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Santa Barbara

Quantification of groundwater discharge to San Ysidro Creek discharge using continuous 222Rn measurements during a storm

A Thesis submitted in partial satisfaction of the

Requirements for the degree Master of Science

in Earth Science

by

Jared William Wilson

Committee in charge:

Professor Jordan F. Clark, Chair

Professor Matthew G. Jackson

Professor Edward A. Keller

Professor Syee Weldeab

January 2018

The thesis of Jared William Wilson is approved.

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Dr. Edward Keller

_____

Dr. Syee Weldeab

_____

Dr. Matthew Jackson

_____

Dr. Jordan Clark, Committee Chair

January 2018

Quantification of groundwater discharge to San Ysidro Creek discharge using continuous 222Rn measurements during a storm

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By

Jared William Wilson

ACKNOWLEDGEMENTS

I would like to thank my parents who have supported my desire to achieve an advanced degree since I was shockingly young and who have bolstered my love for earth science with many beautiful experiences. I would also like to thank my advisor Dr. Clark, who with much patience has helped a geologist coming into the field of hydrology learn many things which I had never considered prior. I would also like to thank Menso de Jong, my fellow lab member at UCSB for being a great friend and tea snob during some stressful times. My gratitude also goes out to the MRL facility and Staff especially Amanda Strom who walked me through learning to use their ICP spectrometer. Finally, I would like to thank my best friend and loving companion Michelle Tibay for helping me survive the hectic life of grad school while also soldiering through on her nursing degree. This one is for you.

ABSTRACT

Quantification of groundwater discharge to San Ysidro Creek discharge using continuous 222Rn measurements during a storm

By

Jared William Wilson

This study utilizes high temporal resolution ^{222}Rn activity data to create a chemical hydrograph in order to better quantify the influx of groundwater, soil water, and rain water into a stream during precipitation events. Three tests were conducted during separate storm events within the area of Montecito, CA along San Ysidro Creek throughout the 2016 and 2017 Water Years. These tests analyzed ^{222}Rn activities, $\delta^{18}O$ and $\delta^{2}H$ ratios and silica concentrations with the goal of testing whether ^{222}Rn activities measured through the use of the RAD7 system would provide similar hydrograph data to the other two methods.

^{222}Rn activities showed trends in a higher temporal resolution than the other methods used despite low activities caused by rapid diffusion of ^{222}Rn gas from the stream into the atmosphere. ^{222}Rn data, dissolved silica data, and stable isotope data all showed steady increases in groundwater during the first test (Mar. 5, 2016). No distinguishable trends were noticed in the second test (April 10, 2016). Strong trends were shared between the ^{222}Rn data, dissolved silica data, and stable isotope data during the third test (Mar. 21, 2017) which was conducted with higher resolution discharge data for a significantly longer duration. This shows a positive correlation between the ^{222}Rn data and the other tracers used in this study. Results suggest that with additional testing restrictions: information regarding the definition

of end members within the stream or a more stable study site which is a location of groundwater influx, ^{222}Rn activities would work as a viable proxy for pre-event water during a storm. ^{222}Rn would then provide a more cost effective and less time-consuming means of creating storm chemical hydrographs without having to collect, transport, and analyze multiple water samples.

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I. INTRODUCTION

Sufficiently monitoring and protecting the headwaters of rivers nearby population centers from contaminations ensures reliable fresh water sources for many of the world's cities and agricultural areas. Even though these sources of freshwater are valuable resources, they are also possible sources of mass wasting and flood events, which are often triggered by exceptionally high precipitation in the headwaters of a stream. Therefore, monitoring of rivers nearby urban environments must be conducted carefully and thoroughly.

Previous studies of groundwater discharge into streams have utilized stable isotope ($\delta^{18}O$ and $\delta^{2}H$) data and silica concentrations of stream water (Sklash et al., 1975; Fritz et al., 1976; Hinton and Schiff, 1994). The tracer measurements are interpreted through two end-member mixing models that require time-consuming analyses of stream water. The method being tested in this study would provide high-resolution groundwater discharge data through the measurement of *in situ* ^{222}Rn activities. Time-series measurements of radon-in-water activities should reveal a trend similar to those of the dissolved silica concentrations and stable isotope ratios due to their shared sources and relative abundances within groundwater. Silica and radon are present at negligible levels in the precipitation (event water) and therefore the concentrations and activities of these tracers should decrease as the relative influx of groundwater (pre-event water) decreases.

In contrast, the stable isotope signature of the event water should have a very distinctive value whereas the stable isotope signature of the pre-event water should have a value that is equal to the weighted average of the precipitation over the past few years (Sklash et al., 1975; Fritz et al. 1976; Clark and Fritz, 1997).

Multiple studies have utilized chemical hydrograph data to better determine the relative contributions of event water and pre-event water to a stream during the course of a storm (e.g., Bottomley et al., 1984 and 1986; Hooper and Shoemaker, 1986; Moore, 1989; Wels et al., 1991). This study utilizes the familiar approach of chemical hydrograph analysis through the study of a relatively easy to analyze tracer (^{222}Rn) to provide further data about how pre-event water is discharged into streams and the proposed "pressure wave" that causes large scale discharge of pre-event water into streams upon rapid loading of the water table within a catchment basin. The objective of this study is to test the viability of using ^{222}Rn activity to measure influx rates of groundwater and the associated mixing between the groundwater (pre-event water) and rainwater (event water), as well as to test whether the associated method is comparable to the previously established dissolved tracer and stable isotope methods.

To test the hypothesis that ^{222}Rn is an effective tracer in performing these stream discharge analyses, this study collects and analyzes a variety of data measured during storm events from a local Santa Barbara creek. These ^{222}Rn activities are compared to the previously established methods for quantifying groundwater discharge to streams to test the effectiveness of existing models in creating time series data. A comparison between ^{222}Rn activities, dissolved silica concentrations, and stable isotope ratios of the stream will be employed to test whether the ^{222}Rn method presents a viable, less labor intensive, and less time-consuming method for analyzing groundwater discharge into streams. A lack of correlation between ^{222}Rn activities and both stable isotope and dissolved silica would show that this method is incapable of resolving the groundwater discharge as effectively as the other methods. If there is a weak correlation between ^{222}Rn activities and the stream

hydrochemistry, then a new set of measurements would need to be gathered in order to see if this is due to poor hydrochemistry resolution or insufficient impact from the event water on the water table.

This study employed a newer method of attaining very high temporal resolution chemical hydrograph data that could eventually inform which sections of a creek or a watershed have the lowest rates of groundwater discharge into streams, which sections of a creek have high turbulence that enhances gas loss, or which sections of a creek are gaining or loosing water with respect to their baseflow.

II. THEORY

A. Hydrogeological Background

i. Geologic Setting

The primary study takes place in the Santa Ynez Mountain Range, which is located in Santa Barbara County, California. This mountain range originated from compression caused by the big bend of the San Andreas left lateral fault. This compression has resulted in the uplifting of the Eocene aged oceanic shales and sandstones to create the southern reach of the Santa Ynez Mountains. These mountains contain springs, which are formed by the flow of water through the broken shale aquifers in the area such as the Juncal and Cozy Dell shales; however, they are blocked from flowing through the less permeable sandstone formations such as the Coldwater and Matilija sandstones. This interlayering of sandstone and shale, which makes up the Santa Ynez Mountains, allows for the presence of perennial streams, which are fed by these springs.

Due to this difference in local geology, there should be significant changes in the amount of ^{222}Rn within the stream. Sections of the Santa Ynez streams that flow through the porous, fractured shales have significantly more groundwater interaction from springs. In contrast, reaches of Santa Ynez streams that run through more sandstone-rich beds would have significantly less interactions with groundwater aside from occasional springs located within the Matilija and Coldwater Sandstones. When gas loss is factored in, these reaches of Santa Ynez streams that are disconnected from the local groundwater can become depleted in ^{222}Rn quite rapidly from the rough nature of the stream bed. In this study, these springs will be the source for the pre-event component of stream discharge while the event water component will be measured from captured precipitation that occurs during the tests.

ii. Hydrograph Separation

Hydrographs were initially used as a tool for determining flood discharge and timing through calculations of stream discharge. They have been used to determine information such as the detention volume or water storage capacity of soils within a watershed under the assumption that a certain maximum detention volume would be captured by the watershed before a stream would reach peak discharge (Linsley and Kohler, 1958). In theory, these short duration storm hydrographs could be used to develop hydrographs for longer duration storms through an understanding of these properties (Linsley and Kohler, 1958). Additionally, the peak flow rate and the lag times associated with a storm have been the major points of study for these datasets. Historically, the use of these hydrographs was reserved for small area drainage basins (< 5180 km^2) (Linsley and Kohler, 1958), and the San Ysidro Creek catchment is itself a small area drainage basin (16.8 km^2).

More recent studies of hydrochemistry have produced methods of determining water

sources of discharge for a given storm event. Methods for performing a separation of a hydrograph into its constituent sources have been developed along with the development of isotope measurements in hydrology. However, despite recent advances using these tracers as well as dissolved major ion tracers and conductivity, there are some studies that claim that chemical hydrograph separation is too complex and ambiguous (Beven, 2001; Brutsaert, 2005).

Most studies that employ a two-component mixing model using hydrograph separation require a record of stream discharge, a record of chemical signature, and a distinct chemical signature for both end members of the mixing model (Sklash et al., 1975). Most of these models utilize Isotope Hydrograph Separations (IHS) in which the end members of a model are assigned isotopic values and percentages of those components are calculated. These percentages are then imposed onto a discharge hydrograph to show total volume of the defined components within the stream. Later studies by Kennedy et al. (1986) and DeWalle et al. (1988) showed that the simple two-component hydrograph separation models are sometimes not sufficient for understanding groundwater and surface water interactions and there is a need to further quantify vadose zone soil water in addition to the two primary components. Performing a three component IHS requires additional information about the chemical signature of the vadose zone water as well as either the total discharge of one of the three components or information from a separate independent tracer (DeWalle et al., 1988).

The simple mixing model used in this study is from Pinder and Jones (1969):

$$X = \frac{C_t - C_{pe}}{C_e - C_{pe}} \qquad \text{[Eq. 1]}$$

Where *X* is the fraction of event water in the sample, *C* is the concentration of each solution, and the subscripts "*pe*", "*e*", and "*t*" refer to the pre-event component of the flow, the event component of the flow, and the total flow, respectively. The acquired fractions were then combined with the discharge data in order to attain a storm hydrograph showing both total discharge and the discharge attributed to event water.

This equation was also applied to the dissolved silica and the stable isotope ratios using the respective end member values for pre-event and event waters. These calculations were then compiled into similar hydrographs showing the total discharge and the event water discharge. Pre-event water values for both tracers came from the pre-test samples collected before the precipitation events. The event water values for silica are assumed to be 0 and the event water values for the stable isotopes are elevation corrected from precipitation data collected in Goleta, CA. The data are modified to account for the difference in elevation given the samples are collected about 34 meters above mean sea level (Google Earth) while the San Ysidro Catchment area is on average 720 m above sea level (Fig. 1). The modifications were completed using data from Rademacher et al. (2003), who demonstrated that within the Santa Ynez Mountains there was a 0.2‰/100 m decrease in $\delta^{18}O$ of precipitation, which would be a decrease of 1.44‰ in $\delta^{18}O$ for the San Ysidro Drainage Basin relative to the Goleta station.

B. Methodological Background

i. Stable Isotopes as a Tracer

The first hydrograph separations were conducted using tritium as a tracer to distinguish precipitation from groundwater due to the measured differences of tritium in precipitation and groundwater (Hubert et al., 1969). After these initial tritium studies, many

more IHS papers were published relying on δ^2H and $\delta^{18}O$ ratios of water. δ-notation is obtained by relating the isotopic ratio of a sample to the isotopic ratio of the accepted standard V-SMOW (Vienna Standard Mean Ocean Water) through the equation:

$$\delta\ [‰] = \frac{R_{sample} - R_{standard}}{R_{standard}} * 1000 \qquad \text{[Eq. 2]}$$

where $R = \frac{Amount\ of\ Atypical\ Isotope}{Amount\ of\ Most\ Abundant\ Isotope}$

$\delta^{18}O$ IHS studies were first conducted by Mook et al. (1974) and IHS studies using δ^2H were first performed by Hermann et al. (1978). These studies used the method developed by Hubert et al. (1969) where the component isotopic ratios, total discharge, and end member isotopic ratios are combined to define each component of discharge (Sklash et al., 1975). Studies utilizing natural tracers often require assumptions including that the tracer acts conservatively. This means that the tracer is not modified in the study except through the mixing of the source waters. In order to determine the effectiveness of stable isotope tracers within the San Ysidro study area, these assumptions need to be verified. The main assumptions for IHS studies are (Klaus and McDonnell, 2013):

1. The isotopic content of the event and the pre-event water are significantly different.
2. The event water maintains a constant isotopic signature in space and time, or any variations can be accounted for.
3. The isotopic signature of the pre-event water is constant in space and time, or any variations can be accounted for.
4. Contributions from the vadose zone must be negligible, or the isotopic signature of the soil water must be similar to that of groundwater.

5. Surface storage has little to no contribution to the streamflow.

Temporal variation of these storm isotope ratios is the first factor, which must be assumed negligible in this study due to the limited measurement of precipitation. One sample per storm event is recorded at the station in Goleta, CA and therefore temporal variations are assumed to be constant until such a time that a more robust hourly sampling of storm isotope values become available.

The groundwater isotope ratios are defined in this study as the average of three pre-event stream water samples collected simultaneously for dissolved silica, stable isotopes, and ^{222}Rn activities. Mixing of the event water and pre-event water within the vadose zone is expected to produce similar results to mixing of the event water and pre-event water within the stream. However, influence of the vadose zone could pose a problem if there is a distinct isotopic ratio or silica concentration within this zone. There are no vadose zone measurements here, but the vadose zone component is likely a significant factor in calculating the total IHS. As stated above, there are additional steps that can be taken in order to complete a three-component mixing model, but they require additional information about the vadose zone water component and either the total discharge of one of the three components or an additional independent tracer. This study utilizes multiple tracers in order to compare them to the primary tracer of ^{222}Rn.

Stored surface water has little influence in this drainage basin with the only exception being contribution from small pools of water within the stream itself. The San Ysidro drainage basin sources, it's pre-event waters, are from groundwater and springs and all waters during a storm have essentially no risk of evaporating due to the high humidity associated with storms and relative short residence time of water within the channel. No large

surface water features such as snowpack or lakes are responsible for any discharge within this study site.

ii. Dissolved Silica as a Tracer

Dissolved silica within a stream is sourced almost entirely from silicate weathering of material within the watershed (Berner and Berner 1996). This means that water that comes in contact with the soil or bedrock initiates silicate weathering while precipitation contains little to no silica (Likens et al., 1977). However, Kennedy (1971) showed that rainwater dissolves small amounts of silica during its initial interaction with the soil. This could lead to an underestimate of the new water component of a storm hydrograph if the catchment area is large enough or sparsely vegetated. In contrast, a smaller more vegetated catchment area would have little silica from direct precipitation on soil material. Through assumptions regarding precipitation's capacity to weather silicate minerals and the presence of diatoms within the watershed (which control silica loss in a stream), it is possible to make a chemical hydrograph separation, which shows similar results to IHS methods (Hooper and Shoemaker, 1986).

