentration changes, in turn affecting the reliability of estimates of contaminant flux.

The *In Situ* Sampler (IS2) is an offline solid phase extraction system designed for groundwater sampling. The volume of water processed and the time duration of the sampling event are programmable, enabling both time-averaged sampling and significant *in situ* collection and enrichment of target analytes in the device on the selective sample media presented. Here, an application of the method is presented for a site impacted by aviation fuel, the former Williams Air Force Base near Mesa, Arizona.

E.2 SITE CHARACTERISTICS

E.2.1 Hydrogeology. The former Williams AFB (Figure E-1) covers more than 4,000 acres of land located in Mesa, Arizona, approximately 30 miles southeast of Phoenix.

Williams AFB operated as a flight training school from 1941 until the base was closed under the Base Realignment and Closure (BRAC) in 1993. Much of the converted property is now in use by public and private entities including the Phoenix-Mesa Gateway Airport and the Arizona State University (ASU) Polytechnic Campus.

Figure E.1: Former William AFB, Mesa, AZ. The site of the former fuel storage tanks (ST-12) is highlighted ("Former Williams AFB," 2011).

The Former Fuel Tank Storage Site (ST-12) in Operating Unit (OU)-2 was operated from 1977 to 1989. This site was impacted by up to 1.5 million gallons of JP-4 from leaking underground storage tanks (USTs) and their associated fuel distribution lines. Free-phase recovery, a thermal-extraction pilot plant, and soil vapor extraction have all been performed at this site, which continues to be impacted by BTEX fuel components, benzene and toluene in particular. Contaminants monitored at ST-12 include total petroleum hydrocarbons (TPH, both diesel and gasoline associated), volatile organic compounds (VOCs, including benzene, toluene, and naphthalene), semi-volatile organic compounds (SVOCs), and metals (AFCEE, 2011b).

The former Williams AFB lies at an altitude of 1340 ft on generally flat land that slopes gently to the west. The underlying geology is characterized by alluvium-filled depression. The six geological layers underlying the site, from deepest to shallowest, are crystalline rocks, extrusive rocks, Red Unit, Lower Unit, Middle Unit and the Upper Unit. These layers are described briefly in Tables E.1 and E.2. The Upper, Middle, Lower, and Red Units contain the regional groundwater supplies, with the Middle Unit being the largest and most productive water-bearing unit in the basin. Beneath the former Williams AFB, the Upper and Middle Units are separated by a clay aquitard. Water levels declined markedly during the 1960s and 1970s, but have been rising steadily since 1978. The primary (Middle Unit) aquifer is presently approximately 290 ft bgs (AFCEE, 2011a; AMEC Environment & Infrastructure, 2013).

E.2.2 Well Selection and Contaminants of Interest. Extensive light, non-aqueous phase liquid (LNAPL) contamination at this site resulted from long-term leakage from a former fuel tank farm, and was subsequently smeared by rising groundwater levels. From this source, a dissolved plume of fuel components spreads largely to the west. The contamination is limited to the upper unit by the aquitard that separates it from the middle unit, thus sparing the most important units for water in the community.

In consultation with the site remediation contractor, two wells were selected as potential demonstration sites in the periphery of the plume: W11 and W36 (Table E.3). Considerations included the expected concentration of fuel components, ease of access

Table E.1

Geological formations underlying the Former Williams AFB.

Unit	Deposition	Depth (ft bgs)	Aquifer Type	Stratigraphic Lithology
Upper Unit	Open basin; channel, floodplain, alluvial fan	0 to 300	Unconfined	Gravel, sand, silt, clay.
Middle Unit	Closed basin; playa, alluvial fan, fluvial	<100 to 1,000	Unconfined, leaky confined	Silt, siltstone, silty sand, gravel.
Lower Unit	Closed basin; playa, alluvial fan, fluvial	600 to 10,000+	Unconfined, leaky confined	Clay, silt, mudstone, evaporites, sandstone, gravel, conglomerate, andesitic basalt.
Red Unit	Alluvial fan, fluvial	2,000+	Confined	Breccia, conglomerate, sandstone, siltstone, local basaltic to rhyolitic flows and pyroclastic rocks.

Notes. (AFCEE, 2011a; AMEC Environment & Infrastructure, 2013).

Table E.2

Subunits of the Upper Unit.

Unit	Depth (ft bgs)	Aquifer Type	Stratigraphic Lithology
Vadose Zone	0 - 160	Unconfined	Interbedded coarse- and fine-grained layers
Cobble Zone	145-160	Unconfined	Coarse-grained, permeable
Upper Water Bearing Zone	160-195	Unconfined	Interbedded coarse- and fine-grained layers
Low Permeability Zone	195-210	Unconfined	Silty clay layer
Lower Saturated Zone	210-240	Semi-confined	Interbedded coarse-and fine-grained layers (coarsest and most permeable unit)
Aquitard	240-300	Semi-confined	Low permeability clay

Notes. (AFCEE, 2011a; AMEC Environment & Infrastructure, 2013).

for the investigators, and type of instruments already deployed (e.g., water depth transducers). Both wells are in the upper, unconfined unit, approximately 250 ft deep and screened below 200 ft.

Table E.3

Construction details for candidate wells.

Well	Year Built	Diameter (in)	Depth to Screen (ft bgs)	Screen Length (ft)	Depth to Water (ft)
W11	1989	4	208	40	153 (2010)
W36	2010	4	210	35	156 (2012)

The site is impacted by a significant amount of LNAPL, which is present in many of the monitoring wells. A visit to the site to collect preliminary samples found LNAPL present in W11. The demonstration was therefore performed in W36, since it lies exclusively in the dissolved plume. If W36 had been rendered unavailable by remediation activities at the site, W11 could possibly have been substituted provided that care was taken to remove the free product as much as possible before introducing the IS2 sampler.

The primary analyte of interest was naphthalene, a polycyclic aromatic hydrocarbon (PAH). Naphthalene is considered semivolatile, and the aromatic rings in this compound make it a good candidate for solid phase extraction with a styrene divinylbenzene (SDB). Two other common fuel components (Table E.4) were identified from groundwater sampling data as secondary analytes of interest. It was noted that lighter and more volatile compounds would likely be more difficult to recover effectively than heavier and less volatile compounds

Table E.4

Analytes of interest at Former Williams AFB.

Analyte	CAS No.	MW	BP[a] (°C at 1 atm)	Log K_{OW}[a]
Ethylbenzene	100-41-4	106	136	3.21
Isopropylbenzene	98-82-8	120	152	3.56
Napthalene	91-20-3	128	222	3.45

Notes. (a) Values predicted by the ACD/Labs Suite.

E.3 MATERIALS AND METHODS

E.3.1 The In Situ Sampler. The primary instrument used in this study is an offline solid phase extraction system packaged in a submersible for deployment in groundwater monitoring wells, the *in situ sampler* or IS2. The embodiment of the sampler used in this study was comprised of a peristaltic pump driving three fluid channels, an array of SPE cartridges (three channels, two cartridges in serial on each channel, Figure E.2), and an array of 500 mL fluoropolymer bags for effluent capture, all housed in a 3.5 inch-diameter stainless steel shell.

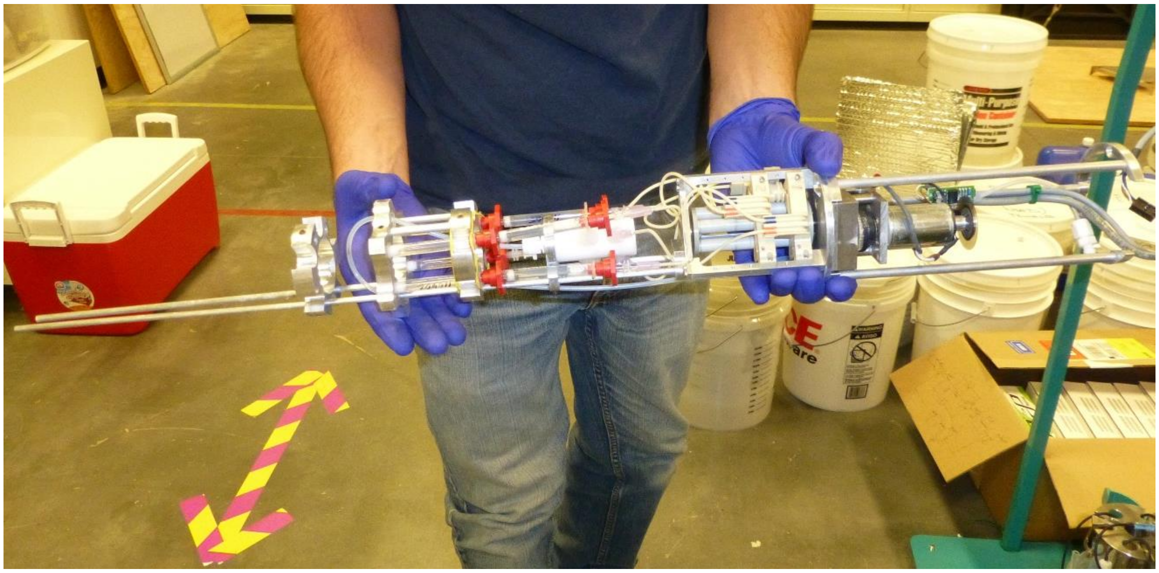

Figure E.2: The IS2 Sampler Deployed at the Former Williams AFB. From left to right: a framework for attaching accessories, an array of six SPE cartridges, and a peristaltic pump driving three channels (Photograph by Sara Murch).

This submersible was suspended from a steel cable secured to the wellhead and connected by a multi-channel waterproof electronic cable to a surface package comprised of a 12-V lead-acid battery pack, a DC-AC inverter, and a pump power supply and controller (Figure E.3).

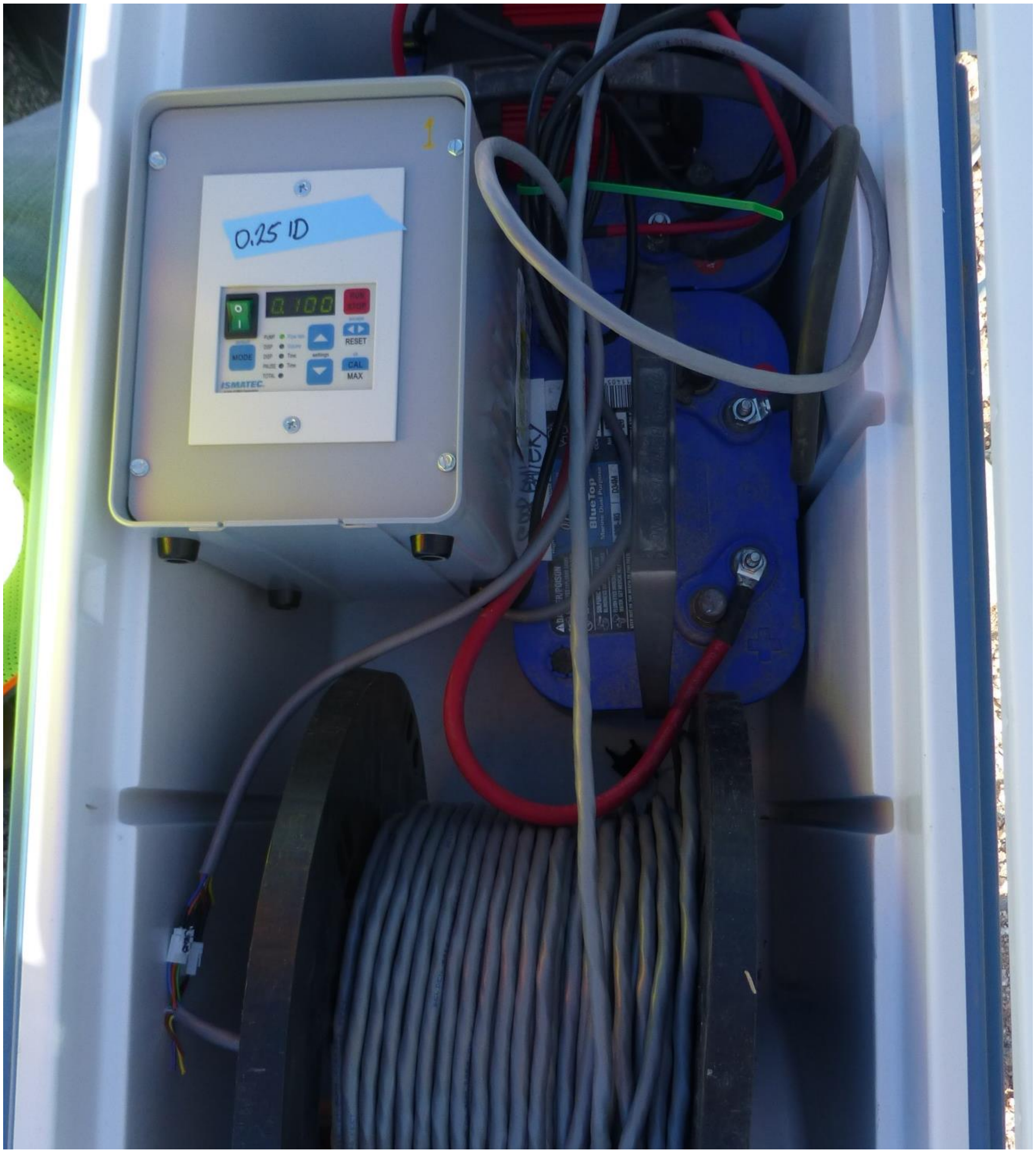

Figure E.3: Surface package for IS2 demonstration at Former Williams AFB. Clockwise from upper left: controller, inverter, batteries, and cable spool (Photograph by the author).

