# Apparatus and method for time-integrated, active sampling of contaminants in fluids demonstrated by monitoring of hexavalent chromium in groundwater
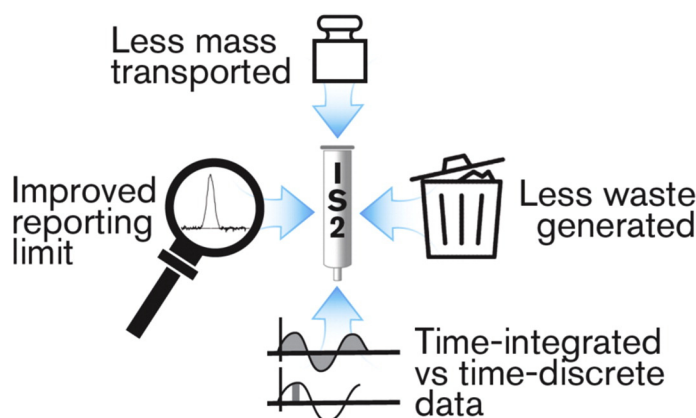
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## HIGHLIGHTS

- A new sampler with solid-phase extraction permits *in situ* aqueous contaminant capture.
- Active sampling and *in situ* processing reduce waste and decrease carbon footprint.
- The sampler provides time-integrated average concentrations.
- Active sampling improves reporting limits 8-fold over conventional techniques.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

## 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 (i.e., inorganics and organics) by the Environmental Security Technology Certification Program (ESTCP) of the U.S. Department of Defense.

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## 1. 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 and Zhang, 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 and 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 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., fully deuterated 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 Zeng, 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., 2014a, 2014b). 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. 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