Another factor with dissolved silica as a tracer is that the old water concentration of silica typically changes throughout a storm because silica directly reflects the flow path of the water rather than the age of the water in contact with soil material (Hinton et. al., 1994). Fluctuating primary pre-event water sources between soil water and groundwater would lead to either an increase or a decrease in total pre-event water concentrations. It is possible that this increase in groundwater concentration can in turn offset the underestimation of event water, but this is something that cannot be determined until the two-component hydrograph separations of the stable isotopes and of dissolved silica are compared.

iii. ^{222}Rn Activity as a Tracer

Initial observations of the abundance of ^{222}Rn in groundwater were reported by Bumstead and Wheeler (1904) and the exact values of this enrichment were determined by multiple more recent papers such as Asikainen (1981), Chung (1981), and King et al. (1982). Krishnaswami et al. (1982) utilizes uranium- and thorium-series isotopes in groundwater to estimate adsorption rates, desorption rates, and retardation factors of aquifer systems. The findings of Krishnaswami et al. (1982) largely confirm the result of Bumstead and Wheeler (1904): that the activities of ^{222}Rn were on the order of three to four magnitudes more abundant than other radionuclides in the groundwater. For example, ^{222}Rn was compared to ^{224}Ra, another alpha particle emitting isotope with a similar half-life to ^{222}Rn from the ^{232}Th decay series rather than the ^{238}U decay series. Krishnaswami et al. (1982) expected a ^{224}Ra/^{222}Rn activity ratio of 1.7 based on the assumption that the ratio of ^{224}Ra/^{222}Rn activities should equal the ratio of their production shown by ^{228}Th/^{226}Ra activities, but they observed ^{224}Ra/^{222}Rn activities 4 orders of magnitude lower than expected. They attributed this difference to the removal of ^{224}Ra from the groundwater through adsorption to the aquifer matrix. This adsorption of radioisotopes from the groundwater happens to all charged ions. The only isotope that showed high activities in the groundwater was ^{222}Rn (Krishnaswami et al. 1982). Other decay products typically were adsorbed back onto the aquifer matrix if recoiled into the aquifer water due to their ionic status, but ^{222}Rn is a noble gas with no ionic charge. In addition to the ionic difference, the gaseous ^{222}Rn is able to dissolve rapidly into nearby groundwater because many of its parent isotopes are concentrated on the outside of aquifer grains (Krishnaswami and Seidemann, 1988).

^{222}Rn has also been described in Schubert et. al. (2005) as a useful natural tracer in hydrology because this isotope occurs naturally in all groundwater systems due to the abundance of ^{238}U in the crust. Common uses for ^{222}Rn in hydrology typically include the application of ^{222}Rn as a naturally occurring tracer for groundwater discharge (Lee and Hollyday, 1987; Genereux et al., 1993; Burnett and Dulaiova, 2003; Cook et al., 2006; 2008; Gleeson et al., 2018) and reaeration studies (Rogers, 1958; Ellins et al., 1990). Using ^{222}Rn activities as a tracer with some other common tracers, mixing models can be created to quantify possible end member sources.

Within the stream, the major sinks of ^{222}Rn are gas loss to the air due to reaeration and ^{222}Rn loss through alpha decay (Cook et al., 2006). The major sources of ^{222}Rn are vadose zone water and groundwater, which both exhibit higher activities of ^{222}Rn than surface waters. Because of this difference in relative activities, the concentration gradient between the air and the stream causes the water to become depleted in ^{222}Rn in reaches of the stream, which are highly aerated such as sections with large waterfalls or shallow rocky beds. Rogers (1958) described the factors which had a major influence on ^{222}Rn dissipation rates within a stream in which ^{222}Rn is lost to the atmosphere in an exponential manner with large spikes in ^{222}Rn activity nearby groundwater sources. Some of the controlling factors on ^{222}Rn gas loss are channel distance from groundwater or spring sources, stream velocity and volume, stream gradient, and the shape of the channel bed (Rogers, 1958). Some examples of this rapid loss of ^{222}Rn can be seen in recent studies such as those by Gleeson et al. (2018) in which there is a reported loss of 0.075 Bq/L of ^{222}Rn activity over a 600-m reach of Sagehen Creek, a small stream on the eastern side of the Sierra Nevada.

One of the first uses of ^{222}Rn as a tracer was conducted by Lee and Hollyday (1987) who found that large concentrations of ^{222}Rn in stream waters were typically linked to areas of high groundwater discharge and those concentrations decreased rapidly downstream of the influx site. The relation between groundwater and surface water was then determined by mass balance assuming only two major sources of ^{222}Rn in the stream and no significant gas loss or decay from the mix of surface water and groundwater (Lee and Hollyday, 1987). In another case, Genereux et al. (1993) created a three end-member model through the measuring of two tracers: [Ca] and ^{222}Rn. Their study took samples from the vadose zone, the soil groundwater, and the bedrock groundwater and used tracers from these three sources as a way of determining which locations provided what percentage of the stream water. ^{222}Rn has also been utilized in hydrology by measuring its activities as a direct indicator of groundwater discharge. Using ^{222}Rn activities, Cook et al. (2008) determined which sections of a wetland were being fed by groundwater and which sections of the wetland were recharging aquifers.

^{222}Rn shares some characteristics with silica in that it is abundant within groundwater and absent within precipitation. In addition to its similarities to silica, ^{222}Rn has multiple other characteristics that make it a viable tracer. It is a noble gas and neither adsorbs nor reacts within the aquifer, which often occurs with many ion tracers. There are no issues with photolytic decomposition that occurs with some fluorescence dye tracers. ^{222}Rn activities do not depend on the pH of the groundwater and remain constant if the source of the water remains constant. Another direct benefit of using ^{222}Rn is that it can be detected at very low activities due to its large decay constant and its alpha-particle emission (Schubert et. al., 2005).

^{222}Rn activity was also used as a tool for calculating the percentage of pre-event water in the stream under the assumption that there were 0.005 Bq/L of ^{222}Rn in the precipitation (an average of the values from Takeyasu et al., 2006) and the pre-event water activity is taken from measurements of San Ysidro Creek taken 20 days after the last storm and right before the storm to be measured. The precipitation value comes from a set of precipitation measurements at Kumatori Village in Osaka, Japan. Takeyasu et al. picked this village due to its proximity to the ocean and its separation from the nuclear power plants within Japan (at least 100 km from any nuclear power station). Kumatori village is also similar to Montecito in its latitude (14 km further north than Montecito) and its proximity to the Pacific Ocean. Takeyasu et al. (2006) also acknowledged the possibility of additional ^{222}Rn coming from natural ^{238}U deposits within the Asian mainland. This would therefore mean that the precipitation activity measured from Takeyasu et al. (2006) might be an overestimation of precipitation within the area of Montecito.

Typically, the sites of groundwater discharge change with time through raising and lowering of the phreatic surface (the top of the fully saturated zone of the soil matrix). Some factors that affect phreatic surface elevation are local air pressure and the loading of the phreatic surface by precipitation. This means that over the course of a storm there are typically changes in ^{222}Rn activities from groundwater sources even though the study location, the stream gradient, the bed roughness, and the stream profile do not change significantly (Ellins et al., 1990). Further complications which may arise through the addition of new groundwater influx sites closer to the measurement site as a result of the raising of the phreatic surface as well as from possible changes in ^{222}Rn gas loss rates due to changes in total discharge within the stream over during a storm (Rogers, 1958; Ellins et al., 1990).

III. MATERIALS AND METHODS

A. Study Location and Materials

Initial lab tests were conducted within the Woodhouse Laboratory at UC Santa Barbara in order to understand the time that it took for the RAD7 device to "start up" and record consistent values as well as the "bleed over" effect that a 15-minute run cycle on the device has on the prior 15-minute run. Field tests were conducted at three sites within California (Fig. 2) Supplemental tests of the radon-in-water method were conducted at the Sierra Nevada Aquatics Research Laboratory (SNARL) and at the Sagehen Creek Research Station. The SNARL test was conducted at the parallel stream channels near Convict Creek in Inyo County, CA. These channels were the downstream of two small weirs that redirected part of Convict Creek's water through the parallel channels (Fig. 3A). This location was used to determine how much ^{222}Rn would be lost from increased aeration of the stream from rapids, falls, and weirs. The Sagehen Creek tests were conducted at the USGS Gaging Station located at the Research Station in Sierra County, CA (Fig. 3C). This location was also used to determine ^{222}Rn loss from aeration caused by the weir that created a fall-like setting at this location.

The main tests of this study were conducted at San Ysidro Creek, which is a creek located in Montecito, CA (Fig. 4A). Two locations within this creek were sampled due to unforeseen changes in stream morphology during the heavy storms in Southern California in the Winter of 2017 (Fig. 4B) The second San Ysidro site is located at a USGS flood control structure just upstream of the highest homes in Montecito that reside off of this creek (928 W Park Ln, Santa Barbara, CA 93108) (Fig. 4C). This study site was chosen for four major reasons: 1) the stream is near UCSB and easily accessed once storms approached; 2) this

creek has a year-round baseflow; 3) a 15 yr record of $\delta^{18}O$ and $\delta^{2}H$ exists for precipitation at a nearby location in Goleta, CA, and 4) San Ysidro Creek has a substantial undeveloped catchment area (16.8 km^2), which ensures that both its infiltration and its spring patterns are not influenced by land use changes beyond the creation of hiking trails and fire roads.

B. Semi-Continuous ^{222}Rn Analyses with a Radon-in-Air-Detector (RAD7)

This study utilizes the Radon-in-Air Detector (RAD7) developed by the Durridge Company. While this system was designed to measure in-air activities of ^{222}Rn, Burnett and Dulaiova (2003) modified it by adding an air-water equilibrator to the inlet of the device, which allows for the quantification of ^{222}Rn activities in water. Calculated Radon-in-air activities were converted to Radon-in-water activities with the provided Durridge capture software. Essentially, the air activities were multiplied by the equilibrium coefficient (Weigel, 1978):

$$\alpha = 0.105 + 0.405 * \exp(-0.0502*T) \qquad \text{[Eq. 3]}$$

Where "α" is the unit-less equilibrium coefficient and T is the temperature in °C. This technique is referred to as the RAD AQUA method.

Schmidt et. al. (2008) improved this modified system by replacing the equilibrator with a membrane contactor. This contactor is a membrane (through which water is pumped) that is lined with hollow polypropylene fibers to allow for rapid gas diffusion. This allows for a lightweight means to transfer in-water radon to in-air radon through a simple equilibrium relationship based on water temperature.

Other methods for analyzing water with the RAD7 device were carried out using an attachment to the RAD7 device known as RAD H_2O. The RAD H_2O attachment is connected to a water sample bottle, which is then aerated. The released ^{222}Rn is subsequently pumped into the RAD7 device and its in-air activity is analyzed. This method suffers from the same drawbacks of the other two methods analyzed in this study in that it requires collection, storage, and later analysis of the water samples.

The RAD7 device utilizes a solid-state silicon alpha detector in order to count ^{222}Rn daughter ^{218}Po decays. The detector is a conductive material that converts the energy from alpha particles into an electrical signal. This makes it possible to identify which isotopes are counted through radioactive decay. The RAD7 pulls air through a filter located within the device, which excludes any charged aerosol from the analysis such as the radioactive parents and daughters of ^{222}Rn.

The RAD7 device counts radioactive decay within a 0.7 liter hemisphere chamber. The alpha detector is located within the center of this chamber. ^{222}Rn that decays within this chamber produces its daughter isotope of ^{218}Po, which is positively charged. The device charges the inside coating of the hemisphere to 2000 to 2500V higher than the voltage of the alpha detector. This creates an electric field throughout the inside of the detection chamber. This electric field propels any particles that have positive charges (such as the ^{222}Rn decay products) towards the detector in the middle of the chamber. When ^{218}Po decays within the detection chamber, it produces an alpha particle that has a 50% probability of being ejected into the detector. This decay produces an electrical signal that has a voltage directly proportional to the energy released from alpha decay. Later radioactive decay of ^{218}Po daughter isotopes produces either beta-decays or alpha decays of a different energy that the

detector can distinguish from the ^{218}Po decay, so they are not counted. The RAD7 collector amplifies, filters, and sorts the signals according to their strength (Durridge, 2015).

Proving the similarities between the membrane contactor method which was used in this study and the RAD AQUA method – which utilizes a spray chamber equilibrator similar to the one developed by Burnett and Dulaiova (2003) – was the focus of Schmidt et. al. (2008). The RAD7 device measures ^{222}Rn activity not by measuring the decay of ^{222}Rn to ^{218}Po, but by measuring the decay of ^{218}Po, which needs to reach secular equilibrium before consistent data is made available. The theoretical lower limit on how long it takes the equipment to reach this equilibrium state between ^{222}Rn and ^{218}Po is about 15 minutes which is five half-lives of ^{218}Po (Schmidt et. al., 2008). This equilibrium time was tested by Schmidt et al. (2008), and they showed a minimum equilibration time of around thirty minutes for a water flow rate of 2.5 L/min and around forty to fifty minutes for a water flow rate of 1.0 L/min (Fig. 5A). In this study, a similar trend is visible with a faster equilibrium time due to the use of the maximum allowed flow rate for the membrane contactor of 3 L/min (Fig. 5B)

During this study, the radon measurements consist of multiple cumulative 10-minute cycles during Test 1 and Test 2 and cumulative 15-minute cycles during Test 3.

C. Field Methods

Background radon measurements have been conducted at the Sierra Nevada Aquatic Research Laboratory (SNARL) and the Sagehen Creek Field Station. No large precipitation events were observed within 20 days prior to these studies, which were conducted to examine the sensitivity of the equipment used and to gain greater insight into how reaeration may affect ^{222}Rn activities.

Three tests were conducted at San Ysidro Creek. The data was collected March 5, 2016, April 10, 2016, and March 21, 2017. The setup used in the collection of the radon data is consistent with the method developed by Schmidt et al (2008) with two portable filters attached to the inflow pump to ensure the membrane contactor does not get clogged by debris from the creek (Fig. 6). The filtered and degassed water then exits the system. The filtered water is collected at hourly intervals for analysis of dissolved silica. Samples for stable isotope analysis are collected directly within the stream before the water goes through the membrane contactor. This is because the aeration of the water could fractionate the stable isotope ratios while it passed through the membrane contactor.

Transport of materials to and from the field site was done by car and a single trip from the car to the stream site. All of the equipment can be carried within a simple storage container or a backpack. Measurements were performed either in the field or later at contract laboratories. The initial in-field analysis was carried out for two hours in order to attain a baseline measurement for the stream to use as the pre-event end member values. This was done 16 to 20 days (approximately 5 half-lives of ^{222}Rn) after the last rainfall in Montecito so that the newly introduced groundwater was able to come to secular equilibrium with the ^{222}Rn parent isotope, ^{226}Ra, within the soil and aquifer matrices. These results were then used as a base level for the main focus of this study: the time series measurements during a storm.