E.3.2 Preparation of Sampling Materials. EPA methods 8260B and 8270C were selected for quantification of these compounds from liquid samples. The types and quantity of samples to be taken were selected according to quality control requirements, and a sampling matrix (Table E.5) generated.

Table E.5

Sampling matrix for IS2 demonstration at Former Williams AFB.

Container	Quantification	Data Type	Quantity	Holding Time (days)[a]
Strata SDB-L, 1mL, 25 mg (Appendix C.1)	ASU GC-MS (Appendix C.2)	Quantification	3	14
		Breakthrough	3	14
		Field Blank	1	14
		Trip Blank	1	14
		Method Blank	1	N/A
40 mL VOA Vial	EPA 8260B	Quantification	3	14
	EPA 8260B	Trip Blank	1	14
1 L Amber Bottle	EPA 8270C	Quantification	2	14

Notes. (a) Maximum allowable holding time at 4°C.

The method used to extract aromatic fuel components from groundwater was as follows, and was executed using the materials described in Table E.6.

1. Condition cartridge with 8 mL neat methanol by gravity feed without allowing the resin bed to run dry.
2. Rinse with 1 mL ultrapure water by gravity feed and fill the syringe with 1 mL ultrapure water.
3. Cap cartridges and refrigerate until installation in sampler.
4. Uncap and install cartridges in sampler.
5. Load 200 mL groundwater at up to 1 mL/min.
6. Uninstall cartridges from sampler; cap and refrigerate until analysis.

7. Uncap and dry under gentle vacuum for no more than five minutes.

8. Elute with 2 mL neat hexane.

Table E.6

Materials for SPE method for aromatic fuel components.

Material	Supplier
Strata SDB-L Styrene Divinylbenzene Polymer, (100 µm, 260A) 25 mg/1 mL	Phenomenex (Torrance, CA, USA)
Water, 18 MΩ·cm (ultrapure)	ELGA LabWater (High Wycombe, UK)
Methanol, reagent-grade	Sigma-Aldrich (St. Louis, MO, USA)
Hexane, MS-grade	Sigma-Aldrich (St. Louis, MO, USA)

The cartridges were loaded into the sampling mechanism prior to delivery to the site. Three sampling channels were prepared, each with a quantification cartridge in series with a breakthrough detection cartridges. A field blank cartridge was loaded into the sampler but not connected to a liquid handling line. A trip blank cartridge was carried with the team to the site but not loaded into the sampler. A method blank was retained at the laboratory and later loaded with deionized water to provide a method blank.

E.3.3 GC-MS Method for Aromatic Fuel Components. An Agilent DB-5MS column (30 m-long x 0.250 mm-inner diameter x 25 µm-film thickness) was used with helium carrier gas regulated by flow at 1.2 ml/min. A 0.5 µL aliquot of the hexane extract was injected into an Agilent split/splitless inlet held at 280°C in splitless mode. The column temperature at injection was held for three minutes at 50 °C, increased by 2 °C/min to 66 °C, increased by 10 °C/min to 160 °C, and finally increased by 40 °C to 300 °C and held for six minutes. The first quadrupole of the MS operated in single ion monitoring (SIM) mode from 3 min post-injection to the end of the oven cycle, scanning the *m/z* values presented in Table E.7 with a dwell time of 100 ms and a gain of 10. The source temperature was set at 230 °C and the ionization energy was -70 eV. After every injection, the autosampler syringe was cleaned sequentially with neat methanol and hexane.

Table E.7

Ions monitored in GC-MS method for aromatic fuel components.

Analyte	m/z
Ethylbenzene	91 and 109
Isopropylbenzene	105 and 120
Napthalene	128

3.3.3 Sampling. The IS2 sampler was inserted to 200 ft bgs (50 ft underwater) on November 7, 2013 (Table E.8). Due to the depth required to reach the target formation at this site, the use of a crane was required for safety in handling the large weight of cable (Figure E.4). The sampler was programmed to continuously dispense 250 mL over 24 hours, and was recovered and returned to the laboratory shortly after the control unit indicated that the dispensation had been completed. The sample cartridges were removed from the sampler, capped to prevent them from drying out, and refrigerated until they were extracted. The volume of water collected in the storage bag for each channel was determined gravimetrically and recorded. After allowing the well to equilibrate for another day, a disposable bailer was used to collect the liquid samples, which were immediately returned to a commercial laboratory for analysis. An additional data set was obtained from the site remediation contractor, who sampled the same well with a gas-operated bladder pump on November 4, 2013. The depths at which each group of samples were obtained is presented in Table E.8.

Table E.8

Dates and sampling depths for demonstration at Former Williams AFB.

Method	Sampling Date	Screen Depth (ft bgs)	Sampling Depth (ft bgs)
Bladder Pump	11-04-2014	210	215
IS2	11-07-2014	210	200
Bailer	11-08-2014	210	155

Figure E.4: Deployment of the IS2 sampler into W36 at the former Williams AFB, November 2013. Clockwise from left: 1) insertion of the sampler by crane, 2) the surface package being programmed, and 3) the deployment hanger on the well head (Photographs by Sara Murch).

E.4 RESULTS AND DISCUSSION

E.4.1 Metered Operation of Pump. The volume of water dispensed per channel was greater than expected (Table E.9), particularly for channel 3. This was a significant concern, as the sampler is intended to be used in some cases without effluent capture, and inaccurate dispensation would significantly affect the results generated in those cases. This source of this dispensation error was investigated, as a number of conditions can result in poor accuracy including pump wear, communication problems via the control line, overpressure of the inlet, and initial calibration error.

Table E.9

Fluid volume dispensed by the IS2 peristaltic pump.

Channel	Programmed (mL)	Dispensed (mL)
1	250	285
2	250	268
3	250	470

Overpressure of the pump from the inlet was determined to be the problem by placing the sampling unit in a pressure chamber and observing empty effluent bags for evidence of passive flow through the pump. The inlet pressure was varied over the range of pressures that the submersible would have experienced during the deployment and it was determined that pressure as low as 5 psi (approximately 12 ft of head) could cause leakage of the pumps. While it is believed that this would not be a problem in a flow-through system (*i.e.* one where the inlet and outlet of the pump are at equal pressure, as on the surface), this conclusion lead directly to a redesign of the pump system to improve tolerance of inlet overpressure, through the application of a reciprocating pump with check valves.

E.4.2 Analysis of Samples. After elution, the concentration of concentrations of naphthalene, ethylbenzene, and isopropylbenzene in the eluate were determined by GC-MS. It was noted that the concentration of the analytes in the breakthrough cartridges was below the limit of detection, indicating that the quantification cartridge had sufficient capacity to collect all of the analyte mass without breakthrough. The quality control cartridges were also noted to contain no detectable concentration of the analytes.

For all of the analytes, a reporting limit was determined by multiplying the lowest calibrated concentration for the analyte by the ratio of the prescribed volume of the eluate (2 mL) to the prescribed volume of water programmed for the channel (250 mL). With the lowest calibrated concentration for all three analytes being 10 μg/L, the reporting limit for the IS2 is conservatively estimated at approximately 0.1 μg/L for this study. Compared to the reporting limits provided by the commercial labs which analyzed liquid samples, this is a significant improvement of between 1 and 2 orders of magnitude (Figures E.5 and E.6).

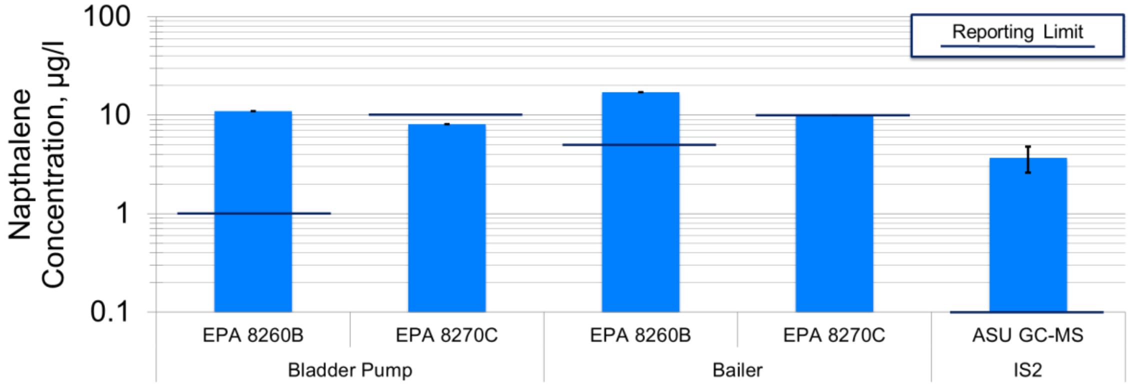

Figure E.5: Concentrations and reporting limits of naphthalene. Values were reported for demonstration well using samples generated by a bladder pump, a bailer, and the IS2, and analysis by EPA methods 8260B, 8270C, and the ASU GC-MS method.

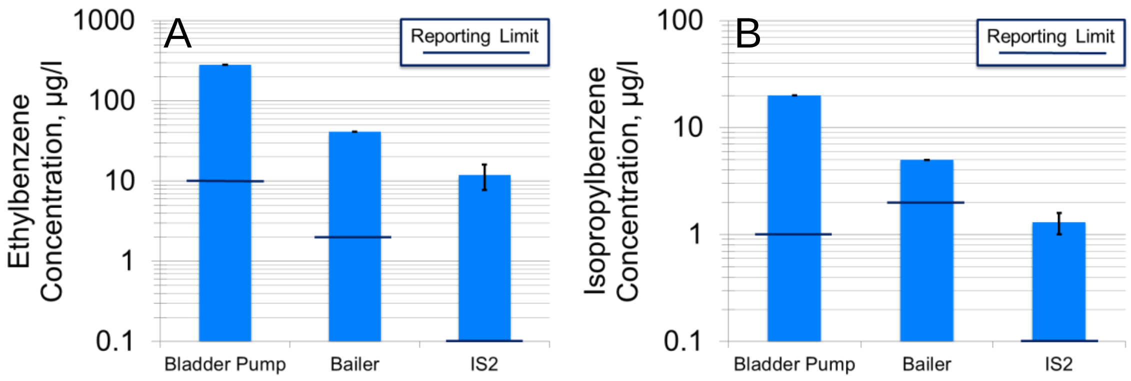

Figure E.6: Concentrations and reporting limits of ethylbenzene and isopropylbenzene. Values for ethylbenzene (A) and isopropylbenzene (B) were reported for demonstration well using samples generated by a bladder pump, a bailer, and the IS2, and analysis by EPA methods 8260B and the ASU GC-MS method.

The concentration of the primary analyte of interest, naphthalene, reported by the IS2 and the ASU GC-MS method was observed to be within an order of magnitude of that reported by samples generated by the bladder pump and the bailer, and analyzed by EPA methods 8260B and 8270C. As expected, the reported values of the more volatile ethylbenzene and isopropylbenzene were lower. However, it should be noted that there are many inconsistencies between the methods that could drive these differences, including the date of sample collection, the depth of sample collection, the use of a 24-hour composite sample vs time-discrete sampling, material differences between the samplers, and handling techniques of the different sampling teams.

While the recovery of the IS2 technique could likely be improved, the differences between techniques and the natural variation in concentration between sampling events make direct comparison of concentrations a challenge. It should be noted that for concentrations below the reporting limit of the other techniques, the IS2 should have a significant advantage.

