**Apparatus and Method for Time-integrated, Active Sampling of Contaminants in Fluids
Demonstrated by Monitoring of Hexavalent Chromium in Groundwater**

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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 $75 \pm 6\%$ 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%). The IS2 is compatible with commercial SPE resins and standard extraction methods, and has been certified for more general use (e.g., monitoring of jet fuel components) by the Environmental Security Technology Certification Program (ESTCP) of the U.S. Department of Defense.

Keywords

time-integrated; active sampling; water sampling; solid-phase extraction; environmental characterization; hexavalent chromium

1.0 Introduction

Characterization and monitoring accounts for up to 25% of the \$8 billion in annual expenditures for contaminated site remediation in the United States (USEPA 2004; Frost and Sullivan, 2005). Resultant characterization and monitoring data inform the design, implementation, and ultimately the overall expense of remediation for hazardous waste cleanup sites; therefore, a significant impetus exists to effectively reduce the cost of sampling and improve on the quality of monitoring data (ITRC 2010; Zhang et al., 2012; Verreydt et al. 2014). 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 (U.S. Government 2007, 2009, 2015).

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 and Le Pape, 1987; Zhang et al. 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 and 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 (Verreydt et al., 2014; Woodrow et al., 1986; Coes et al., 2014; Jacquet et al., 2014; Shaw and Mueller, 2009).

Integrative sampling approaches are an attractive approach to these challenges. Integrative samplers collect the contaminant of interest from a volume of environmental water at a predictable, linear uptake rate (R_s) (ASTM 2014; Vrana et al. 2005). Once the device is calibrated, 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; Woodrow et al., 1986; Shaw and Mueller, 2009). 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 and Le Pape, 1987; Woodrow et al., 1986; Pankow et al., 1984). By collecting the analyte separately from the environmental phase, a time-integrated sample eliminates the liquid handling steps associated with discrete samples and reduces the overall volume of material (sample, packaging, and activity-derived waste) generated by the sampling event (Woodrow et al., 1986; Pankow et al., 1984; Kot et al. 2000; Namieśnik et al., 2005; Senseman et al., 1995), thereby reducing cost and improving sustainability.

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 environmental waters over periods of several weeks Shaw and 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 (Jacquet et al., 2014; Vrana et al., 2001; Seethapathy et al., 2008; Huckins et al., 1999; Villanueva et al., 2013). 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 measure the volume of water from which the analyte was quantitatively extracted 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 sample technician. 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 (Russell, 1975; Brown and Purnell, 1979; Ras et al., 2009). 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; Tran and Zheng, 1997; Stephens and Müller, 2007; Green et al., 1986). Submersible devices capable of sampling small volumes water over

longer timescales are available for surface water applications (Llorca et al., 2009; Sánchez et al., 2014^{a,b}). These devices use pre-programmable circuit boards to control peristaltic pumps that deliver a constant, low flow of water to the instrument-specific glass capture system with sorbent. The device functionality envisioned here would add to recent advances in the abovementioned devices, but provide increased user options, including instrument-plumbing materials, commercially available extraction methods and variable fluid flows (e.g., pause/pump). Currently, active sampling devices designed for *in situ* groundwater sampling also are limited, likely due to the restricted diameter of the typical groundwater monitoring well (10 cm).

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 (Halden and Roll, 2015).

2.0 Experimental Section

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. The pump then passes the acquired fluid through

commercial solid-phase extraction (SPE) cartridges, to generate simultaneously at least three 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 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.

2.2 Demonstration Site Description.

Field demonstration data were collected in a coastal freshwater lens on Coronado Island in San Diego Bay, CA. 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 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 below ground surface (bgs); depth to water is approximately 1.2 m. 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); maximum contaminant level for Cr(VI) is 0.01 mg/L. Hydrogeological parameters are provided in Table S1 and information on the reporting limit of the methods used in Table S6 of the Supporting Information. Samples were diluted as necessary to stay within the calibrated range of the method (e.g., 0.01 to 1 mg/L or 0.1 to 10 mg/L depending on metal species investigated.) Additional

information on the performance of the analytical methods used has been made available elsewhere (Halden and Roll, 2015).

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 below ground surface (bgs), which is 3.4 m below the water table. Sampling commenced at 11:00 on October 4, 2014 and ended at 9:00 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 website (NOAA, 2015).

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).

2.5 Estimation of Transportation Cost and Carbon Impact.

Overnight shipping costs were estimated from the 2015 rate tables for a major international shipping company (FedEx, 2015). Carbon emissions were estimated using a method and parameters provided by the U. S. Environmental Protection Agency (USEPA, 2008).

3.0 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 (Figure 1). 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.