Three separate time series datasets have been collected with the initial study (March 5, 2016) being cut short due to an insufficiently charged battery that caused the 12V pump to fail after 3 hr. The second dataset (April 10, 2016) was collected during a period of little rain and resulted in insubstantial data (0.05 cm over 24 hours). The third dataset (March 21, 2017) was taken during a period with two separate intense precipitation periods, which were

recorded in an hourly precipitation value. The first set of measurements for field tests were collected during a relatively dry period: no rain for at least 20 days (~ 5 half-lives of ^{222}Rn), which should allow the radon activity in the groundwater to reach secular equilibrium. This set of measurements initially aimed to produce a maximum radon activity of the stream at this location because it was expected to provide a measurement of nearly pure groundwater not diluted by storm water. The initial stream measurements were originally collected as the groundwater end member for the mixing model. This changed when later analysis revealed this method led to situations where the pre-event water would sometime account for more than 100% of the stream discharge, a result of having a pre-event activity significantly lower than the actual pre-event activity.

An alternative activity for groundwater was then acquired through the Montecito Water District 2008 Water Quality Report and that value was used to determine the final ^{222}Rn activity hydrograph. Knowing the pre-event groundwater ^{222}Rn activity and assuming that event water contains little to no ^{222}Rn (because of radon's low solubility and mixing ratio in the atmosphere), a two-end member mixing model was created.

Pre-event and event water end members for all tracers in this study were collected from multiple sources. Pre-event water values were determined through analysis of pre-storm San Ysidro Creek water after a dry period of no less than 16 days to ensure stream water is sourced exclusively from groundwater. ^{222}Rn activity and silica concentration of the event water is assumed to be near zero. Stable isotope event water values are determined through collection and analysis of precipitation from storms collected from a nearby station in Goleta (694 Edgewood Drive; 34 m amsl (Google Earth)). These values are then corrected for elevation.

During the initial two tests collect in 2016, stream discharge was measured manually and compiled at an hourly basis. Test 3 utilized a rating curve created from previous storm discharge measurements and a Solinst Levelogger tool, which recorded stream depth every minute. These values were then combined into averaged 5-minute data points for stream discharge.

D. Lab Methods

The unfiltered samples for stable isotope analysis were transferred from 60 mL glass bottles with poly-seal caps into 2 mL glass bottles with septa caps in the laboratory and were then sent to the UC Davis Stable Isotope Laboratory. UC Davis analyzed the samples for oxygen and hydrogen stable isotope ratio values on their Water-Vapor Isotope Analyzer, which was designed by Los Gatos Research Instruments (an off-axis Integrated Cavity Output Spectrometer). The dissolved silica concentrations were analyzed at the UCSB Materials Research Laboratory ICP-AES facility during two separate measurement periods. The first and second measurement periods included, respectively, Test 1 and Test 2 from 2016 and Test 3 from 2017 as well as some background spring data from the old Mission Tunnel and from Hot Springs Road. During each measurement period, standards purchased from High Purity Standards in North Charleston, SC, were analyzed.

Analyses of soil ^{222}Rn emanation rates were completed using an incubation process described by Goodridge and Melack (2014). Samples were incubated with deionized water for 20 days. During this time, all ^{222}Rn initially within the water and soil before incubation will have decay to insignificant levels. Therefore, the measured ^{222}Rn will have been produced by the soil collected from the streambed. After the incubation period, the samples were analyzed using the RADH_2O setup (Durrige, 2015). The methods of Goodridge and

Melack (2014) stated that the samples were run on a continuous closed air loop for 1.25 to 3 hours on 15-minute sample collection times. For degassing the samples in this test, the method used was the RADH_2O program on the RAD7 device. In this method all the radon is expected to be removed from the water during the initial 30-minute "bubbling" stage of measurement, but the pore water might not be fully degassed through this method as typically the RADH_2O program is used exclusively with samples with no soil component. This may result in a lower emanation rate than the natural emanation value.

IV. RESULTS

A. Background Laboratory Test

The first series of background tests with the RAD7 device were designed to determine basic capabilities and limitations of the modified procedure. The first test was completed to confirm the lower limit of time needed to reach equilibrium. Schmidt et al. (2008) found this lower limit to be 15 minutes, similar to the time required for ^{18}Po to reach secular equilibrium with ^{222}Rn. Multiple tests conducted on local tap water suggested that consistent data started at roughly 30 minutes after the RAD7 began testing (Fig. 5B). When the device had been running for more than an hour before hand, this time was reduced by almost 10 minutes creating consistent measurements from the end of the second measurement period.

B. Background Field Tests

The background field studies were a test to determine the effect that turbulence and waterfalls had on the activities of ^{222}Rn in a stream. Initial measurements were taken at

SNARL in the parallel stream channels near Convict Creek (May 28, 2016). These channels were the downstream section of two small weirs that directed part of Convict Creek's flow through the parallel channels. After an hour of data collection, the RAD7 device was reading virtually no ^{222}Rn (0.001 ± 0.023 Bq/L) (Figure 7B). ^{222}Rn was then measured above the first weir in the bypass channel itself. These tests also came back with values similar to dry air (0.005 ± 0.014 Bq/L) (Fig. 7A).

The second background study (September 9, 2016) was at Sagehen Creek Field Station, about 15 km north of Truckee, CA to see if a new location would yield different results. A similar experiment to the one at SNARL was conducted by measuring the activities of ^{222}Rn upstream and downstream of the constructed USGS Gaging Station located on Sagehen Creek. The two tests ran for 80 minutes each and there was significantly more ^{222}Rn in Sagehen Creek than in Convict Creek. The upstream measurements at Sagehen for radon activities was 0.10 ± 0.04 Bq/L (Fig. 8A) whereas just downstream of the weir the average activity was 0.09 ± 0.04 Bq/L (Fig. 8B). These values agree with ^{222}Rn activities measured by Gleeson et al. (2018) who found a steady change in ^{222}Rn activity from 0.07 Bq/L to 0.15 Bq/L over a 600 m reach of Sagehen Creek.

C. Initial Values

i. March 5, 2016 Test

Tests of ^{222}Rn activities in San Ysidro Creek were conducted on three separate occasions, both of which had a preliminary analytical period when typical levels of ^{222}Rn activity without storm input were determined. During Test 1 baseflow was measured five days before the main test on February 28, 2016. The base level of Test 1 was found to be 0.31 ± 0.05 Bq/L after two hours of data collection (Fig. 9A). The activity measured during

the March 5, 2016 test (20:00 to 23:00 PST) ranged from 0.37 ± 0.08 to 0.51 ± 0.09 Bq/L (Fig. 9B) with no apparent trends (*i.e.*, the high activities and low activities were not temporally related to anything in the test). This time series was cut short because the battery powering the water pump was drained. Creek discharge increased throughout the test and there was slight variation in ^{222}Rn activity.

The precipitation rate is measured at MTIC1 weather station in Montecito (2.3 km from the San Ysidro Creek field location at 493 m above sea level) during the March 5, 2016 test was about 0.28 cm/hr. The samples collected on March 5th have initial silica concentrations of 8.81 ± 0.04 ppm (Fig. 10A), but during the period of greatest rainfall these values drop to 8.49 ± 0.05 ppm (Fig. 10B). The dissolved silica data of Test 1 shows significant depletion of dissolved silica before reaching a minimum at the end of the test (Fig. 10B) (when the battery failed).

The Stable Isotope data also shows similar trends to that seen in the dissolved silica data. The March 5, 2016 test dataset shows a steady decrease in $\delta^{18}O$ and in $\delta^{2}H$, which is a departure from the pre-event water value (-6.3‰ for $\delta^{18}O$ and -37‰ for $\delta^{2}H$) (Fig. 11A – B) towards the less depleted values of the event water (-4.1‰ for $\delta^{18}O$ and -16‰ for $\delta^{2}H$). The initial values for the test were -6.2‰ for $\delta^{18}O$ and -37‰ for $\delta^{2}H$ and the final sample showed values of -5.7‰ for $\delta^{18}O$ and -33‰ for $\delta^{2}H$ (Fig. 11C – D).

ii. April 10, 2016 Test

Test 2 was collected in the field for six hours (13:46 – 19:46 PST) and initial activities collected on April 9, 2016 for the pre-event water were found to be 0.341 ± 0.08 Bq/L (Fig. 12A). During Test 2, activities fluctuated from 0.33 ± 0.08 to 0.21 ± 0.05 Bq/L

but did not produce any significant trends (Fig. 12B). This dataset has been analyzed and it is believed that due to the low rainfall during this 6-hour test (0.05 cm total precipitation) the results are inconclusive (0.33 ± 0.08 to 0.21 ± 0.06 Bq/L falls within standard error). Slight similarities do seem to exist between some of these measurements and when precipitation occurred, but never enough to outweigh the large counting errors associated with the RAD7 device.

The dissolved silica data from Test 2 shows little variation and a slight increase in overall concentration during the test. The background test on April 9, 2017 produced an average silica concentration of 8.91 ± 0.07 ppm (Fig. 13A). The samples collected on April 10, 2016 have initial silica concentrations of 8.74 ± 0.15 ppm and range from this initial concentration to 8.85 ± 0.07 ppm throughout the test (Fig. 13B).

The Stable Isotope data collected during the April 10, 2016 test shows sporadic variability in the $\delta^{18}O$ and in $\delta^{2}H$ ratios that fall around the average of the pre-event water values (-6.1‰ for $\delta^{18}O$ and -35.4‰ for $\delta^{2}H$) (Fig.14A - B). The values for this test ranged from -6.2‰ to -5.9‰ for $\delta^{18}O$ and ranged from -35.8‰ to -34.5‰ for $\delta^{2}H$ (Fig. 14C - D). The precipitation rates during the April 10, 2016 test were low enough that no precipitation sample was collected at the Goleta station.

iii. March 21, 2017 Test

During Test 3 on March 21, 2017, there were two intense periods of precipitation which were recorded at the nearby weather station (MTIC1): The first period went from 7:47 to 10:47 PST and dropped 0.92 cm/hr of precipitation and the second period went from 11:47 to 12:47 PST and dropped 0.53 cm/hr of precipitation. This creek dataset was recorded at the

second location nearby the flood control structure in San Ysidro Creek and the results are different than the results attained at the earlier study site. The pre-test ^{222}Rn activity of baseflow was measured on Mar. 19, 2016 at 0.061 ± 0.01 Bq/L (Fig. 15A) and the ^{222}Rn activities during the main test ranged from 0.038 ± 0.021 Bq/L to 0.099 ± 0.031 Bq/L. Activities were lower from 6:30 to 10:30 PST and higher between 10:45 to 16:15 PST (Fig. 15B). This time series ran over the course of 11 hours (from 5:15 to 16:15 PST) and data collection concluded once the rain had been over for 3 hours.

The dissolved silica concentration was 10.0 ± 0.1 ppm in the pre-event water and the event water is expected to have a silica concentration of 0 ppm (Fig. 16A). The initial concentration of Test 3 was 9.68 ± 0.08 ppm, which over the test decreased exponentially during precipitation events, leveled off between precipitation events, and started to increase back to pre-storm levels once the precipitation ended with a minimum in creek value of 8.92 ± 0.03 ppm (Fig. 16B).

The stable isotope data for the March 21, 2017 test shows results that follow similar trends to the dissolved silica data with pre-event δ^2H ratio of -36 ± 1‰ and an elevation corrected δ^2H ratio of -28 ± 1‰ (Fig. 17A) and a pre-event $\delta^{18}O$ ratio of -6.1 ± 0.2‰ and an elevation corrected $\delta^{18}O$ ratio of -5.5 ± 0.2‰ (Fig. 17B). Stable isotope values closest to pre-event water levels were seen after the second major precipitation event.

D. Flux and Hydrograph Data

i. March 5, 2016 Test

During Test 1, the constant ^{222}Rn activities show a steadily increasing trend over the three hours (Fig. 18A). From an analytical viewpoint, this could be caused by the discharge

within San Ysidro Creek steadily increasing throughout the storm, which means that the increase in discharge would have been almost entirely composed of groundwater and would have contained little soil or event water. This is because ^{222}Rn activities remained steady while total discharge in the creek increased. In comparison, the silica flux also showed a steady increase in stream silica during Test 1 (Fig. 18B)

The poorly recorded discharge of this initial test resulted in a set of hydrographs, which are governed by seemingly constant increases in total stream discharge due to low frequency (hourly) discharge measurements. All the March 5, 2016 hydrographs show a steady increase in event water discharge during the test with initial event water discharges of nearly zero (Fig. 19A – D). The ^{222}Rn data also seems to show that this event water component is skewed to a negative discharge by the increase in total ^{222}Rn flux from a change in the pre-event water activity. The expected pre-event water ^{222}Rn activity was 0.31 Bq/L but the very first measurement after the RAD7 had warmed up was already greater than this value, which in turn produces a hydrograph with a negative discharge value for the event water, assuming the event water ^{222}Rn activity remained constant and the pre-event water ^{222}Rn activity increased during the test.

ii. April 10, 2016 Test

During Test 2, ^{222}Rn activities were constant throughout the test with all values falling within typical analytical error of the RAD7 device (Fig. 13B). However, when the ^{222}Rn activities are converted to ^{222}Rn flux, the resulting data starts to create a series of peaks and valleys, which might be linked to increased rainfall in the upper reaches of the San Ysidro Watershed (Fig. 20A). The ^{222}Rn flux seems to agree well with the silica flux values despite the low precipitation (Fig. 20B). The observed 0.05 cm of rainfall measured at

weather station MTIC1 occurred within the time frame of 15:47 to 17:47 PST. The ^{222}Rn flux does show an increase and eventual decline during this time frame. This could be indicative of a surge of groundwater into the creek caused by a minor pressure wave from the precipitation in the upper sections of the watershed, but again the analytical errors of the RAD7 device make this trend difficult to resolve.

The chemical hydrographs created for the April 10, 2016 test were of a higher temporal resolution due to greater sampling of stream discharge throughout the test. The ^{222}Rn activity hydrograph shows a constant level of event water discharge (ranging from 1 to 3 L/s) throughout the seven-hour test (Fig. 21A). Despite changes in total discharge, the percentage of event water remains at 20% to 25% of total discharge. The dissolved silica hydrograph also shows a similar trend with constant levels of event water discharge (ranging from 1 to 2 L/s) throughout the seven-hour test (Fig. 21B). This suggests that all event water quickly recharged the aquifer, which in turn allowed all the stream discharge to come from the pre-event water source. The first period of minimum event water discharge occurs during a period of peak discharge within the stream at 15:56 PST while the second minimum occurs at 17:56 PST, which corresponds with a minimum in total discharge. No stable isotope hydrographs were created for the April 10, 2016 tests because no precipitation samples were collected at the Goleta station due to the low levels of precipitation that day.

iii. March 21, 2017 Test

During Test 3, the ^{222}Rn flux increased from a pre-event value of 0.47 Bq/s to a final value of 1.62 Bq/s (Fig. 22A). The flux of silica shows a similar trend to the ^{222}Rn flux in that it starts at 55.4 mg/s and increases to a maximum two hours after precipitation ended of 158.5 mg/s (Fig. 22B). The ^{222}Rn flux increases almost instantaneously to its second value

(over a 15-minute period) whereas the silica flux increases gradually over two hours. The ^{222}Rn flux increases 3.5x while the silica flux increases 2.9x and both flux graphs exhibit a stable period after the periods of precipitation.