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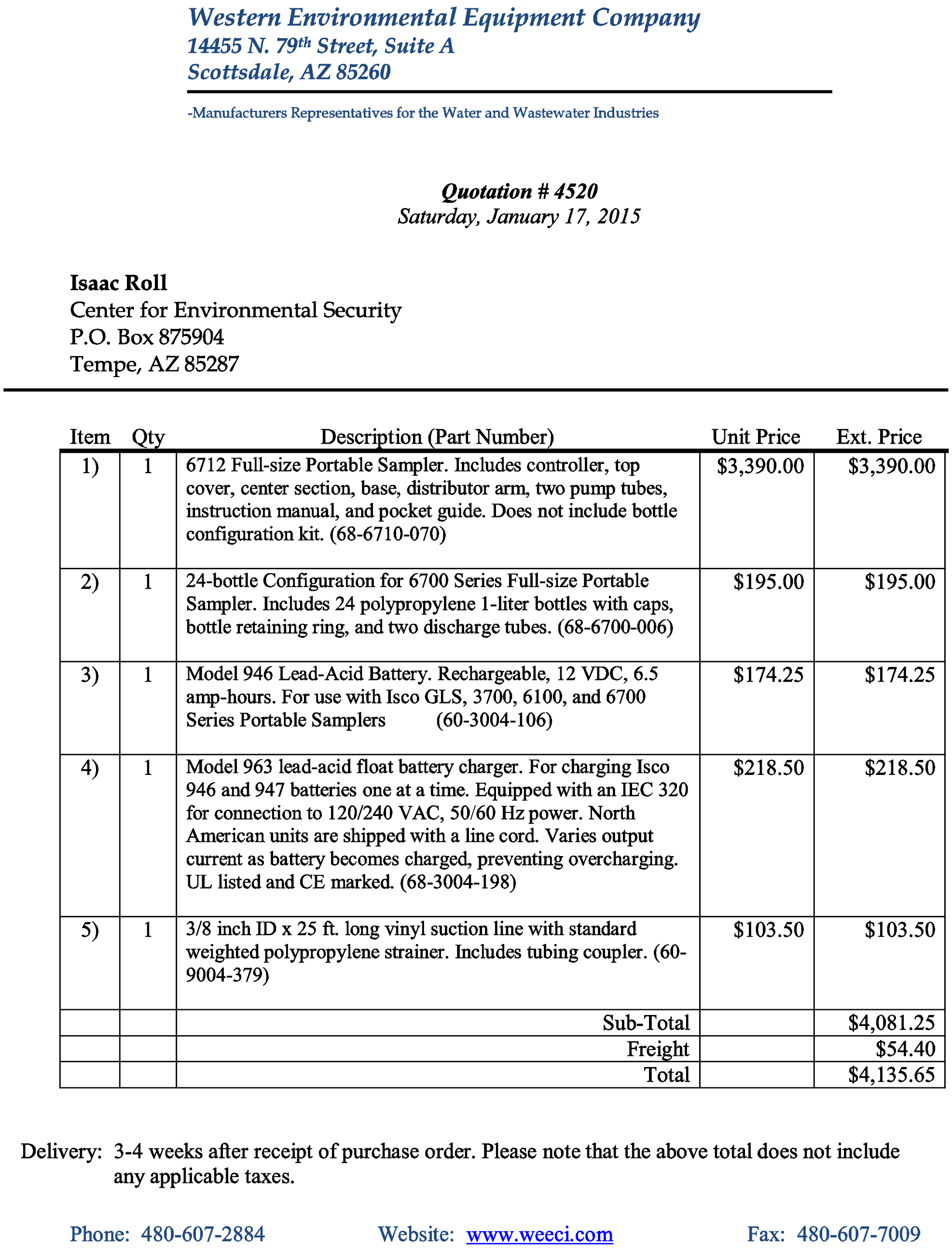
APPENDIX F

SUPPLEMENTARY MATERIAL FOR CHAPTER 4



Western Environmental Equipment Company
14455 N. 79th Street, Suite A
Scottsdale, AZ 85260

-Manufacturers Representatives for the Water and Wastewater Industries

Quotation # 4520
Saturday, January 17, 2015

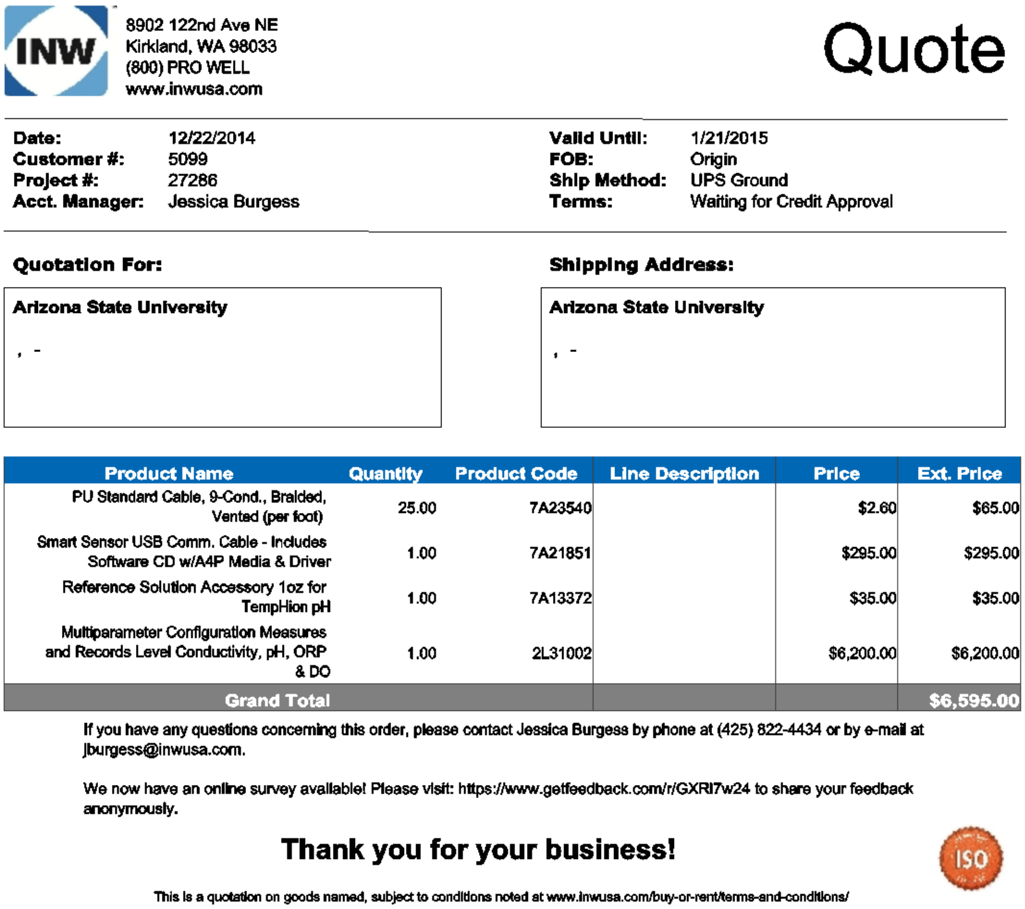
Isaac Roll
Center for Environmental Security
P.O. Box 875904
Tempe, AZ 85287

Item	Qty	Description (Part Number)	Unit Price	Ext. Price
1)	1	6712 Full-size Portable Sampler. Includes controller, top cover, center section, base, distributor arm, two pump tubes, instruction manual, and pocket guide. Does not include bottle configuration kit. (68-6710-070)	$3,390.00	$3,390.00
2)	1	24-bottle Configuration for 6700 Series Full-size Portable Sampler. Includes 24 polypropylene 1-liter bottles with caps, bottle retaining ring, and two discharge tubes. (68-6700-006)	$195.00	$195.00
3)	1	Model 946 Lead-Acid Battery. Rechargeable, 12 VDC, 6.5 amp-hours. For use with Isco GLS, 3700, 6100, and 6700 Series Portable Samplers (60-3004-106)	$174.25	$174.25
4)	1	Model 963 lead-acid float battery charger. For charging Isco 946 and 947 batteries one at a time. Equipped with an IEC 320 for connection to 120/240 VAC, 50/60 Hz power. North American units are shipped with a line cord. Varies output current as battery becomes charged, preventing overcharging. UL listed and CE marked. (68-3004-198)	$218.50	$218.50
5)	1	3/8 inch ID x 25 ft. long vinyl suction line with standard weighted polypropylene strainer. Includes tubing coupler. (60-9004-379)	$103.50	$103.50
		Sub-Total		$4,081.25
		Freight		$54.40
		Total		$4,135.65

Delivery: 3-4 weeks after receipt of purchase order. Please note that the above total does not include any applicable taxes.

Phone: 480-607-2884 Website: www.weeci.com Fax: 480-607-7009

Figure F.1. Quote for ISCO fluid autosampler.



8902 122nd Ave NE
Kirkland, WA 98033
(800) PRO WELL
www.inwusa.com

Quote

Date:	12/22/2014	**Valid Until:**	1/21/2015
Customer #:	5099	**FOB:**	Origin
Project #:	27286	**Ship Method:**	UPS Ground
Acct. Manager:	Jessica Burgess	**Terms:**	Waiting for Credit Approval

Quotation For:

Arizona State University

, -

Shipping Address:

Arizona State University

, -

Product Name	Quantity	Product Code	Line Description	Price	Ext. Price
PU Standard Cable, 9-Cond., Braided, Vented (per foot)	25.00	7A23540		$2.60	$65.00
Smart Sensor USB Comm. Cable - Includes Software CD w/A4P Media & Driver	1.00	7A21851		$295.00	$295.00
Reference Solution Accessory 1oz for TempHion pH	1.00	7A13372		$35.00	$35.00
Multiparameter Configuration Measures and Records Level Conductivity, pH, ORP & DO	1.00	2L31002		$6,200.00	$6,200.00
Grand Total					**$6,595.00**

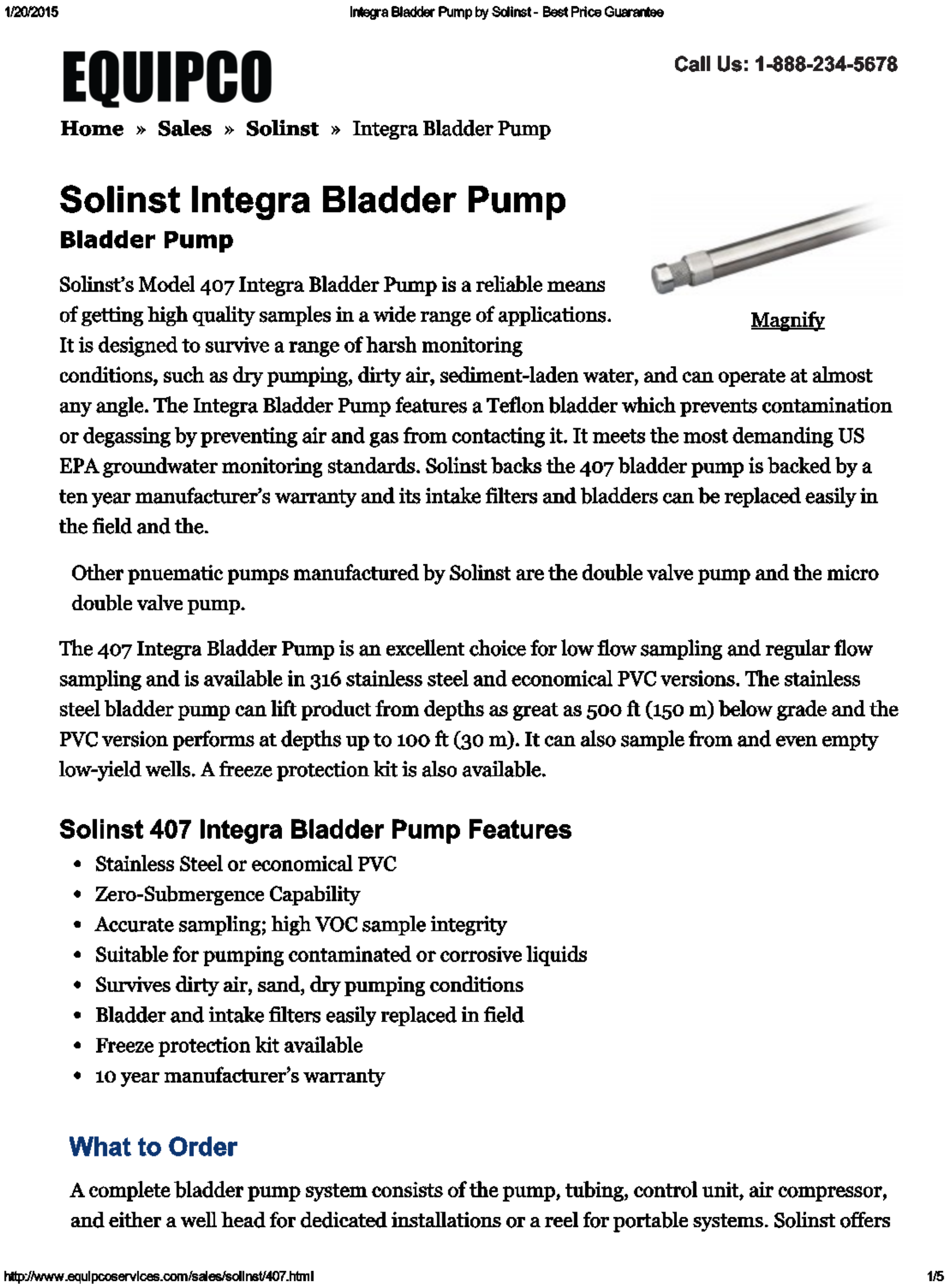
If you have any questions concerning this order, please contact Jessica Burgess by phone at (425) 822-4434 or by e-mail at jburgess@inwusa.com.