3.1 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 inner diameter monitoring wells (Figures 2 and 3). 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 S2 of the Supporting Information.

In a typical configuration of the tool, the pump, fluid train, and SPE cartridges are housed in an 8.9 cm outer diameter, 90 cm 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. This configuration was optional and implemented in this work only to unambiguously determine the actual amount of water processed by the device. For routine use of the IS2, calibration of the pumps and consideration of the programmed volume processed may suffice to obtain an estimate of the concentration of analytes in environmental waters sampled.

3.2 Baseline Field Data: Time-discrete Sampling Series.

Depth to water (1.25 m) did not change appreciably in the study well over a 24-h period; however, Cr(VI) concentrations exhibited distinctive trends (Figure 4). In field and trip blanks, chromium species were never found at detectable levels. In site groundwater, 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.

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 113 km of San Diego County on the California coast using the GeoTracker application revealed nearly 1700 monitoring wells within 1 km of the shoreline (California EPA, 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 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 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 $75\% \pm 6\%$ 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 $82.1\% \pm 3.8\%$ to $96.3\% \pm 2.4\%$ (3 mL at 30 mg/L in buffered solution) (Bowen, 2014), $92\% \pm 3\%$ (6.4 L at 1.4 $\mu\text{g/L}$ in drinking water) (Inui et al., 2010), and $76.8\% \pm 5.8\%$ to $104\% \pm 5.2\%$ (500 mL at 1.0 $\mu\text{g/L}$ in river, rain, spring, and tap waters) (Inui et al., 2010).

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, down to a rounded value of 0.01 mg/L (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 $\mu\text{g/L}$ 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).

3.4.1 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 (Inui et al., 2010); however, these studies were conducted using time-discrete samples, and were not subjected to the significant holding time of the present study samples.

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 and active samplers for a diversity of target species and ambient conditions, as reviewed recently (Roll and Halden, 2016). One study reported a range of RSD values 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%

(Jacquet et al., 2014), a third using the Semipermeable Polymeric Membrane Device (SPME) showed values of 1 to 33% (Huckins et al., 1999), and a final study employing Diffusive Gradient Thin Films showed values varying from 2-49% (Villanueva et al., 2013).

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 S4 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 (Roll and Halden, 2016).

3.5 Economic and Environmental Implications.

In the present study, 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 this study represented more than 400 g of sampled water each (more than 1.2 kg total), giving an approximately 100-fold reduction in mass. With a sampling volume of 250 mL, sampling at two-hour intervals over 28 days would have required the transportation and disposition of as much as 84 kg of hazardous materials. 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 (Figure S3 of the Supporting Information). As the number of samples generated by a site increases, *in situ* sampling with the IS2 provides significant advantages in reducing carbon emissions (Table 1; 98% reduction), shipping costs (90% or greater reduction), and hazardous waste disposal (98% reduction).

3.6 Limitations.

Many of the limitations of the present sampling system are shared by contemporary alternatives. The present instrument, while more complex than most liquid aliquot sampling systems, is expected to have capital costs similar to contemporary environmental autosamplers and similar equipment (Table S5 of the Supporting Information). 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. For applications in low-permeability environments different from the one studied here (Table S1), care should be taken to keep the daily exchanged volume in the borehole at more than 10 times the groundwater volume sampled, to avoid bias from *in situ* analyte depletion. 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.

4.0 Conclusions

The instrument and method presented here, collectively the IS2 technology, represent an advancement in the monitoring of 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 and as demonstrated here, 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 to the laboratory. 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, and the IS2 technology recently underwent third-party independent validation and was certified for use by the U.S. Department of Defense (Sánchez et al., 2014).

Application areas of the IS2 and derivative technologies are varied and may reach across different water sources and planetary environments, while reductions in carbon emissions will benefit air quality. Established application areas include monitoring of groundwater, surface water, and pore water (Supowit et al., 2016). Potential applications include drinking water, and other process water flows from the built environment, including but not limited to the runoff from buildings, and the condensate stream produced by air handling systems from processing of indoor air (Roll et al., 2015).

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6.0 Appendix A. Supplementary data

Tables providing site hydrogeologic data (Table S1), a detailed materials list (Table S2), results of a paired sample study (Table S3), sampling rates for each channel during the present study (Table S4), and estimates of the capital costs for comparable equipment (Table S5) as well as reporting limits of the methods used (Table S6) are provided in the Supporting Information. Figures include a screenshot of the program interface (Figure S1), a photograph of the interior of the surface package that supports the sampler (Figure S2), and modeled estimates of sample mass reductions for scaled use of the IS2 technology (Figure S3) are similarly provided.

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GRAPHICAL ABSTRACT