Similar results have been seen in the dissolved silica data during the March 5, 2016 test that showed a change of 0.5 ppm or 24 mg/s in only three hours of testing (Fig. 10B and 18B) whereas the April 10, 2016 test that shows only 0.15 ppm variability or 5 mg/s throughout the entire 6-hour test period (Fig. 13B and 20B). Likewise, the stable isotopes show ±0.3‰ variability for $\delta^{18}O$ and ±1‰ variability for $\delta^{2}H$ whereas the March 5 test showed twice that variation over half the time and it had a visible trend to it (Fig. 11C - D; Fig. 14C - D).

The March 21, 2017 test produced a set of four chemical and isotope hydrographs, which show the variations of event water discharge throughout the time series (Fig. 23A – D). Brief spikes in stream discharge were recorded 30 minutes after the onset of both major precipitation events and the greatest discharge was recorded two hours after the final precipitation event had occurred (Fig. 23A).

E. Final Stream Sediment and Alternate Pre-event Source Analyses

The analysis of the two soil activity samples collected at the second San Ysidro Study site provided incubated ^{222}Rn emanation rates of 0.21 and 0.28 Bq/s with an associated error of ± 0.20 Bq/s. In comparison, a sample of local UCSB tap water (which is groundwater sourced) collected and analyzed after these samples finished showed an activity of 0.9 ± 0.4 Bq/L.

An alternate groundwater ^{222}Rn activity for hydrograph separation was collected from deep pool of stagnant water which appeared to be a groundwater source located just downstream of the initial San Ysidro Creek study site. This deep pool was sampled on January 18, 2017 and had an activity of 0.35 ± 0.06 Bq/L. An additional groundwater ^{222}Rn activity was collected by the Montecito Water District and published in a 2008 water quality report (Montecito Water District, 2008). This report indicates an average activity of the sampled groundwater wells of 2.26 Bq/L with values that ranged from 0 Bq/L to 11.5 Bq/L. After discussions with the Montecito Water District, no standard deviation or sample size was made available for this report, but it is still a possible value of interest for the groundwater within the catchment area.

V. DISCUSSION

The major complications of this study were the changes to groundwater discharge as well as variations in channel distance from groundwater discharge sites. During these field studies, the distance to groundwater discharge sites becomes a complex issue. Typically, these discharge sites are places where the phreatic surface intercepts the surface, which is often associated with natural groundwater springs. This study measured ^{222}Rn activity at a defined site along San Ysidro Creek, which is an unknown distance from nearby static groundwater influx points (or reaches) in this stream. While taking background measurements under dry conditions, that distance is not a variable unless the phreatic surface drops from low groundwater recharge. During a storm, this distance as well as total stream discharge becomes highly variable. Discharge can be measured and partially accounted for, but distance from groundwater influx can be strongly influenced by loading and subsequent

rising of the phreatic surface by precipitation and by changes in the formation through which groundwater is discharged. Increased phreatic surface elevation results in a larger area of contact between groundwater and the surface, which in turn increases ^{222}Rn flux into the stream.

Some complications and uncertainties regarding IHS also affect the use of ^{222}Rn activity in performing a hydrograph separation. The main complications are from temporal variation of pre-event water throughout the storm and from the influence on the stream ^{222}Rn activity by the vadose zone and soil water. Temporal variations in the pre-event water signature were not measured during this study. If multiple samples of soil and groundwater ^{222}Rn activity were collected at the same frequency of the stream sampling device, then this problem could be solved through clearly defined end members. Alternatively, a measurement of activities at the head of a spring or other major groundwater source could remove complications from the soil water component. Vadose and hyporheic zone waters are also both known to have an influence on stream ^{222}Rn activity (Dörr and Munnich, 1990; Cook et al., 2006; Lamontagne and Cook, 2007). This influence is due to the transition between air and groundwater ^{222}Rn activities in the vadose zone and the transition and transfer between river and groundwater ^{222}Rn activities in the hyporheic zone. While these values could be measured using three-component mixing models, they would require an end-member value for vadose zone water. Alternatively, the event water or groundwater discharge would need to be measured at a similar frequency to the total stream discharge.

Silica also has complications that are separate from those of gaseous tracers. Given the depth of the soils and alluvial fan deposits within the Santa Ynez mountain range, silica may not remain a conservative tracer within the watershed as depth of soil leads to longer

soil water flow paths and higher silica concentrations (Hinton et al., 1994). The small area of the San Ysidro watershed and the lack of sunlight during storm events should minimize diatom growth within the stream. This allows silica, which is typically not a conservative tracer to behave in a near-conservative manner in the creek. Silica also seems to produce a chemical hydrograph separation similar to that of the conservative stable isotope tracers.

Of all the hydrograph separation methods involved in the San Ysidro Creek ^{222}Rn study, the most likely tracers to remain conservative throughout the storm event are the stable isotopes and the dissolved silica. Complications may arise if the stable isotope ratios of the pre-event water or the event water change throughout the storm duration, which is a factor that could be addressed through multiple analyses of event water (collected throughout the storm) as well as analyses of changes in mean elevation of precipitation. The precipitation is not necessarily constant over the catchment area and if the majority precipitates at a lower elevation or higher elevation that will affect the enrichment of the lighter isotopes in the event water.

Two-component hydrograph separation has been most commonly done with the stable isotopes unless one of the assumptions about the event water had been proven to be incorrect (Hubert et al., 1969; Mook et al., 1974; Sklash et al., 1975; Hermann et al., 1978). When that happens, silica is usually the next most conservative tracer for hydrograph separation studies. For silica to be a conservative tracer within the San Ysidro watershed there are two major assumption that must be met: there must be little difference between pre-event silica before the storm and during the storm, and the event water must pick up little to no silica after falling within the watershed. Complications arise from the introduction of precipitation into soil water, which is typically part of the pre-event water during initial stream chemistry

surveys. Results from recent ICP tests show that there is negligible difference between stream water and direct spring water within the watershed, which shows that the effect of diatoms on silica is negligible.

The studies at SNARL and Sagehen provided two major findings that are relevant to the ^{222}Rn fieldwork. The first is that there are scenarios in which the use of ^{222}Rn as a proxy for groundwater influx is not reliable. Gas loss due to natural diffusion from the creek throughout the reaches of the stream seemed to have caused the rapid loss of the likely already scarce ^{222}Rn found in the melted snow water of the eastern Sierra Nevada Mountains that is the primary water source of Convict Creek. The combination of snow melt source coupled with severe turbulence in the upper reaches of Convict Creek made ^{222}Rn undetectable with the RAD7 membrane contactor method. There is also the possibility that Convict Creek is not a gaining stream (a stream which is actively receiving groundwater from local aquifers), but a losing stream (a stream that is recharging local aquifers with its water). If that were the case, then it would make sense that there was minimal ^{222}Rn activity because there would be almost no discharge of groundwater within the creek. This seems possible considering the source waters of Convict Creek is Convict Lake, whereas the source water of both Sagehen Creek and San Ysidro creek are springs and baseflow.

Nonetheless, there are also significant benefits to using the RAD7 device rather than stable isotope and dissolved tracer analysis. Aside from the issue of mobility and cost, the Sagehen test indicates that the RAD7 device is more sensitive to the environment of a stream than other methods. The Sagehen test also shows the severe effect of gas loss within a stream due to normal stream processes. ^{222}Rn activity dropped by 0.01 ± 0.04 Bq/L over a five-meter reach of the stream (Fig. 8B) and it has been shown to drop up to 0.075 Bq/L over a 600 m

reach of Sagehen Creek (Gleeson et al., 2018). This rapid loss of ^{222}Rn activity deeply complicates the time series tests conducted in this study due to changes in both pre-event water sources as well as changes in ^{222}Rn gas loss during the storms.

The San Ysidro Creek tests showed that the ^{222}Rn activity alone was not capable of showing the same trends that were observable with the other geochemical tracer data. Both Test 1 and Test 2 showed no significant variation in the ^{222}Rn activity even though the decrease in dissolved silica was apparent. One critical result attained through the ^{222}Rn study of Test 1 is that the baseflow measurements attained five days prior to the major storm test showed lower ^{222}Rn activities than what was observed during the storm event. Two possible explanations of this result are that either 1) there are more than two sources of ^{222}Rn into the stream and that they are being affected differently by the storm event, or 2) that the total amount of ^{222}Rn lost to gas exchange decreased once there was a greater discharge during the storm which increased the ^{222}Rn activity of the stream

Typical baseflow is not strictly composed of groundwater supplied from aquifers. There is a component of baseflow that is made up of soil or vadose zone water. Previous studies using ^{222}Rn as a tracer have mentioned that it is important to understand the relative fluxes of both groundwater and soil water and how their combined values make up baseflow (Hinton et al., 1994). The result from Test 1 suggests that during the large storm, there was a larger relative concentration of groundwater to soil water in the stream, which was seen as higher activities of ^{222}Rn.

The ^{222}Rn hydrograph separation of the March 21, 2017 test shows a constant increase in both event water and pre-event water during periods of precipitation with minor "pulses" which occur during periods of peak discharge. Further analyses also show that the

percentage of discharge, which is attributed to event water decreases with time whereas the percentage of discharge attributed to pre-event water increases with time (Fig. 23A). The findings from the other geochemical tracer studies suggest that Test 1 has a strong influx of event water into the stream, which caused stream water to show more event-water like characteristics. This finding is in agreement with the Test 1 ^{222}Rn activity hydrograph in that during the initial precipitation event there is an increase in total event water discharge, which is associated with the low activities. This may be due to the difference between ground and soil water ^{222}Rn activities and the smaller variation between these two sources with regards to the natural dissolved silica. The RAD7 device seems capable of attaining the correct trends for ^{222}Rn flux but a longer measurement duration of each individual run (from 10 min to 15 min or longer) will decrease the analytical error because it would increase the number of decays the device could measure before determining the activity.

The dissolved silica Test 3 hydrograph shows an increase in event water discharge from near 0 L/s to 1 L/s during the first precipitation event and to 2 L/s during the second precipitation event (Fig. 23B). The stable isotope hydrographs show increases in event water during periods of recorded precipitation in the catchment area while also showing a return to pre-event levels during periods in which little to no precipitation occurred (Fig. 23C – D). The δ^{18}O Test 3 hydrograph also shows a steady increase in event water discharge from 0 L/s to 1 L/s during the first period of intense rainfall which then increased to 2 L/s during the second period (Fig. 23D). The δ^{2}H Test 3 hydrograph shows a similar trend with near 0 L/s event water discharge at the start of the test which increases to 2 L/s during the first precipitation event at which time there is a quick dip between precipitation events before a return to higher event water discharge at just under 4 L/s within the second precipitation

event (Fig. 23C). The “peak discharge” correlates with a large increase in pre-event water and a significant decrease in event water discharge for the δ^2H hydrograph (Fig. 23C). The $\delta^{18}O$ values do not show this decrease, but there is a noticeable flat period, which appears a half an hour before precipitation ended (Fig. 23D).

Multiple ^{222}Rn hydrograph separations can be produced depending on which pre-event activity is used. The hydrograph that most closely resembles the dissolved silica hydrograph and the stable isotope hydrographs utilizes the baseflow value for pre-event water. The ^{222}Rn activity hydrograph created using the groundwater pool activity but without taking into account ^{222}Rn gas loss designates a constant 75 to 85 percent of the stream water is event water (Fig. 24A). The Montecito Water District’s reported groundwater ^{222}Rn activities from drinking water wells between 0 to 11.54 Bq/L. The value of the groundwater feeding San Ysidro Creek could therefore be any activity within that range. The average activity, 2.29 Bq/L, can also be used in this study as a pre-event activity and the associated hydrograph separation again without taking into account ^{222}Rn gas loss designates 96% to 99% of total discharge to event water (Fig. 24B). This seems to be a product of the strong effect that gas diffusion has on the creek ^{222}Rn activity coupled with the mixing of dilute headwaters with ^{222}Rn rich spring water.

The Test 3 ^{222}Rn hydrograph shows a similar trend to the Test 1 hydrograph in which higher activities are measured during the storm than were measured as the pre-event water value. The Test 3 hydrograph shows increases in event water discharge during periods of precipitation with decreases in event water discharge towards the end of precipitation events. During those times of minimum or low precipitation, the relative amount of pre-event water discharge increases. These pre-event water end-members attributed negative discharges to

event water during intense period of precipitation and both of these tests show a negative discharge of roughly -6 L/s at their minimum (Fig. 19A and 23A). This trend seems to be a result of unknown locations of the major groundwater sources along the stream coupled with ^{222}Rn loss from the creek throughout the storm hydrograph. The other methods used in this study either have no complications from gas loss (dissolved silica) or have minimal complications from gas loss (fractionation during evaporation). These ^{222}Rn hydrographs were able to show high temporal resolution trends in event and pre-event water discharge, but were not able to show realistic discharge values such as those seen in the silica and stable isotope hydrographs. To properly calculate these event water and pre-event water discharges using the ^{222}Rn activity hydrographs a study would need to know how the locations of groundwater influx into a stream change during a storm (through loading and raising of the phreatic surface by rain water) and how ^{222}Rn gas loss changes during a storm.

Another concern regarding these hydrograph separations is the lack of a clearly defined end member for the geochemical tracers. ^{222}Rn has difficult end member values to define as seen in the results of Test 1. Utilizing ^{222}Rn as a tracer for two-component hydrograph separation has severe complications associated with its end members, namely, the lack of a soil water activity component. The soil water component is variable and dependent on the depth of the phreatic surface. The soil water component affects hydrograph separation in that it further complicates the quantification of the pre-event end-member composition. Further quantification of the event water ^{222}Rn activity would also be useful since the pre-event water can typically range from 0.001Bq/L to 0.01Bq/L based on proximity to nuclear power planks (Takeyasu et al., 2006).

VI. CONCLUSIONS

The results show the RAD7 system can collect the necessary data to determine the discharge rate of groundwater and soil water into a stream given accurate end-member activities. The results show that the sampling duration for collecting ^{222}Rn activities does not seem to reduce errors unless there is insufficient ^{222}Rn within the stream (1^{st} study site vs 2^{nd} study site). Even if the testing duration required a 30 to 60-minute run time, it would still hold some advantages over the stable isotope and dissolved tracer methods. The ^{222}Rn activities are attainable after a brief post-processing rather than after lab analysis. The time and money saved by this method is further coupled by the possible un-studied benefits of the heightened sensitivity of the RAD7 device. The only inherent problem with these tests was the lack of sufficient ^{222}Rn activity within the second study site in order to produce a hydrograph with small errors. The given errors collected from the RAD7 system produce event water discharge errors of almost ± 3 L/s.