We now have an online survey available! Please visit: https://www.getfeedback.com/r/GXRI7w24 to share your feedback anonymously.

Thank you for your business!

This is a quotation on goods named, subject to conditions noted at www.inwusa.com/buy-or-rent/terms-and-conditions/

Figure F.2. Quote for multi-parameter data logger.



1/20/2015 Integra Bladder Pump by Solinst - Best Price Guarantee

EQUIPCO

Call Us: 1-888-234-5678

Home » **Sales** » **Solinst** » Integra Bladder Pump

Solinst Integra Bladder Pump

Bladder Pump

Magnify

Solinst's Model 407 Integra Bladder Pump is a reliable means of getting high quality samples in a wide range of applications. It is designed to survive a range of harsh monitoring conditions, such as dry pumping, dirty air, sediment-laden water, and can operate at almost any angle. The Integra Bladder Pump features a Teflon bladder which prevents contamination or degassing by preventing air and gas from contacting it. It meets the most demanding US EPA groundwater monitoring standards. Solinst backs the 407 bladder pump is backed by a ten year manufacturer's warranty and its intake filters and bladders can be replaced easily in the field and the.

> Other pnuematic pumps manufactured by Solinst are the double valve pump and the micro double valve pump.

The 407 Integra Bladder Pump is an excellent choice for low flow sampling and regular flow sampling and is available in 316 stainless steel and economical PVC versions. The stainless steel bladder pump can lift product from depths as great as 500 ft (150 m) below grade and the PVC version performs at depths up to 100 ft (30 m). It can also sample from and even empty low-yield wells. A freeze protection kit is also available.

Solinst 407 Integra Bladder Pump Features

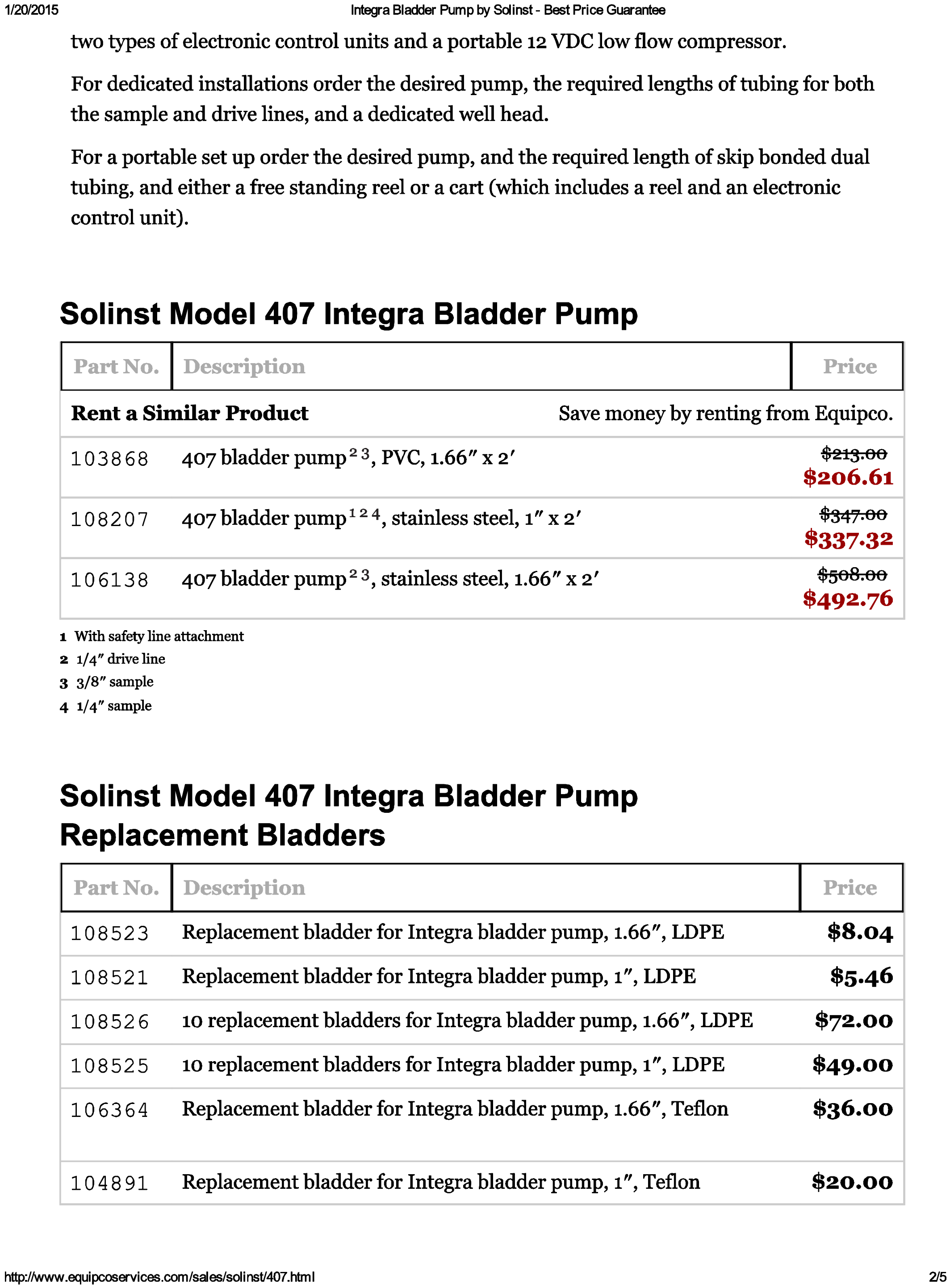
- Stainless Steel or economical PVC
- Zero-Submergence Capability
- Accurate sampling; high VOC sample integrity
- Suitable for pumping contaminated or corrosive liquids
- Survives dirty air, sand, dry pumping conditions
- Bladder and intake filters easily replaced in field
- Freeze protection kit available
- 10 year manufacturer's warranty

What to Order

A complete bladder pump system consists of the pump, tubing, control unit, air compressor, and either a well head for dedicated installations or a reel for portable systems. Solinst offers

http://www.equipcoservices.com/sales/solinst/407.html 1/5

Figure F.3-A. First page of Solinst 407 price sheet.



1/20/2015 Integra Bladder Pump by Solinst - Best Price Guarantee

two types of electronic control units and a portable 12 VDC low flow compressor.

For dedicated installations order the desired pump, the required lengths of tubing for both the sample and drive lines, and a dedicated well head.

For a portable set up order the desired pump, and the required length of skip bonded dual tubing, and either a free standing reel or a cart (which includes a reel and an electronic control unit).

Solinst Model 407 Integra Bladder Pump

Part No.	Description	Price
Rent a Similar Product	Save money by renting from Equipco.	
103868	407 bladder pump[2,3], PVC, 1.66″ x 2′	~~$213.00~~ **$206.61**
108207	407 bladder pump[1,2,4], stainless steel, 1″ x 2′	~~$347.00~~ **$337.32**
106138	407 bladder pump[2,3], stainless steel, 1.66″ x 2′	~~$508.00~~ **$492.76**

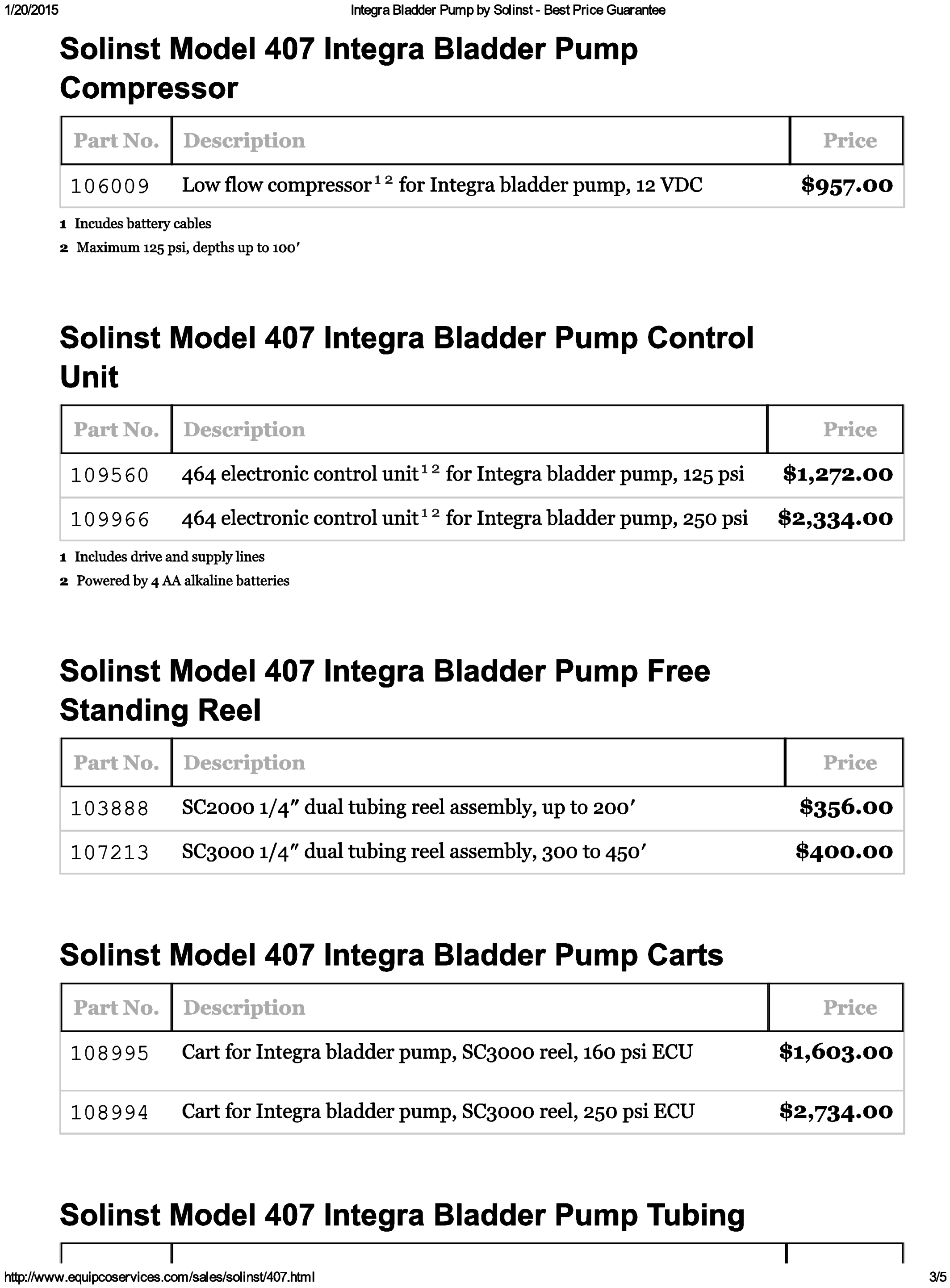
1 With safety line attachment
2 1/4″ drive line
3 3/8″ sample
4 1/4″ sample

Solinst Model 407 Integra Bladder Pump Replacement Bladders

Part No.	Description	Price
108523	Replacement bladder for Integra bladder pump, 1.66″, LDPE	**$8.04**
108521	Replacement bladder for Integra bladder pump, 1″, LDPE	**$5.46**
108526	10 replacement bladders for Integra bladder pump, 1.66″, LDPE	**$72.00**
108525	10 replacement bladders for Integra bladder pump, 1″, LDPE	**$49.00**
106364	Replacement bladder for Integra bladder pump, 1.66″, Teflon	**$36.00**
104891	Replacement bladder for Integra bladder pump, 1″, Teflon	**$20.00**

http://www.equipcoservices.com/sales/solinst/407.html 2/5

Figure F.3-B. Second page of Solinst 407 price sheet.



1/20/2015 Integra Bladder Pump by Solinst - Best Price Guarantee

Solinst Model 407 Integra Bladder Pump Compressor

Part No.	Description	Price
106009	Low flow compressor[1] [2] for Integra bladder pump, 12 VDC	**$957.00**

1 Incudes battery cables
2 Maximum 125 psi, depths up to 100′

Solinst Model 407 Integra Bladder Pump Control Unit

Part No.	Description	Price
109560	464 electronic control unit[1] [2] for Integra bladder pump, 125 psi	**$1,272.00**
109966	464 electronic control unit[1] [2] for Integra bladder pump, 250 psi	**$2,334.00**

1 Includes drive and supply lines
2 Powered by 4 AA alkaline batteries

Solinst Model 407 Integra Bladder Pump Free Standing Reel

Part No.	Description	Price
103888	SC2000 1/4″ dual tubing reel assembly, up to 200′	**$356.00**
107213	SC3000 1/4″ dual tubing reel assembly, 300 to 450′	**$400.00**

Solinst Model 407 Integra Bladder Pump Carts

Part No.	Description	Price
108995	Cart for Integra bladder pump, SC3000 reel, 160 psi ECU	**$1,603.00**
108994	Cart for Integra bladder pump, SC3000 reel, 250 psi ECU	**$2,734.00**

Solinst Model 407 Integra Bladder Pump Tubing

http://www.equipcoservices.com/sales/solinst/407.html 3/5

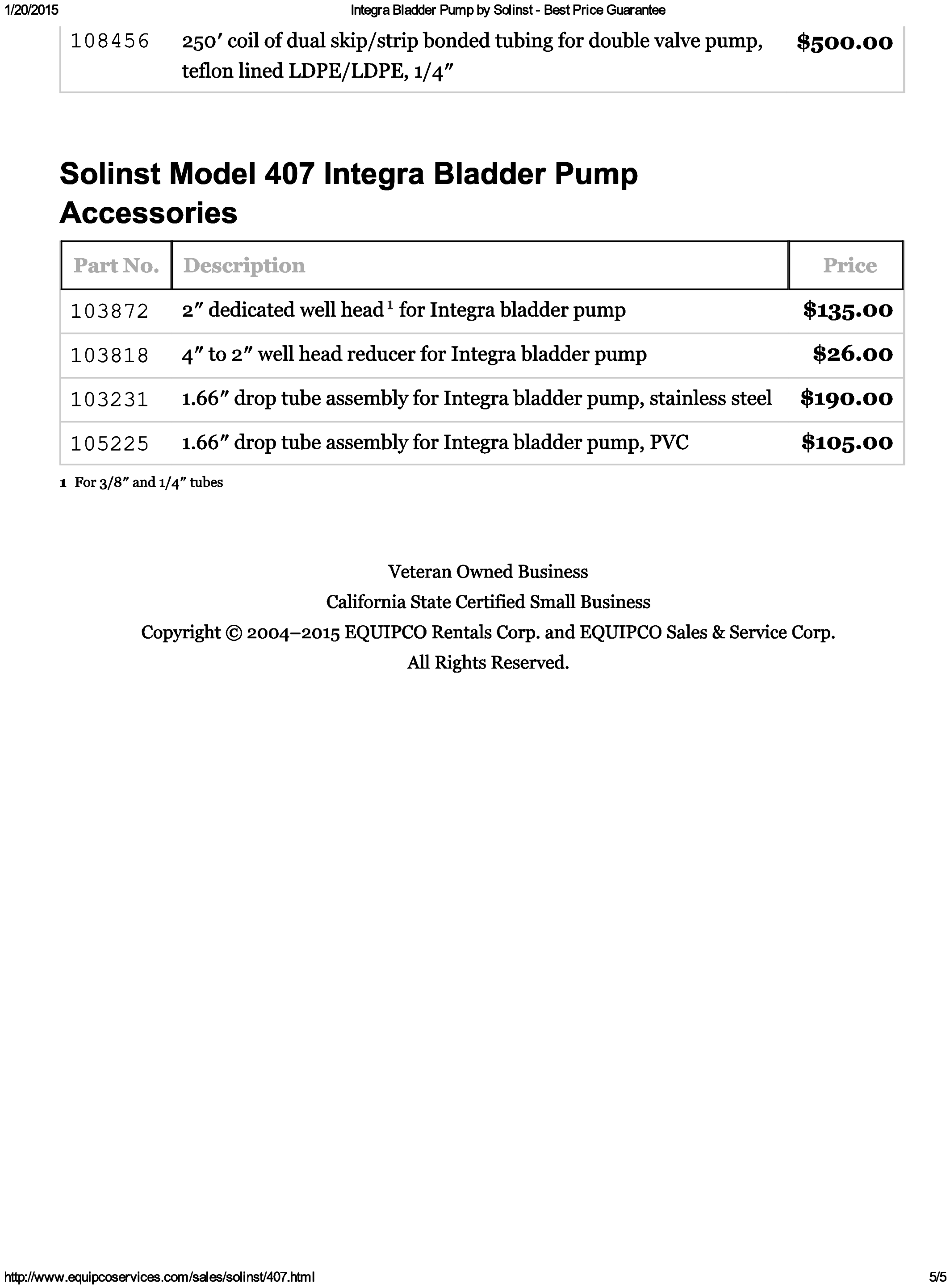
Figure F.3-C. Third page of Solinst 407 price sheet.

1/20/2015 Integra Bladder Pump by Solinst - Best Price Guarantee

Part No.	Description	Price
109465	100′ coil of tubing for Integra bladder pump, natural LDPE, 1/4″ x 0.17″	~~$19.00~~ $18.43
109464	250′ coil of tubing for Integra bladder pump, natural LDPE, 1/4″ x 0.17″	~~$48.00~~ $46.56
109463	500′ coil of tubing for Integra bladder pump, natural LDPE, 1/4″ x 0.17″	~~$96.00~~ $93.12
109457	100′ coil of tubing for Integra bladder pump, red LDPE, 1/4″ x 0.17″	$20.00
109456	250′ coil of tubing for Integra bladder pump, red LDPE, 1/4″ x 0.17″	$42.00
109455	500′ coil of tubing for Integra bladder pump, red LDPE, 1/4″ x 0.17″	$84.00
109471	100′ coil of tubing for Integra bladder pump, LDPE, 3/8″ x 1/4″	$30.00
109470	250′ coil of tubing for Integra bladder pump, LDPE, 3/8″ x 1/4″	$75.00
109469	500′ coil of tubing for Integra bladder pump, LDPE, 3/8″ x 1/4″	$150.00
109468	100′ coil of tubing for Integra bladder pump, teflon lined LDPE, 3/8″ x 1/4″	$144.00
109466	250′ coil of tubing for Integra bladder pump, teflon lined LDPE, 3/8″ x 1/4″	$360.00
109454	100′ coil of tubing for Integra bladder pump, teflon lined LDPE, 1/4″ x 0.17″	$124.00
109444	250′ coil of tubing for Integra bladder pump, teflon lined LDPE, 1/4″ x 0.17″	$310.00
109430	100′ coil of dual skip/strip bonded tubing for Integra bladder pump, LDPE/LDPE, 1/4″	$71.00
109429	250′ coil of dual skip/strip bonded tubing for Integra bladder pump, LDPE/LDPE, 1/4″	$178.00
109421	500′ coil of dual skip/strip bonded tubing for Integra bladder pump, LDPE/LDPE, 1/4″	$356.00
109402	100′ coil of dual skip/strip bonded tubing for Integra bladder pump, teflon lined LDPE/LDPE, 1/4″	$192.00

http://www.equipcoservices.com/sales/solinst/407.html 4/5

Figure F.3-D. Fourth page of Solinst 407 price sheet.



108456	250′ coil of dual skip/strip bonded tubing for double valve pump, teflon lined LDPE/LDPE, 1/4″	**$500.00**

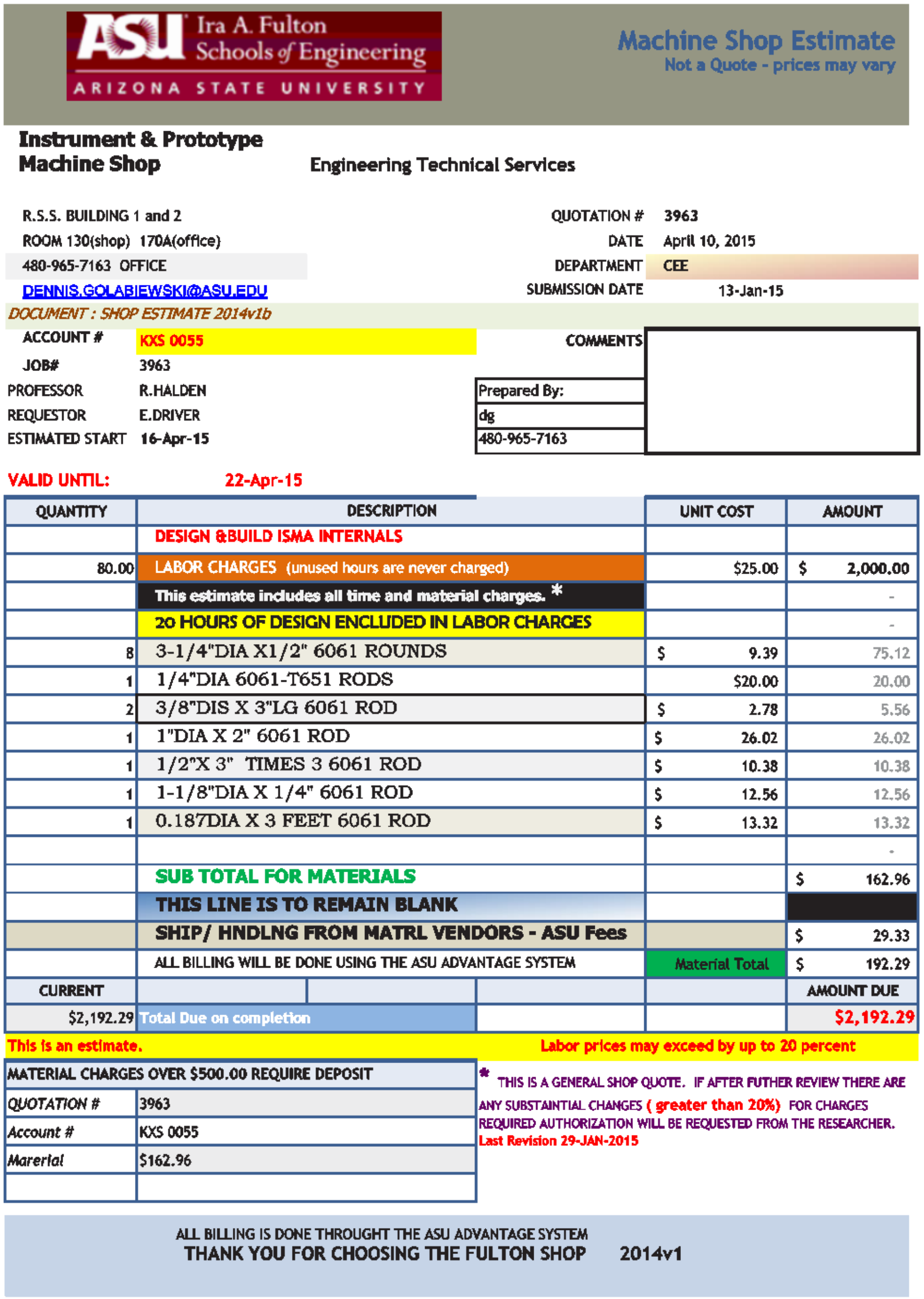
Solinst Model 407 Integra Bladder Pump Accessories

Part No.	Description	Price
103872	2″ dedicated well head[1] for Integra bladder pump	**$135.00**
103818	4″ to 2″ well head reducer for Integra bladder pump	**$26.00**
103231	1.66″ drop tube assembly for Integra bladder pump, stainless steel	**$190.00**
105225	1.66″ drop tube assembly for Integra bladder pump, PVC	**$105.00**

[1] For 3/8″ and 1/4″ tubes

Veteran Owned Business
California State Certified Small Business

Figure F.3-E. Fifth page of Solinst 407 price sheet.