Another implementation of this study is that this method could be used to produce high spatial resolution groundwater discharge information. The introduction of this method as an effective way to collect time series baseflow data should allow hydrologists to collect more data in less time. The measurements made during this study and similar studies with this equipment will not work in all locations. Whether the stream is gaining or losing or whether the stream comes from an aquifer or lacustrine sources are questions hydrologists need to consider when using the membrane contactor-RAD7 ^{222}Rn-in-Air system. The best examples of this are the differences between the Sagehen Creek and Convict Creek study areas. However, this method could allow for very high spatial resolution hydrologic data that could inform which sections of a creek or a watershed have the lowest rates of groundwater

influx into streams, which sections of a creek have high turbulence, or which sections of a creek are gaining or loosing water.

The detailed hydrograph separations created from the March 21, 2017 Test 3 showed that there are significant trends visible within the event water discharge that are nearly identical to both the stable isotope and the dissolved silica hydrographs. The ^{222}Rn activity hydrograph shows these increases and decreases in event water discharge. The unknown factor that would have produced a clear and consistent ^{222}Rn activity hydrograph is a clearly defined groundwater activity and a clearly defined vadose zone activity. With those values, a three-component hydrograph separation could be created and the problem of the stream water activity exceeding the pre-event activity value from Test 1 and Test 3 would no longer be applicable.

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FIGURES

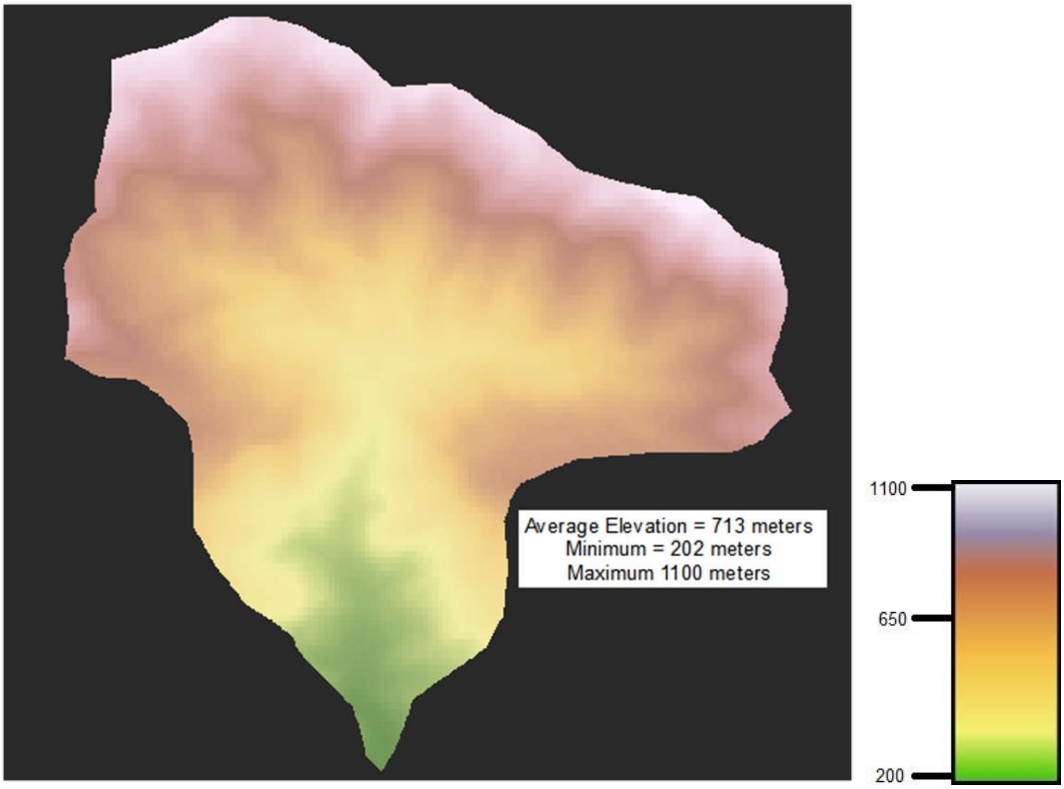


Figure 1: DEM showing San Ysidro Creek catchment area and elevation within the basin.

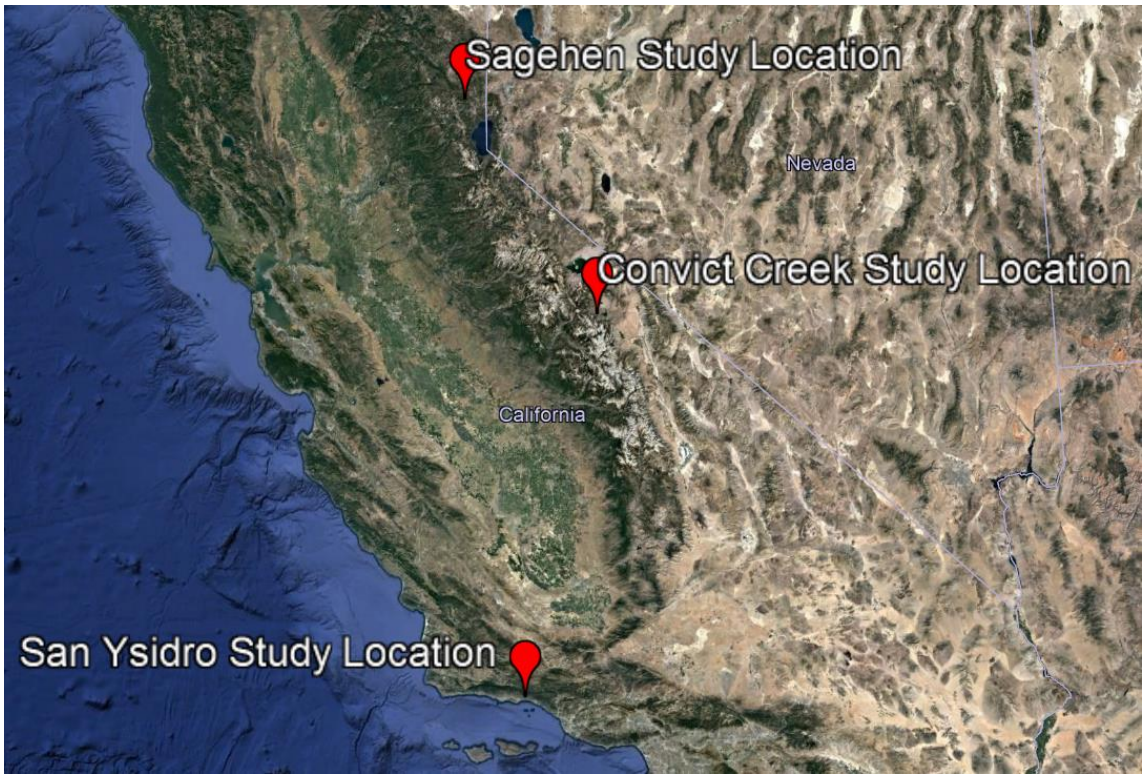


Figure 2: Locations of the three study sites within California (Google map).

Figure 3: (A) Convict Creek parallel channel study location (N37°36’45.2”–W118°49’50.2”). (B) Sagehen Creek study location (N39°25’53.2”–W120°14’16.2”).


A
B

Figure 4: San Ysidro Creek study location (N34°27’24.3”–W119°37’23.4”) before (A) and after (B) December 2016 and January 2017 storms. (C) San Ysidro Creek second study location (34°26'58.5"N 119°37'22.3"W).

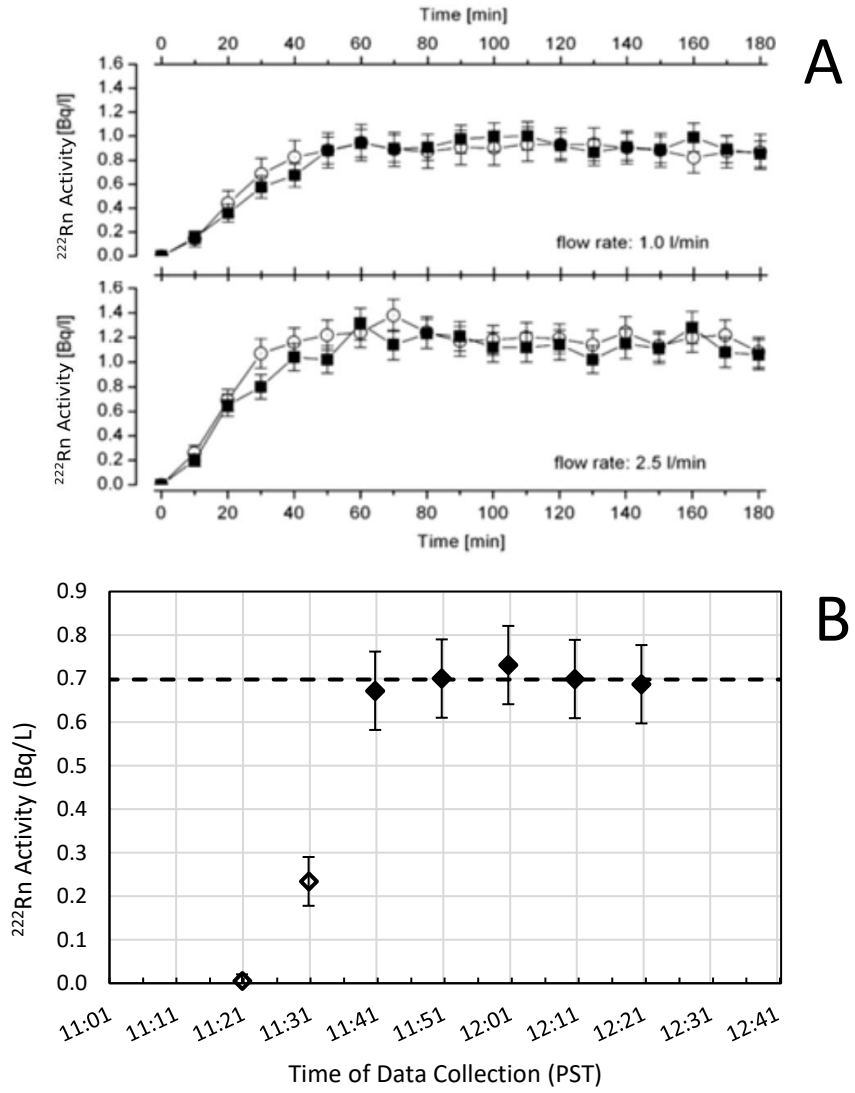


Figure 5: (A) Schmidt et al. (2008) data comparing radon-in-water activities at both low and high water flow rates showing equilibrium time. The solid squares represent activities measured using the membrane contractor method (used in this study) while the empty circles represent activities measured using the similar RAD AQUA device.
(B) Measurement of radon-in-water activities with error bars taken from initial laboratory tests of equilibration time using UCSB tap water. This data shows a similar "warm-up" time to what was seen in the study by Schmidt et al. in 2008. Data collection began at 11:11 PST and ran for 70 minutes. Open diamonds show values measured before the RAD7 device equilibration time (30 min).

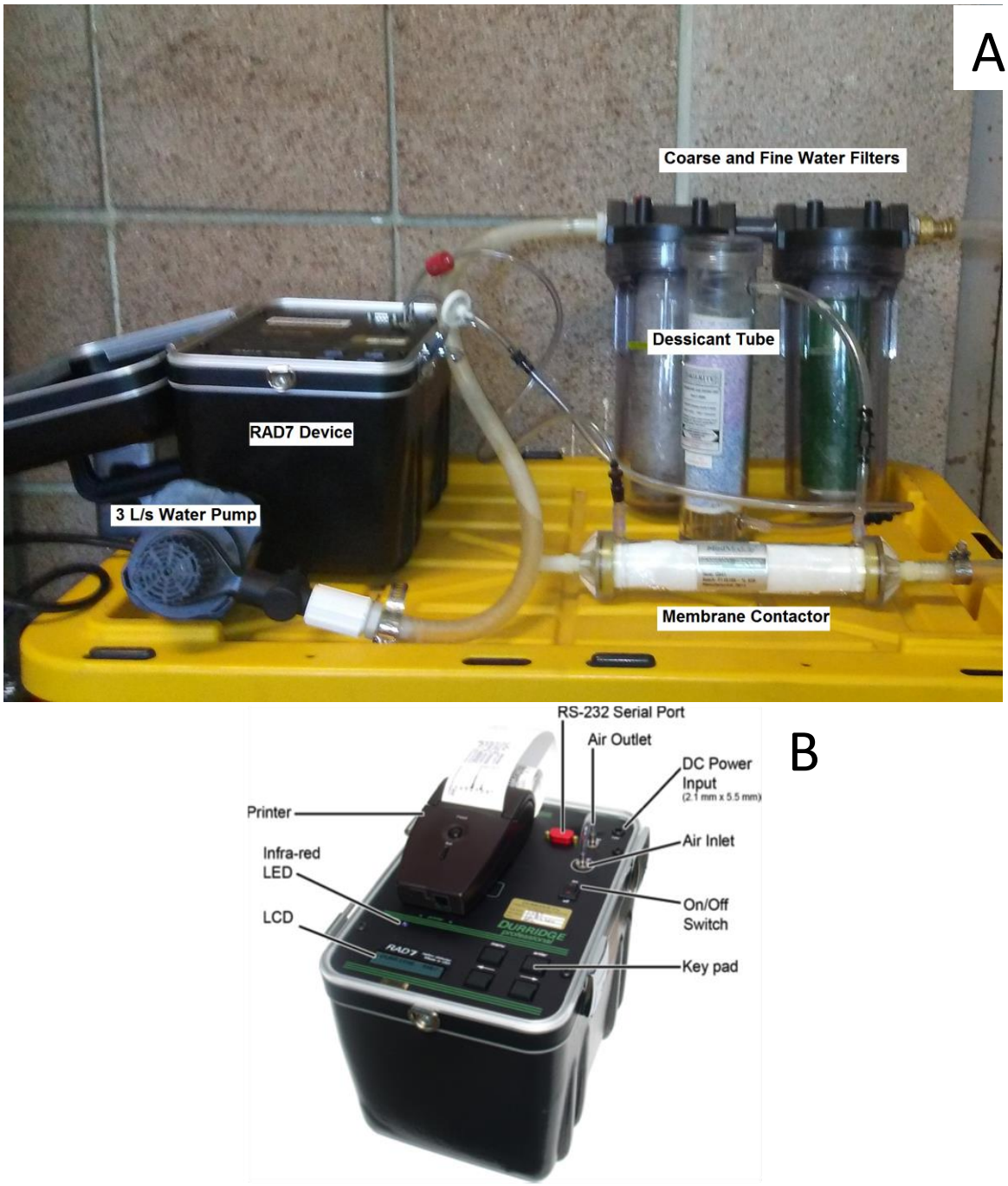


Figure 6: RAD7 device setup in conjunction with the membrane contactor and desiccant tube to ensure no water vapor enters into the RAD7 sensor chamber. (A) Setup developed by Schmidt et al. (2008) and (B) example of RAD7 device controls and air inlet / outlet.