ASU Ira A. Fulton Schools of Engineering
ARIZONA STATE UNIVERSITY

Machine Shop Estimate
Not a Quote - prices may vary

Instrument & Prototype Machine Shop

Engineering Technical Services

R.S.S. BUILDING 1 and 2
ROOM 130(shop) 170A(office)
480-965-7163 OFFICE
DENNIS.GOLABIEWSKI@ASU.EDU

QUOTATION #	3963
DATE	April 10, 2015
DEPARTMENT	CEE
SUBMISSION DATE	13-Jan-15

DOCUMENT : SHOP ESTIMATE 2014v1b

ACCOUNT #	KXS 0055
JOB#	3963
PROFESSOR	R.HALDEN
REQUESTOR	E.DRIVER
ESTIMATED START	16-Apr-15

COMMENTS

Prepared By:
dg
480-965-7163

VALID UNTIL: 22-Apr-15

QUANTITY	DESCRIPTION	UNIT COST	AMOUNT
	DESIGN &BUILD ISMA INTERNALS		
80.00	LABOR CHARGES (unused hours are never charged)	$25.00	$ 2,000.00
	This estimate includes all time and material charges. *		-
	20 HOURS OF DESIGN ENCLUDED IN LABOR CHARGES		-
8	3-1/4"DIA X1/2" 6061 ROUNDS	$ 9.39	75.12
1	1/4"DIA 6061-T651 RODS	$20.00	20.00
2	3/8"DIS X 3"LG 6061 ROD	$ 2.78	5.56
1	1"DIA X 2" 6061 ROD	$ 26.02	26.02
1	1/2"X 3" TIMES 3 6061 ROD	$ 10.38	10.38
1	1-1/8"DIA X 1/4" 6061 ROD	$ 12.56	12.56
1	0.187DIA X 3 FEET 6061 ROD	$ 13.32	13.32
			-
	SUB TOTAL FOR MATERIALS		$ 162.96
	THIS LINE IS TO REMAIN BLANK		
	SHIP/ HNDLNG FROM MATRL VENDORS - ASU Fees		$ 29.33
	ALL BILLING WILL BE DONE USING THE ASU ADVANTAGE SYSTEM	Material Total	$ 192.29
CURRENT			AMOUNT DUE
$2,192.29	Total Due on completion		$2,192.29

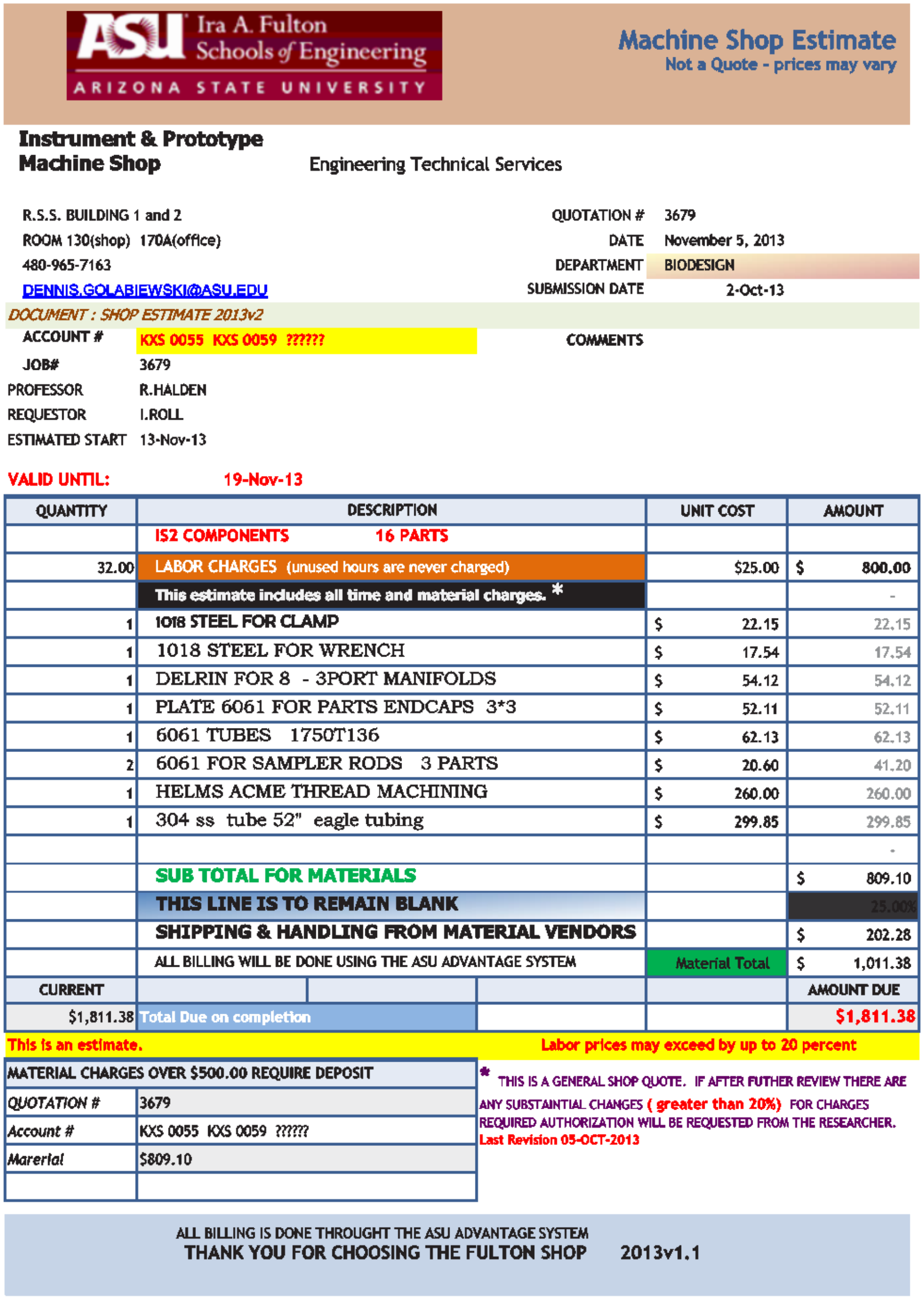
This is an estimate. Labor prices may exceed by up to 20 percent

MATERIAL CHARGES OVER $500.00 REQUIRE DEPOSIT	
QUOTATION #	3963
Account #	KXS 0055
Marerial	$162.96

* THIS IS A GENERAL SHOP QUOTE. IF AFTER FUTHER REVIEW THERE ARE ANY SUBSTAINTIAL CHANGES (greater than 20%) FOR CHARGES REQUIRED AUTHORIZATION WILL BE REQUESTED FROM THE RESEARCHER.
Last Revision 29-JAN-2015

ALL BILLING IS DONE THROUGHT THE ASU ADVANTAGE SYSTEM
THANK YOU FOR CHOOSING THE FULTON SHOP 2014v1

Figure F.4. Quote for the construction of a programmable syringe pump and internal accessories for the IS2.



ASU Ira A. Fulton Schools of Engineering
ARIZONA STATE UNIVERSITY

Machine Shop Estimate
Not a Quote - prices may vary

Instrument & Prototype
Machine Shop
Engineering Technical Services

R.S.S. BUILDING 1 and 2
ROOM 130(shop) 170A(office)
480-965-7163
DENNIS.GOLABIEWSKI@ASU.EDU

QUOTATION #	3679
DATE	November 5, 2013
DEPARTMENT	BIODESIGN
SUBMISSION DATE	2-Oct-13

DOCUMENT : SHOP ESTIMATE 2013v2

ACCOUNT #	KXS 0055 KXS 0059 ??????	COMMENTS
JOB#	3679	
PROFESSOR	R.HALDEN	
REQUESTOR	I.ROLL	
ESTIMATED START	13-Nov-13	

VALID UNTIL: **19-Nov-13**

QUANTITY	DESCRIPTION	UNIT COST	AMOUNT
	IS2 COMPONENTS 16 PARTS		
32.00	LABOR CHARGES (unused hours are never charged)	$25.00	$ 800.00
	This estimate includes all time and material charges. *		-
1	1018 STEEL FOR CLAMP	$ 22.15	22.15
1	1018 STEEL FOR WRENCH	$ 17.54	17.54
1	DELRIN FOR 8 - 3PORT MANIFOLDS	$ 54.12	54.12
1	PLATE 6061 FOR PARTS ENDCAPS 3*3	$ 52.11	52.11
1	6061 TUBES 1750T136	$ 62.13	62.13
2	6061 FOR SAMPLER RODS 3 PARTS	$ 20.60	41.20
1	HELMS ACME THREAD MACHINING	$ 260.00	260.00
1	304 ss tube 52" eagle tubing	$ 299.85	299.85
			-
	SUB TOTAL FOR MATERIALS		$ 809.10
	THIS LINE IS TO REMAIN BLANK		25.00%
	SHIPPING & HANDLING FROM MATERIAL VENDORS		$ 202.28
	ALL BILLING WILL BE DONE USING THE ASU ADVANTAGE SYSTEM	Material Total	$ 1,011.38
CURRENT			AMOUNT DUE
$1,811.38	Total Due on completion		$1,811.38

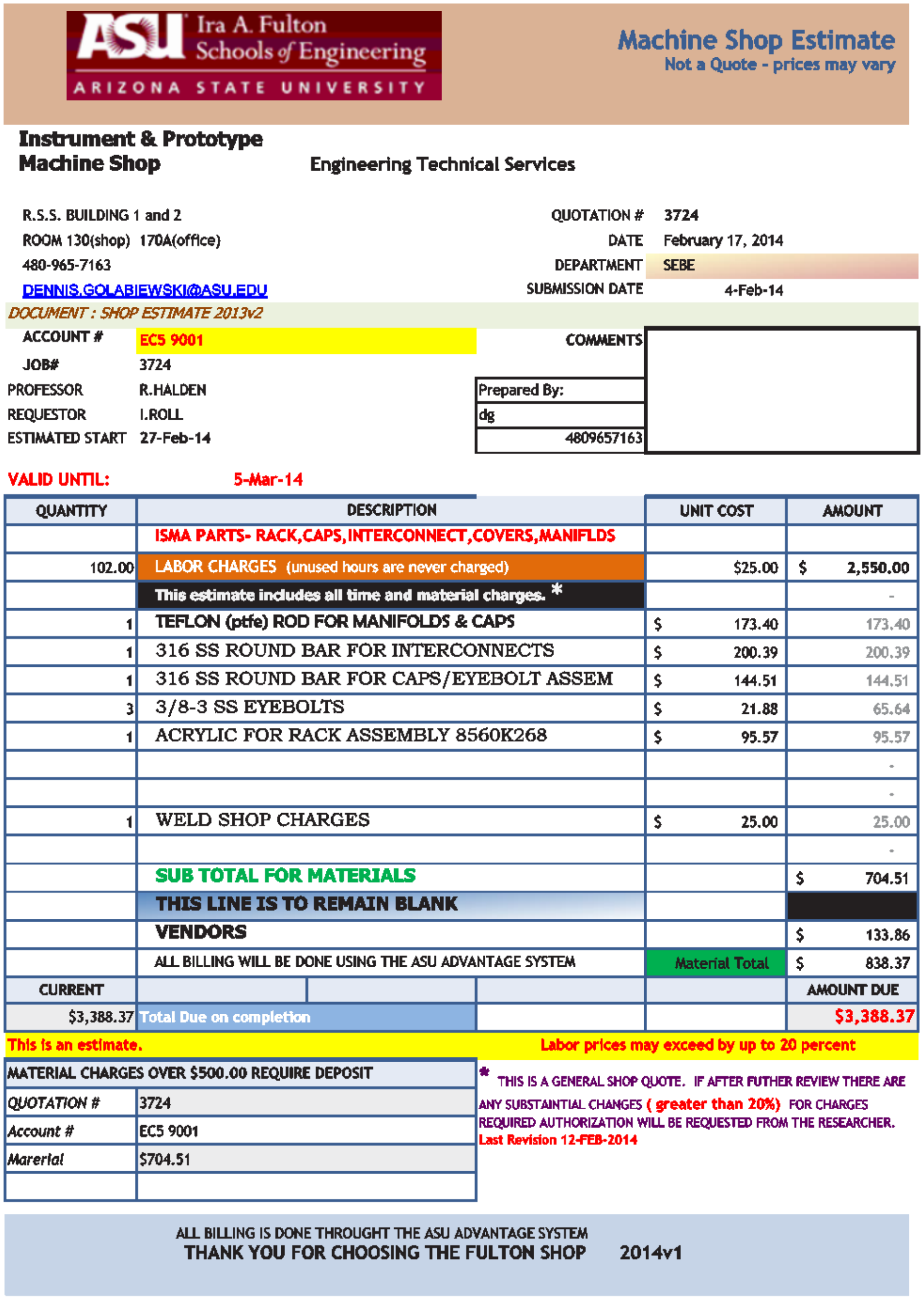
This is an estimate. Labor prices may exceed by up to 20 percent

MATERIAL CHARGES OVER $500.00 REQUIRE DEPOSIT	
QUOTATION #	3679
Account #	KXS 0055 KXS 0059 ??????
Marerial	$809.10

* THIS IS A GENERAL SHOP QUOTE. IF AFTER FUTHER REVIEW THERE ARE ANY SUBSTAINTIAL CHANGES (greater than 20%) FOR CHARGES REQUIRED AUTHORIZATION WILL BE REQUESTED FROM THE RESEARCHER.
Last Revision 05-OCT-2013

ALL BILLING IS DONE THROUGHT THE ASU ADVANTAGE SYSTEM
THANK YOU FOR CHOOSING THE FULTON SHOP 2013v1.1

Figure F.5. Quote for the construction of parts, including the watertight shell, for the IS2.