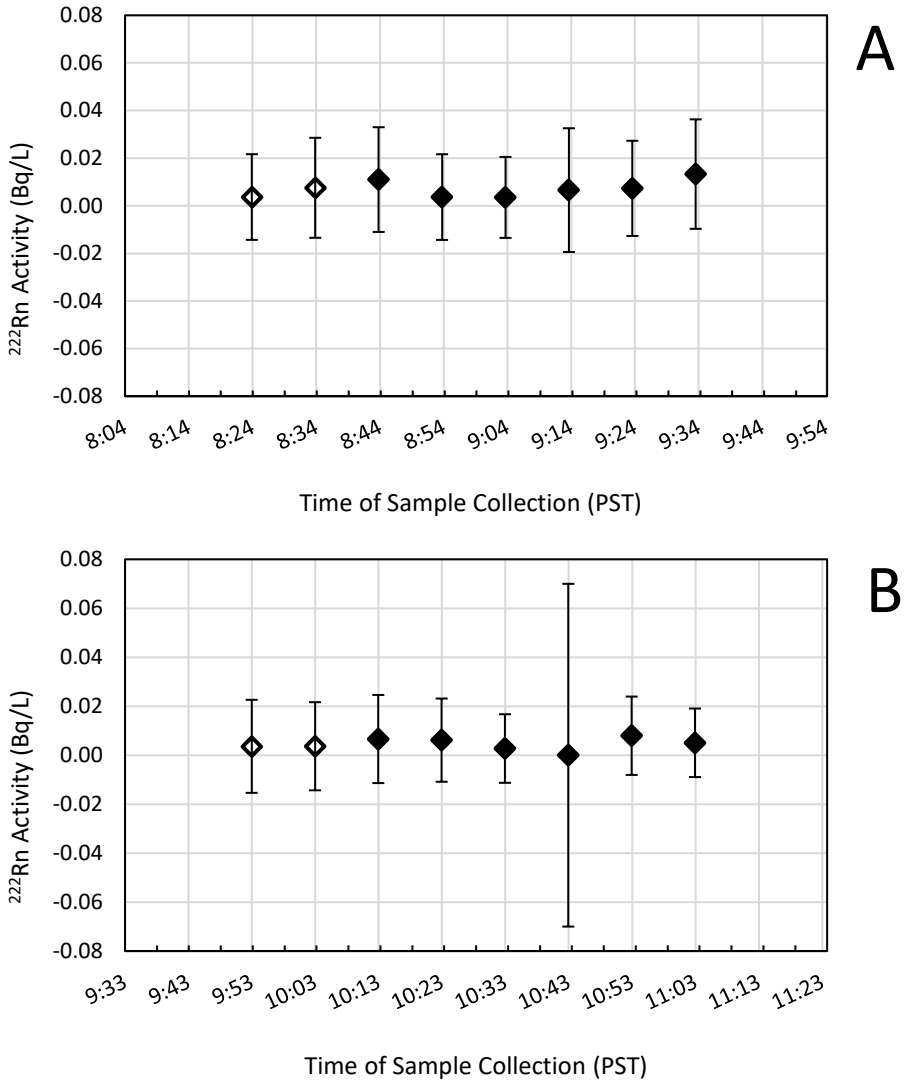


Figure 7: Radon activities from Convict Creek study showing near-zero values (A) upstream of the two flow control weirs and (B) downstream of the weirs. Open diamonds show values measured before the RAD7 device warm-up time (Fig. 5B).

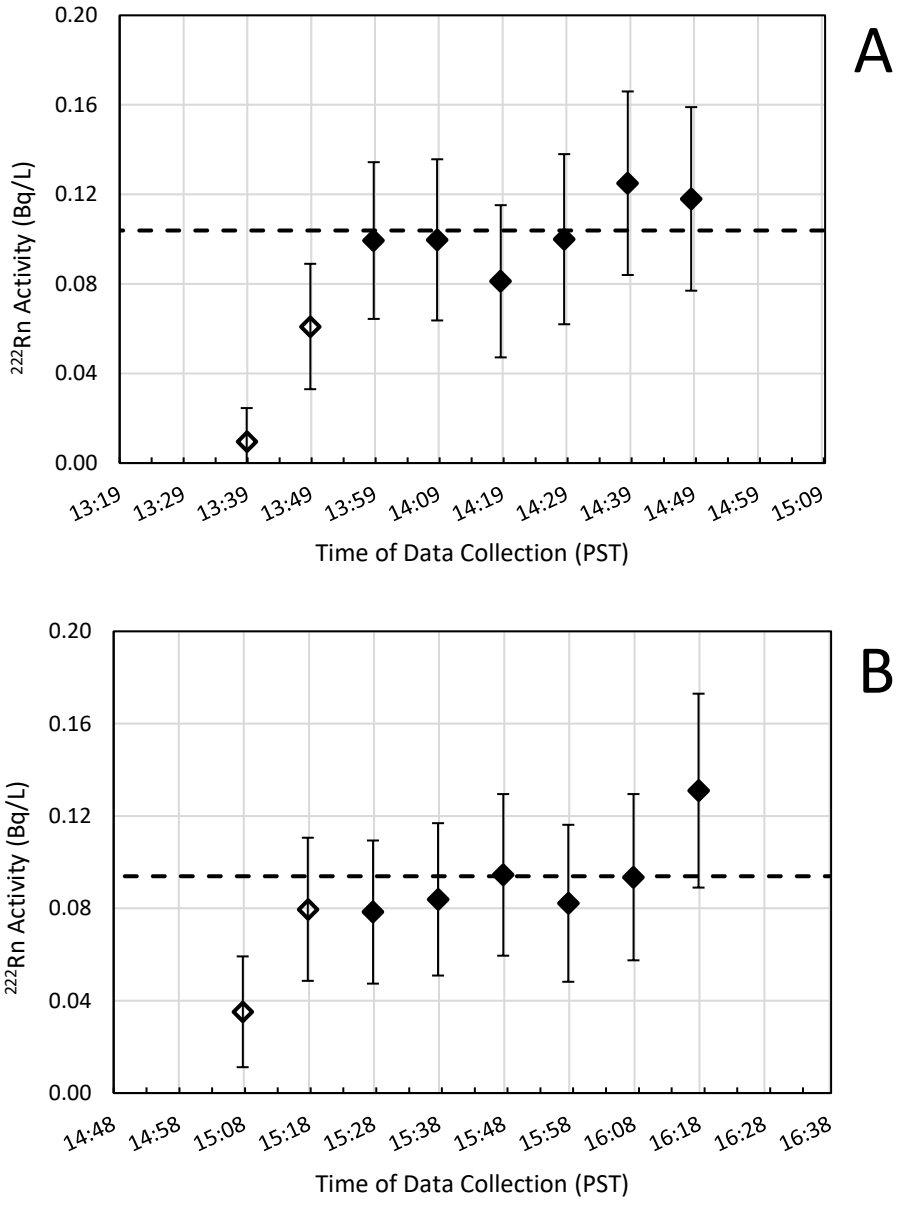


Figure 8: Radon activities from (A) above (0.104 ± 0.041 Bq/L) and (B) below (0.094 ± 0.042 Bq/L) the USGS Weir in Sagehen Creek (Fig. 2B). Dashed horizontal lines represent the mean ^{222}Rn activities. Measurements show a decrease in mean activities of approximately 0.01 ± 0.04 Bq/L due to gas loss caused by the approximate 15 cm fall. Open diamonds show values measured before the RAD7 device warm-up time (Fig. 5B).

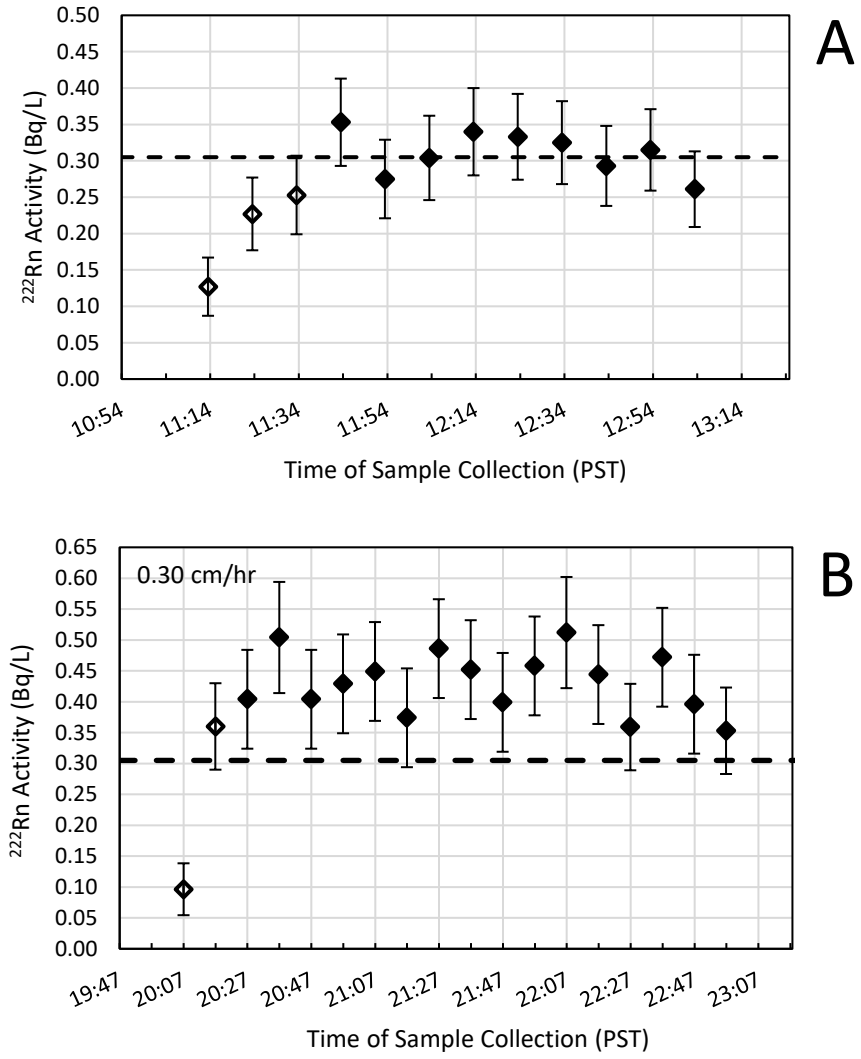


Figure 9: (A) Baseflow ^{222}Rn activities measured on Feb. 28, 2016. (B) Test 1 time-series data of ^{222}Rn activities measured during Test 1 on March 5, 2016. Open diamonds show values measured before the RAD7 device warm-up time (Fig. 5B). Average baseflow ^{222}Rn activity is shown by the dashed horizontal line (0.305 ± 0.06 Bq/L). Average precipitation during Test 1 was 0.3 cm/hr.

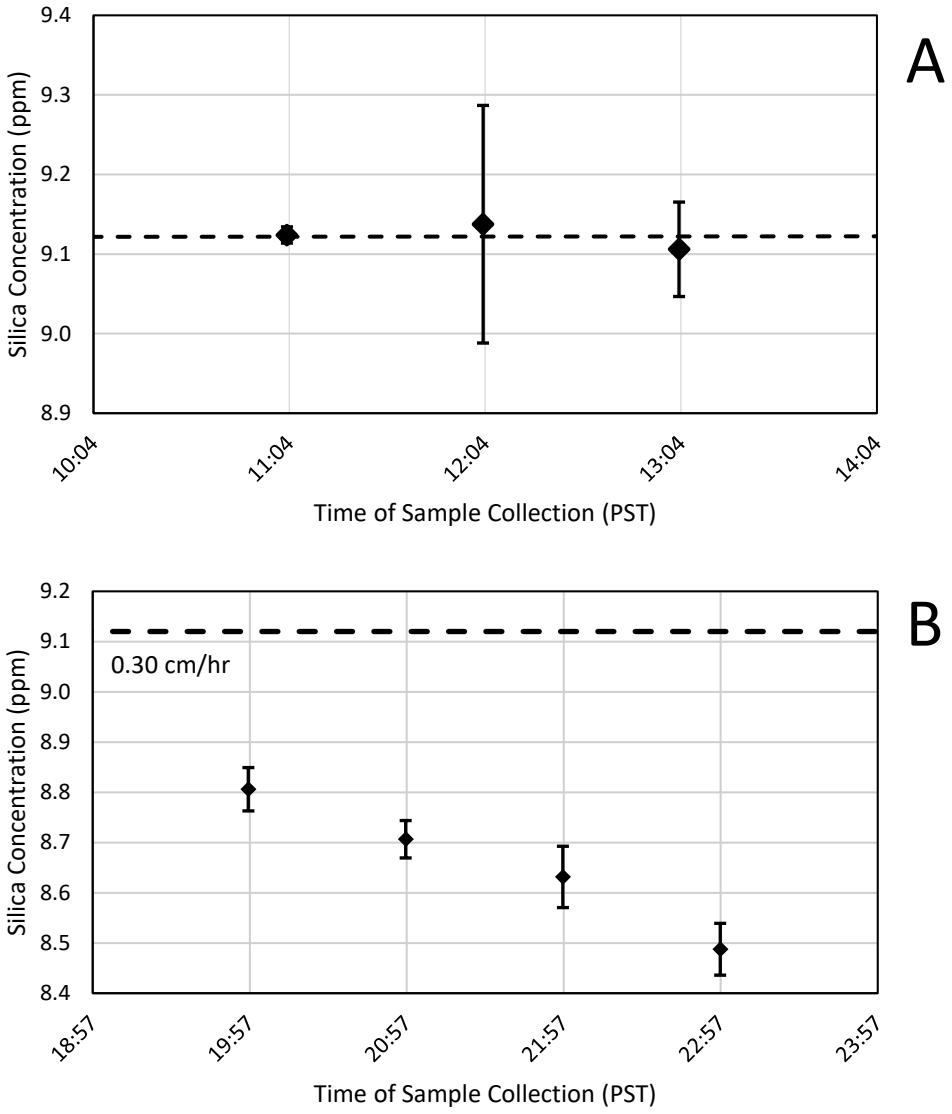
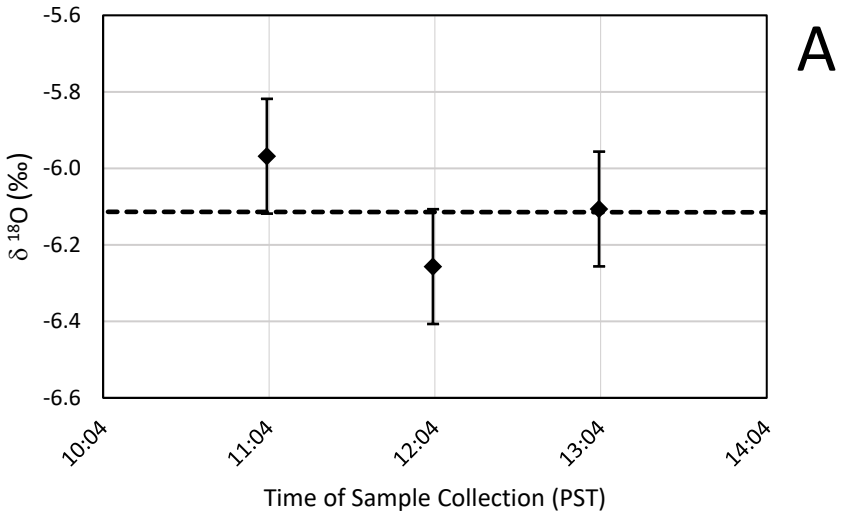
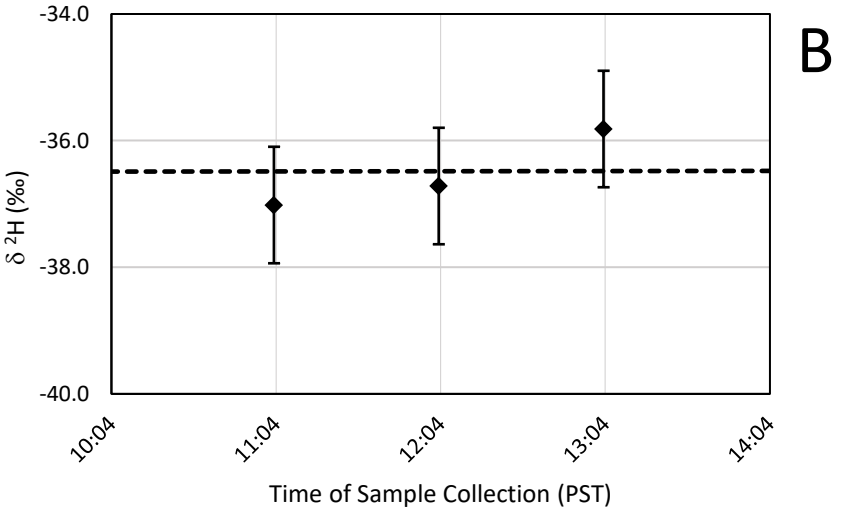