Ira A. Fulton Schools of Engineering
ARIZONA STATE UNIVERSITY

Machine Shop Estimate
Not a Quote - prices may vary

Instrument & Prototype
Machine Shop
Engineering Technical Services

R.S.S. BUILDING 1 and 2
ROOM 130(shop) 170A(office)
480-965-7163
DENNIS.GOLABIEWSKI@ASU.EDU

QUOTATION # 3724
DATE February 17, 2014
DEPARTMENT SEBE
SUBMISSION DATE 4-Feb-14

DOCUMENT : SHOP ESTIMATE 2013v2

ACCOUNT # EC5 9001
JOB# 3724
PROFESSOR R.HALDEN
REQUESTOR I.ROLL
ESTIMATED START 27-Feb-14

COMMENTS

Prepared By:
dg
4809657163

VALID UNTIL: 5-Mar-14

QUANTITY	DESCRIPTION	UNIT COST	AMOUNT
	ISMA PARTS- RACK,CAPS,INTERCONNECT,COVERS,MANIFLDS		
102.00	LABOR CHARGES (unused hours are never charged)	$25.00	$ 2,550.00
	This estimate includes all time and material charges. *		-
1	TEFLON (ptfe) ROD FOR MANIFOLDS & CAPS	$ 173.40	173.40
1	316 SS ROUND BAR FOR INTERCONNECTS	$ 200.39	200.39
1	316 SS ROUND BAR FOR CAPS/EYEBOLT ASSEM	$ 144.51	144.51
3	3/8-3 SS EYEBOLTS	$ 21.88	65.64
1	ACRYLIC FOR RACK ASSEMBLY 8560K268	$ 95.57	95.57
			-
			-
1	WELD SHOP CHARGES	$ 25.00	25.00
			-
	SUB TOTAL FOR MATERIALS		$ 704.51
	THIS LINE IS TO REMAIN BLANK		
	VENDORS		$ 133.86
	ALL BILLING WILL BE DONE USING THE ASU ADVANTAGE SYSTEM	Material Total	$ 838.37
CURRENT			AMOUNT DUE
$3,388.37	Total Due on completion		$3,388.37

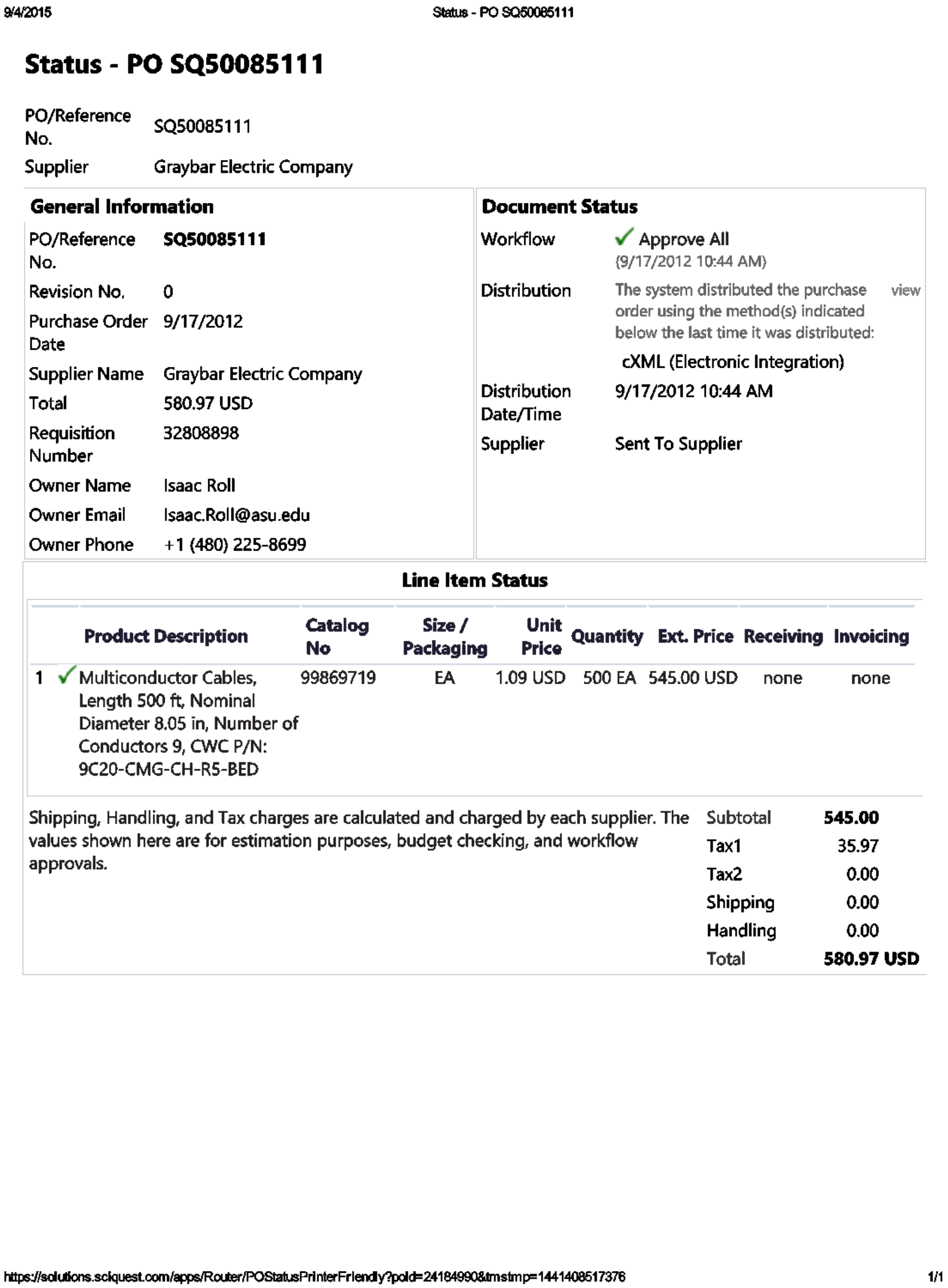
This is an estimate. Labor prices may exceed by up to 20 percent

MATERIAL CHARGES OVER $500.00 REQUIRE DEPOSIT	
QUOTATION #	3724
Account #	EC5 9001
Marerial	$704.51

* THIS IS A GENERAL SHOP QUOTE. IF AFTER FUTHER REVIEW THERE ARE ANY SUBSTAINTIAL CHANGES (greater than 20%) FOR CHARGES REQUIRED AUTHORIZATION WILL BE REQUESTED FROM THE RESEARCHER.
Last Revision 12-FEB-2014

ALL BILLING IS DONE THROUGHT THE ASU ADVANTAGE SYSTEM
THANK YOU FOR CHOOSING THE FULTON SHOP 2014v1

Figure F.6. Quote for the construction of parts, including the shell end caps, for the IS2.



9/4/2015 Status - PO SQ50085111

Status - PO SQ50085111

PO/Reference No.	SQ50085111
Supplier	Graybar Electric Company

General Information

PO/Reference No.	**SQ50085111**
Revision No.	0
Purchase Order Date	9/17/2012
Supplier Name	Graybar Electric Company
Total	580.97 USD
Requisition Number	32808898
Owner Name	Isaac Roll
Owner Email	Isaac.Roll@asu.edu
Owner Phone	+1 (480) 225-8699

Document Status

Workflow	✓ Approve All (9/17/2012 10:44 AM)	
Distribution	The system distributed the purchase order using the method(s) indicated below the last time it was distributed: cXML (Electronic Integration)	view
Distribution Date/Time	9/17/2012 10:44 AM	
Supplier	Sent To Supplier	

Line Item Status

		Product Description	**Catalog No**	**Size / Packaging**	**Unit Price**	**Quantity**	**Ext. Price**	**Receiving**	**Invoicing**
1	✓	Multiconductor Cables, Length 500 ft, Nominal Diameter 8.05 in, Number of Conductors 9, CWC P/N: 9C20-CMG-CH-R5-BED	99869719	EA	1.09 USD	500 EA	545.00 USD	none	none

Shipping, Handling, and Tax charges are calculated and charged by each supplier. The values shown here are for estimation purposes, budget checking, and workflow approvals.

Subtotal	**545.00**
Tax1	35.97
Tax2	0.00
Shipping	0.00
Handling	0.00
Total	**580.97 USD**

https://solutions.sciquest.com/apps/Router/POStatusPrinterFriendly?poId=24184990&tmstmp=1441408517376 1/1

Figure F.7. Purchase order for multi-channel communication cable for the IS2.

APPENDIX G

SUPPLEMENTARY MATERIAL FOR CHAPTER 5

G.1 LC-MS/MS INSTRUMENT PARAMETERS

The LC was operated with MS-grade water and methanol at a flow of 0.4 mL/min. The solvent gradient program started with 60% methanol ramped to 90% methanol over 7 min, held at 90% methanol for 2 min, returned to 60% methanol over 1 min, and held at 60% methanol for 3 min. Samples were diluted 1:1 with MS-grade water and 100 µL was injected. The analytes of interest were separated on a Waters X-Bridge 4.6 × 150 mm C8 column with 3.5 µm particle size preceded by an equivalent guard column. A switching valve allowed sample to flow to the MS/MS between 4 and 12 min of each 13 min run. The source parameters were set as follows: curtain gas = 25 psi, gas 1 = 70 psi, gas 2 = 50 psi, IS = -4500 eV, temperature = 500ºC, entrance potential (EP) = -10 eV, and collision activated dissociation (CAD) gas = 12 psi. All gases (nitrogen) were provided by a Parker Balston Source 5000 LC/MS Gas Generator.

G.2 GC-MS INSTRUMENT PARAMETERS

An Agilent DB-5MS column (30 m-long x 0.250 mm-inner diameter x 25 µm-film thickness) was used with helium carrier gas regulated by flow at 1.2 ml/min. A 1.0 µL aliquot of the methanol extract was injected into an Agilent split/splitless inlet held at 275°C with a 100:1 split ratio. The column temperature at injection was held for one minute at 50 °C, increased by 10 °C/min to 300 °C and held for five minutes. The first quadrupole of the MS operated in scan mode from 3 min post-injection to the end of the oven cycle, scanning the *m/z* range from 50 to 300 with a step size of 0.1, a scan time of 500 ms, and a gain of 10. After every injection, the autosampler syringe was cleaned sequentially with neat methanol and hexane.