Figure 10: (A) Dissolved silica concentrations measured for baseflow on Feb. 28, 2016. (B) Dissolved silica concentrations measured during Test 1 on Mar. 5, 2016. Average baseflow silica concentration is shown by the horizontal dashed line (9.12 ± 0.14 ppm). Average precipitation during Test 1 was 0.3 cm/hr.


A
-5.6
-5.8
-6.0
-6.2
-6.4
-6.6
δ 18O (‰)
10:04
11:04
12:04
13:04
14:04
Time of Sample Collection (PST)


B
-34.0
-36.0
-38.0
-40.0
δ 2H (‰)
10:04
11:04
12:04
13:04
14:04
Time of Sample Collection (PST)

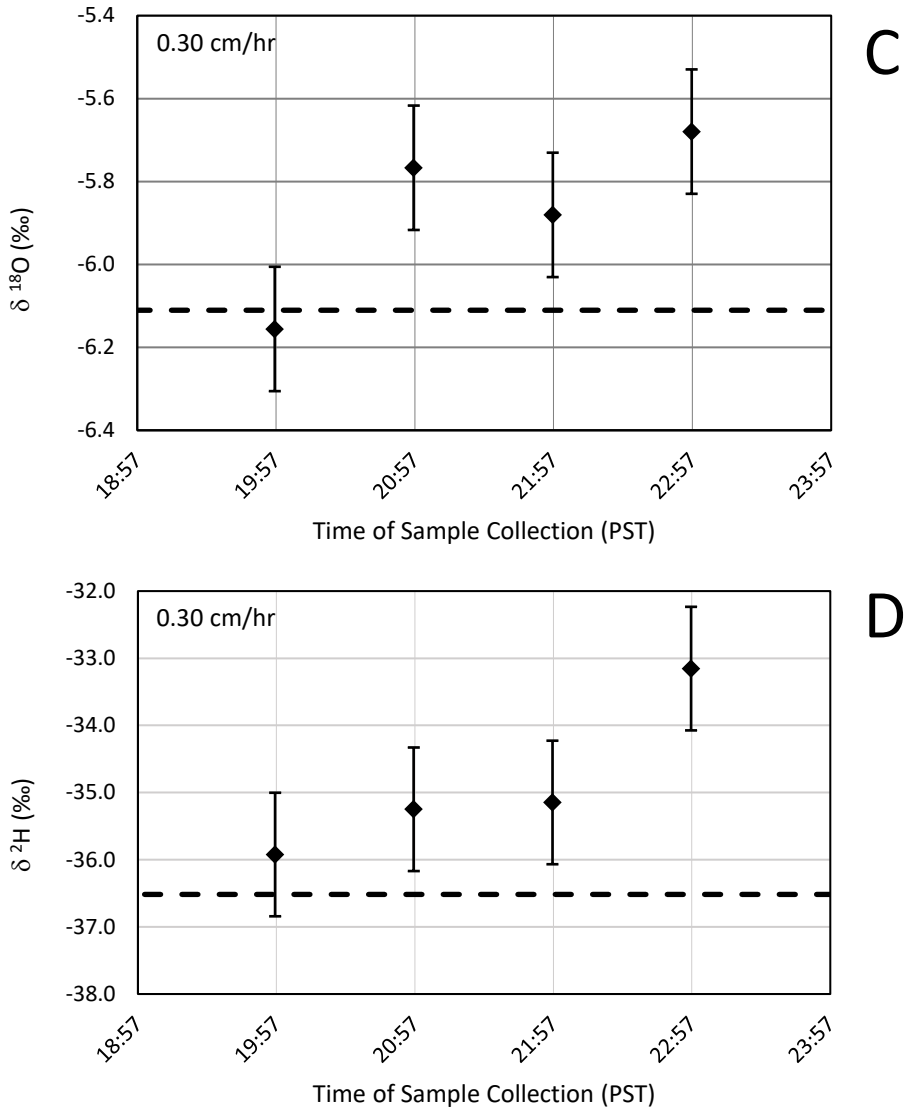


Figure 11: Baseflow values for (A) $\delta^{18}O$ and (B) $\delta^{2}H$ collected on Feb 28, 2016. Test 1 Stable Isotope values for (C) $\delta^{18}O$ and (D) $\delta^{2}H$ collected on Mar. 5, 2016. Average $\delta^{2}H$ is -36.5 ± 0.92 ‰ and the average $\delta^{18}O$ is -6.11 ± 0.15 ‰ which are represented by dashed horizontal lines. $\delta^{2}H$ and $\delta^{18}O$ event water values were, respectively, -15.7 ‰ and -4.1 ‰. Average precipitation during Test 1 was 0.3 cm/hr.

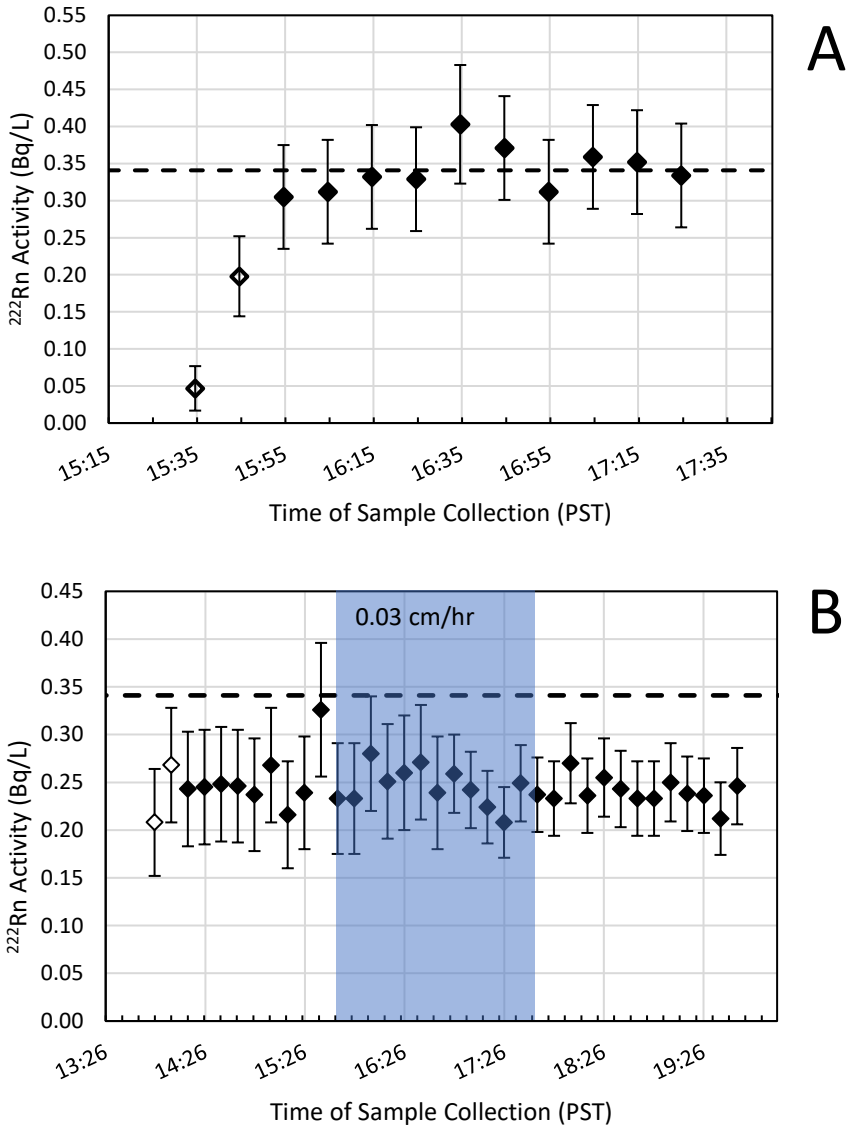


Figure 12: (A) Initial baseflow ^{222}Rn activities for Test 2 collected on Apr. 9, 2016. (B) ^{222}Rn activities during Test 2 collected on Apr. 10, 2016. Open circles show values measured before the RAD7 device warm-up time (Fig. 5B). Average baseflow ^{222}Rn activity is shown by the dashed horizontal line (0.341 ± 0.08 Bq/L). The shaded area represents the most intense period of precipitation.

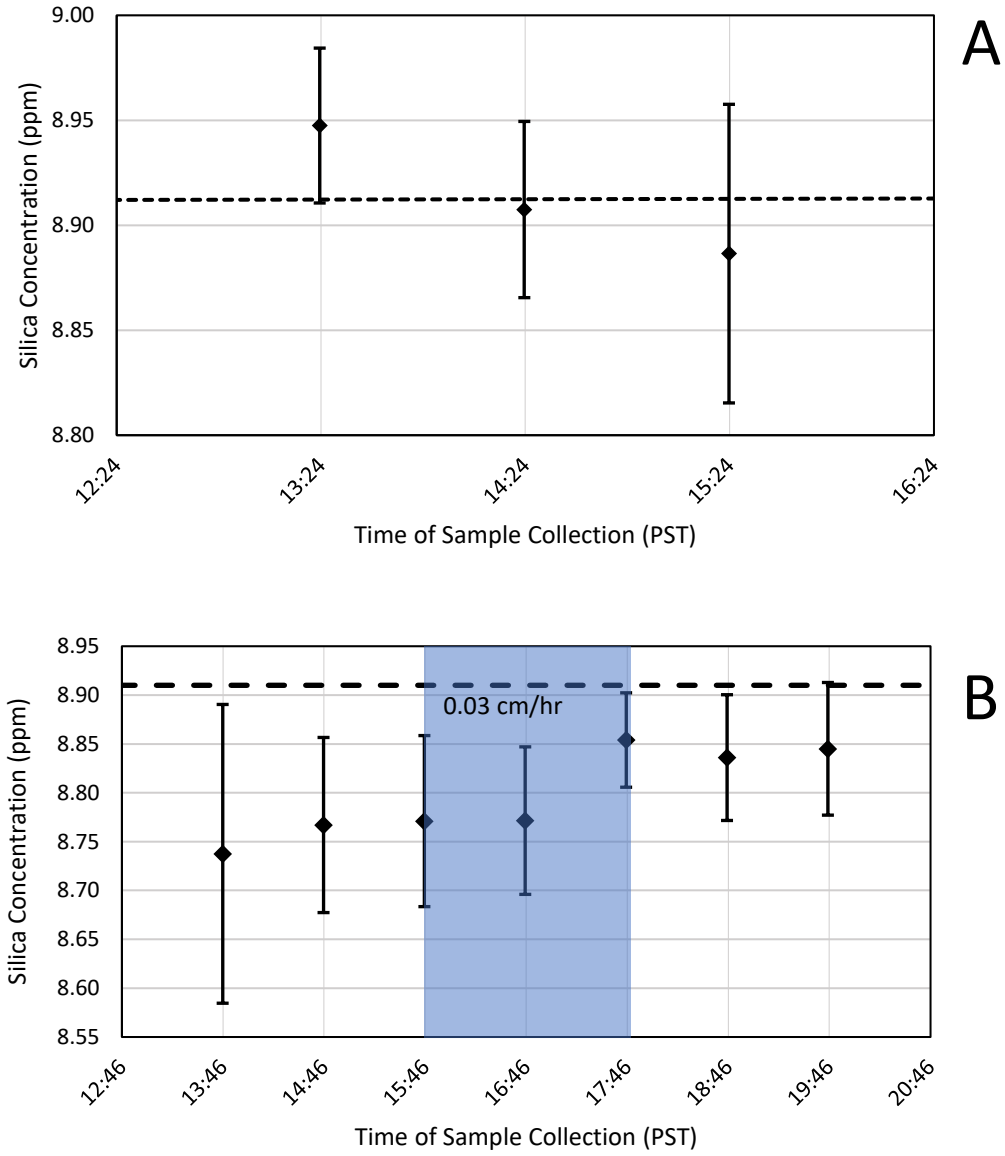
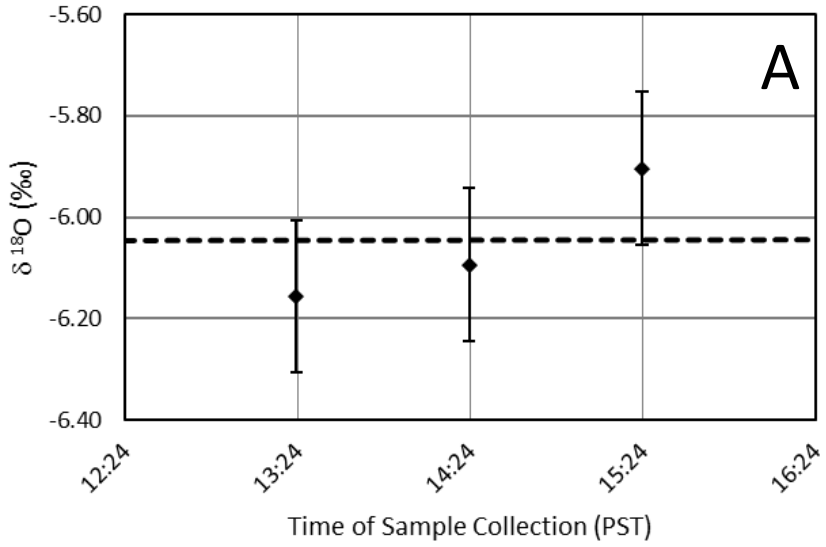
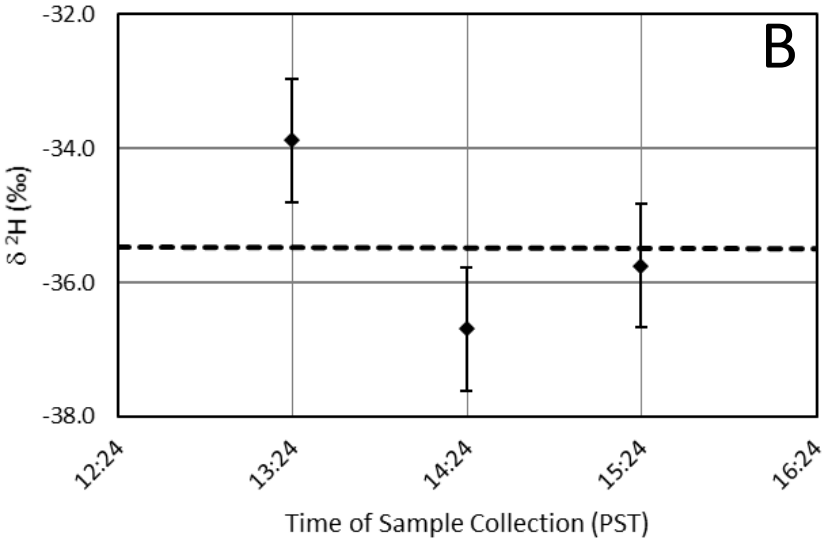