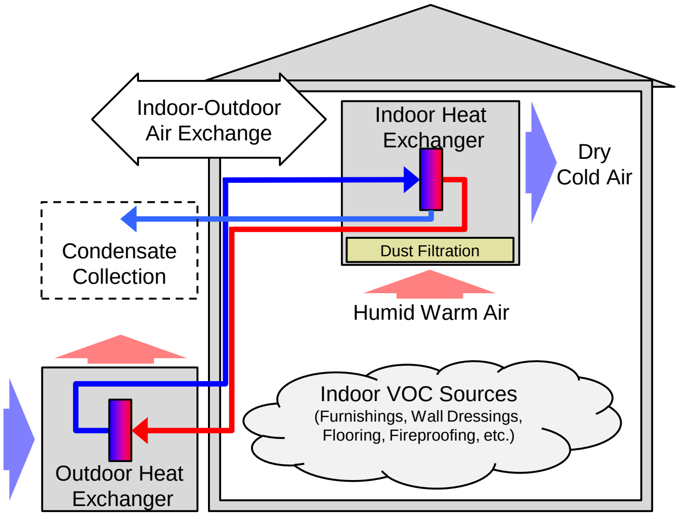


Figure G.1. Schematic representation of an air conditioning system as installed in the study structures. Indoor air laden with humidity and volatile organic compounds (VOCs) from a variety of sources enters the indoor heat exchanger through a dust filter. Condensate formed on the cold coils of the indoor heat exchanger is conducted out of the system. Condensate was collected at the exit point of the drainage line.

Table G.1

Standards and reagents used during the study and associated CAS numbers and vendors.

Compound	CAS No.	Vendor
Bisphenol A (BPA)	80-05-7	Cambridge Isotope Laboratories (Andover, MA)
$^{13}C_{12}$ BPA	-	Cambridge Isotope Laboratories (Andover, MA)
Dibutyl phthalate	84-74-2	Supelco (Sigma-Aldrich, St. Louis, MO)
Diethyl phthalate	84-66-2	Fluka Analytical (Sigma-Aldrich, St. Louis, MO)
2-Ethyl-1-hexanol	104-76-7	Fluka Analytical (Sigma-Aldrich, St. Louis, MO)
Fipronil	120068-37-3	Fluka Analytical (Sigma-Aldrich, St. Louis, MO)
Methyl dihydrojasmonate	24851-98-7	SAFC (Sigma-Aldrich, St. Louis, MO)
4-Methylumbelliferone (MUF)	90-33-5	Cambridge Isotope Laboratories (Andover, MA)
p,α,α-Trimethylbenzyl alcohol	1197-01-9	SAFC (Sigma-Aldrich, St. Louis, MO)
Paraben, methyl- (MePB)	99-76-3	Aldrich (Sigma-Aldrich, St. Louis, MO)
Paraben, (ethyl-, propyl-, butyl-, and benzyl-)	See Table S3	RT Corp (Laramie, WY)
Propylene glycol butyl ether	5131-66-8	Aldrich (Sigma-Aldrich, St. Louis, MO)
Tetrabromobisphenol A (TBBPA)	79-94-7	Cambridge Isotope Laboratories (Andover, MA)
$^{13}C_{12}$ TBBPA	-	Cambridge Isotope Laboratories (Andover, MA)
2,4,7,9-Tetramethyl-5-decyne-4,7-diol (TMDD)	126-86-3	Aldrich (Sigma-Aldrich, St. Louis, MO)
Triclocarban (TCC)	101-20-2	Aldrich (Sigma-Aldrich, St. Louis, MO)
$^{13}C_{13}$-TCC	-	Wellington Laboratories (Guelph, ON, Canada)
Triclosan (TCS)	3380-34-5	Aldrich (Sigma-Aldrich, St. Louis, MO)
$^{13}C_{12}$-TCS	-	Wellington Laboratories (Guelph, ON, Canada)
Tris (chloropropyl) phosphate (TCPP)	13674-84-5	Fluka Analytical (Sigma-Aldrich, St. Louis, MO)
γ-Undecalactone	104-67-6	Aldrich (Sigma-Aldrich, St. Louis, MO)

Table G.2

Condensate samples, sampling locations, and errata.

Sample No.	Sampling Date	Subject (Type, Year Built)	LC	GC	Notes
01	27 Aug 2013	A (House, 1987)	-	U, F	Parafilm shielding during sampling
02	17 Sept 2013	A (House, 1987)	F	U, F	
03	18 Sept 2013	A (House, 1987)	F	U, F	
04	23 Sept 2013	A (House, 1987)	F	U, F	Aliquot acidified for extraction
05	25 Sept 2013	A (House, 1987)	-	U, F	Scented candle introduced to house
06	27 Aug 2013	B (House, 2012)	F	U, F	
07	5 Sept 2013	B (House, 2012)	F	U, F	
08	6 Sept 2013	B (House, 2012)	F	U, F	
09	7 Sept 2013	B (House, 2012)	F	U, F	
10	11 Sept 2013	B (House, 2012)	F	U, F	
11	18 Sept 2013	B (House, 2012)	F	U, F	
12	28 Aug 2013	C (House, 1972)	F	U, F	
13	4 Sept 2013	C (House, 1972)	F	U, F	
14	10 Sept 2013	C (House, 1972)	F	U, F	
15	17 Sept 2013	D (House, 1960)	F	U, F	
16	7 June 2013	E (House, NR)	F	U, F	Parafilm shielding during sampling
17	2 July 2013	F (House, NR)	F	U, F	Parafilm shielding during sampling
18	5 Sept 2013	G (Business, NR)	F	U, F	

Notes. The liquid chromatography (LC) and gas chromatography (GC) table columns indicate whether filtered (F) or unfiltered (U) samples were analyzed on the corresponding instrument.

Table G.3

Compounds selected for analysis by LC-MS/MS and the MS/MS parameters used.

Compound	CAS No.	Precursor Ion	Secondary Ion	DP (V)	EP (V)	CE (V)	CXP (V)
BPA	80-05-7	226.9	133.0	-135	-10	-38	-11
$^{13}C_{12}$ BPA	-	239.0	138.7	-115	-10	-30	-5
Fipronil	120068-37-3	435.0	329.9	-70	-10	-24	-5
		435.0	250.0	-70	-10	-38	-3
MUF	90-33-5	174.9	132.8	-75	-10	-32	-5
Paraben, methyl-	99-76-3	150.9	92.0	-60	-10	-30	-5
Paraben, ethyl-	120-47-8	164.9	92.1	-55	-10	-30	-15
Paraben, propyl-	94-14-3	179.1	92.1	-55	-10	-30	-13
Paraben, butyl-	94-18-8	192.9	92.1	-55	-10	-38	-1
Paraben, benzyl-	94-18-8	227.0	92.0	-65	-10	-36	-1
		227.0	136.1	-65	-10	-22	-5
TBBPA	79-94-7	542.8	78.9	-95	-10	-98	-13
$^{13}C_{12}$ TBBPA	-	554.9	78.9	-110	-10	-96	-11
TCC	101-20-2	312.9	159.9	-80	-10	-18	-9
$^{13}C_{13}$ TCC	-	326.0	166.0	-80	-10	-18	-9
2'-OH-TCC	63348-26-5	328.9	167.9	-65	-10	-18	-9
3'-OH-TCC	63348-28-7	328.9	167.9	-65	-10	-18	-9
3'-Cl-TCC	4300-43-0	346.9	159.9	-80	-10	-22	-11
TCS	3380-34-5	288.8	35.0	-60	-10	-34	-3
$^{13}C_{12}$ TCS	-	301.0	35.0	-60	-10	-34	-3

Notes. DP is declustering potential, EP is entrance potential, CE is collision energy, and CXP is collision cell exit potential. BPA is bisphenol A, MUF is 4-methylumbelliferone, TBBPA is tetrabromobisphenol A, TCC is triclocarban, and TCS is triclosan.

Table G.4

Limits of detection (LOD) and limits of quantification (LOQ) observed for targets of LC-MS/MS analysis.

Compound	LOD (ng/L)	LOQ (ng/L)
BPA	10	33
Fipronil	2	8
Paraben, methyl-	3	9
Paraben, ethyl-	2	8
Paraben, propyl-	2	5
Paraben, butyl-	3	10
Paraben, benzyl-	5	18
TBBPA	8	28
TCC	3	9
2'-OH-TCC	9	31
3'-OH-TCC	10	32
3'-Cl-TCC	4	15
TCS	55	182

Notes. BPA is bisphenol A, TBBPA is tetrabromobisphenol A, TCC is triclocarban, and TCS is triclosan.

Table G.5

Compounds tentatively detected by GC-MS, sorted by molecular weight (MW).

Compound	CAS No.	MW	BP (°C)	log K_{OW}	Note
Diacetamide	625-77-4	101	224	-1.61	A
1,2-dihydro-3H-1,2,4-triazole-3-thione	3179-31-5	101	276	0.18	
2-butoxy-ethanol	111-76-2	118	168	0.80	
N-Ethyl-4-hydroxypiperidine	3518-83-0	129	209	0.01	
2-Ethyl-1-hexanol	104-76-7	130	185	2.82	B
Propylene glycol butyl ether	5131-66-8	132	171	1.14	B
1,2 Benzisothiazole	272-16-2	135	146	1.85	
Benzothiazole	95-16-9	135	227	2.01	
α,α-dimethyl-benzenemethanol	617-94-7	136	202	1.73	
2-phenoxy-ethanol	122-99-6	138	245	1.16	
2-ethyl-hexanoic acid	149-57-5	144	239	2.90	
2,2,4-trimethyl-1,3-pentanediol	144-19-4	146	232	0.88	
2-(hexyloxy)-ethanol	112-25-4	146	206	1.86	
p,α,α-Trimethylbenzyl alcohol	1197-01-9	150	205	2.19	B
m-tert-butyl-phenol	585-34-2	150	240	3.17	
1-Phenoxypropan-2-ol	770-35-4	152	249	1.51	
3,7-dimethyl-1,6-octadien-3-ol	78-70-6	154	198	3.28	
(S)-α,α,4-trimethyl-3-cyclohexene-1-methanol	10482-56-1	154	217	2.79	
α,α4-trimethyl-3-cyclohexene-1-methanol	98-55-5	154	217	2.79	
2,6-dimethyl-7-Octen-2-ol	18479-58-8	156	188	3.08	
dihydro-5-pentyl-2(3H)-furanone	104-61-0	156	267	1.85	

2-(2-butoxyethoxy)-ethanol	112-34-5	162	230	0.44	
3,3'-oxybis-2-butanol	54305-61-2	162	254	0.002	
Triethyl phosphate	78-40-0	182	219	1.08	
Benzophenone	119-61-9	182	305	3.18	
γ-Undecalactone	104-67-6	184	286	2.92	B
Diethyltoluamide	134-62-3	191	297	1.96	
Dimethyl phthalate	131-11-3	194	329	1.13	
N-n-Butylphthalimide	1515-72-6	203	310	3.15	
2-(2-butoxyethoxy)-ethanol acetate	124-17-4	204	245	1.15	
(1-hydroxycyclohexyl) phenyl-methanone	947-19-3	204	339	2.34	
3-methyl-3-phenyl-oxirane carboxylic acid ethyl ester	77-83-8	206	274	2.43	
1-[2-(2-methoxy-1-methylethoxy)-1-methylethoxy]-2-Propanol	20324-33-8	206	271	-0.10	
4,6-di-tert-Butyl-m-cresol	497-39-2	220	284	5.32	
Diethyl Phthalate	84-66-2	222	294	2.7	B
Methyl dihydrojasmonate	24851-98-7	226	308	2.5	B
TMDD	126-86-3	226	253	3.11	B
Oxybenzone	131-57-7	228	370	3.64	
Dibutyl phthalate	84-74-2	278	337	4.82	B
TCPP	13674-84-5	328	358	2.53	B

Notes. Boiling Point is BP and the Octanol-Water Partitioning Coefficient is K_{OW}; these properties were predicted by the ACD/Labs suite. Compounds with note A were selected for confirmation with authentic standards and determined to have been incorrectly identified. Compounds with note B were selected for confirmation with authentic standards and were confirmed in identity. TMDD is 2,4,7,9-tetramethyl-5-decin-4,7-diol, and TCPP is tris(chloropropyl)phosphate.

BIOGRAPHICAL SKETCH

Isaac Benjamin Roll was born in Tucson, Arizona, to the great-grandchildren of homesteaders. He is a fourth generation college graduate on his father's side, with a bachelor's degree in bioengineering and master’s degrees in education and engineering. His first paycheck was $60 for a day’s work as a cowboy on the family ranch. He spent his first few summers out of high school working for civil engineers in highway, floodplain, and survey engineering, and a few years after that teaching Newton's Laws and electron orbitals. When he needed a break from being a teacher, he took a chance on graduate school in engineering, hoping he could spend a few more summers outside building something useful.