Figure 13: (A) Dissolved silica concentrations during baseflow collected onApr. 9, 2016. (B) Dissolved silica concentrations during Test 2 collected on Apr. 10, 2016. Average baseflow silica concentration is shown by the horizontal dashed line (8.91 ± 0.08 ppm). The shaded area represents the most intense period of precipitation.


A
-5.60
-5.80
-6.00
-6.20
-6.40
δ 18O (‰)
12:24
13:24
14:24
15:24
16:24
Time of Sample Collection (PST)


B
-32.0
-34.0
-36.0
-38.0
δ 2H (‰)
12:24
13:24
14:24
15:24
16:24
Time of Sample Collection (PST)

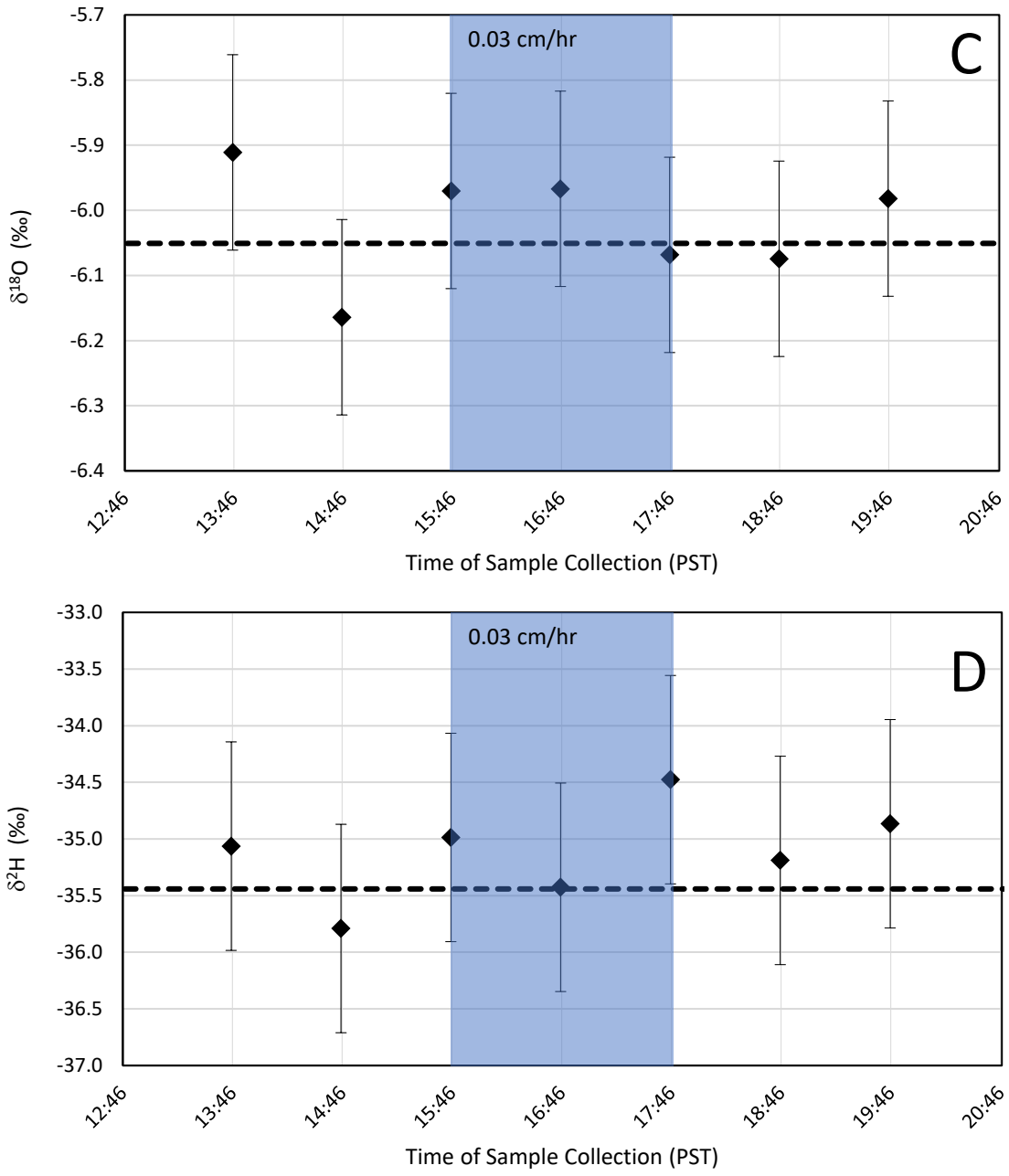


Figure 14: Baseflow (A) $\delta^{18}O$ and (B) $\delta^{2}H$ values collected on Apr. 9, 2016. Test 2 (C) $\delta^{18}O$ and (D) $\delta^{2}H$ values for Test 2 collected on Apr. 10, 2016. Average $\delta^{2}H$ (-35.4 ± 0.92 ‰) and average $\delta^{18}O$ (-6.05 ± 0.15 ‰) are represented by the dashed horizontal lines. The shaded area represents the most intense period of precipitation.

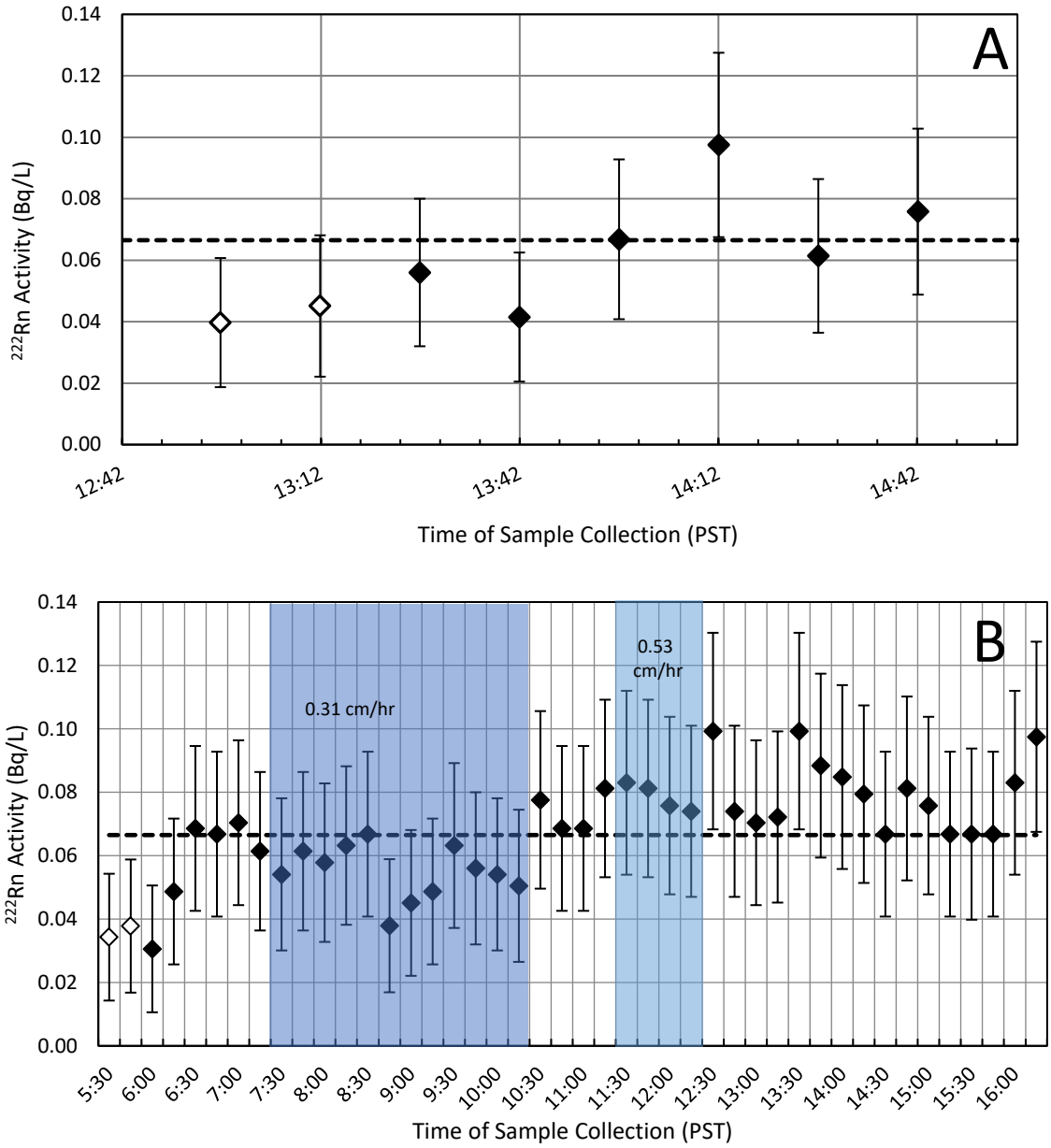


Figure 15: (A) Baseflow ^{222}Rn activities for collected on Mar. 19, 2017. (B) ^{222}Rn activities during Test 3 collected on Mar. 21, 2017. Open diamonds show values measured before the RAD7 device warm-up time (Fig. 5B). The horizontal dashed lines are the average baseflow value of 0.0665 ± 0.03 Bq/L. The shaded areas represent the most intense periods of precipitation.

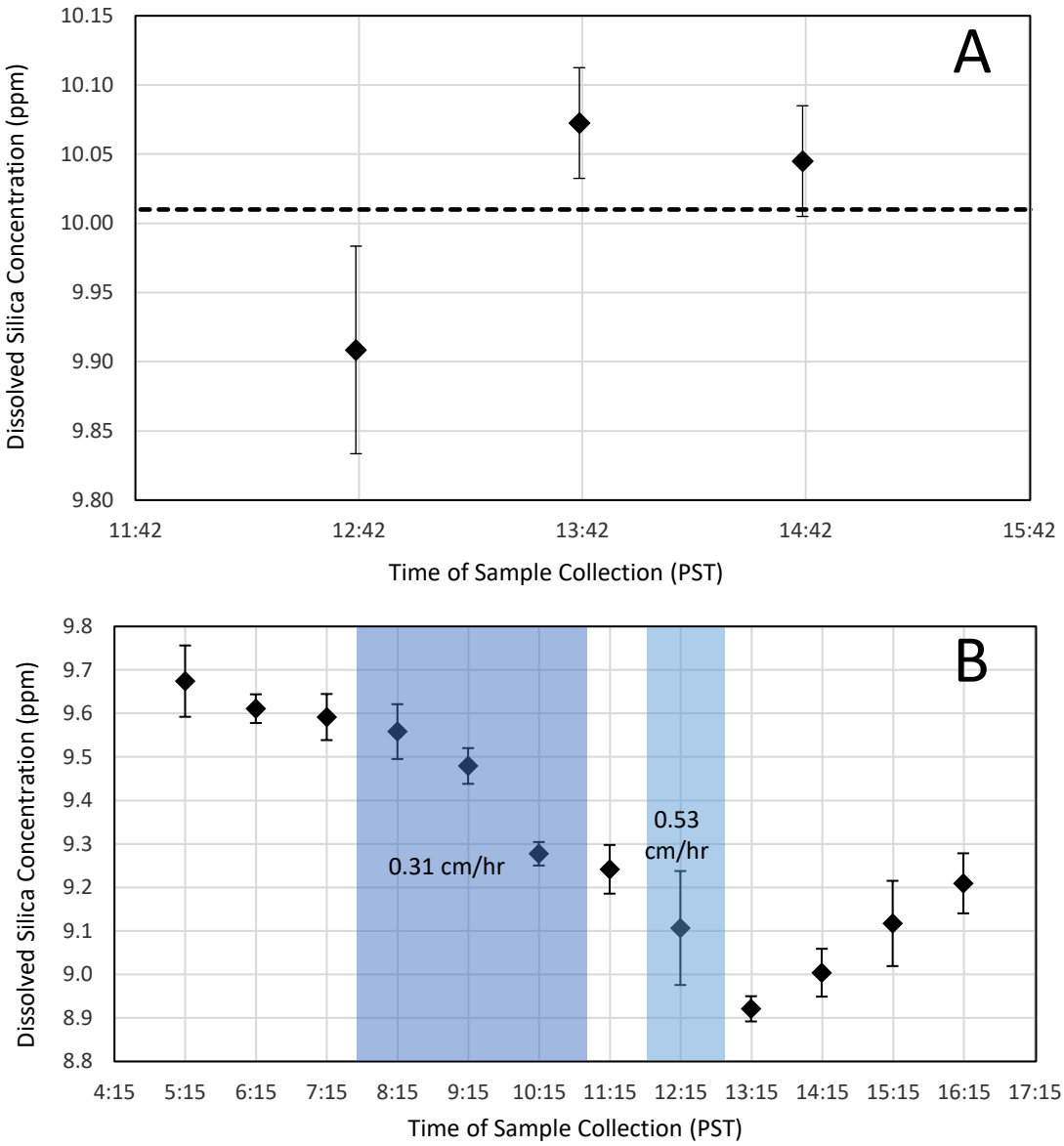
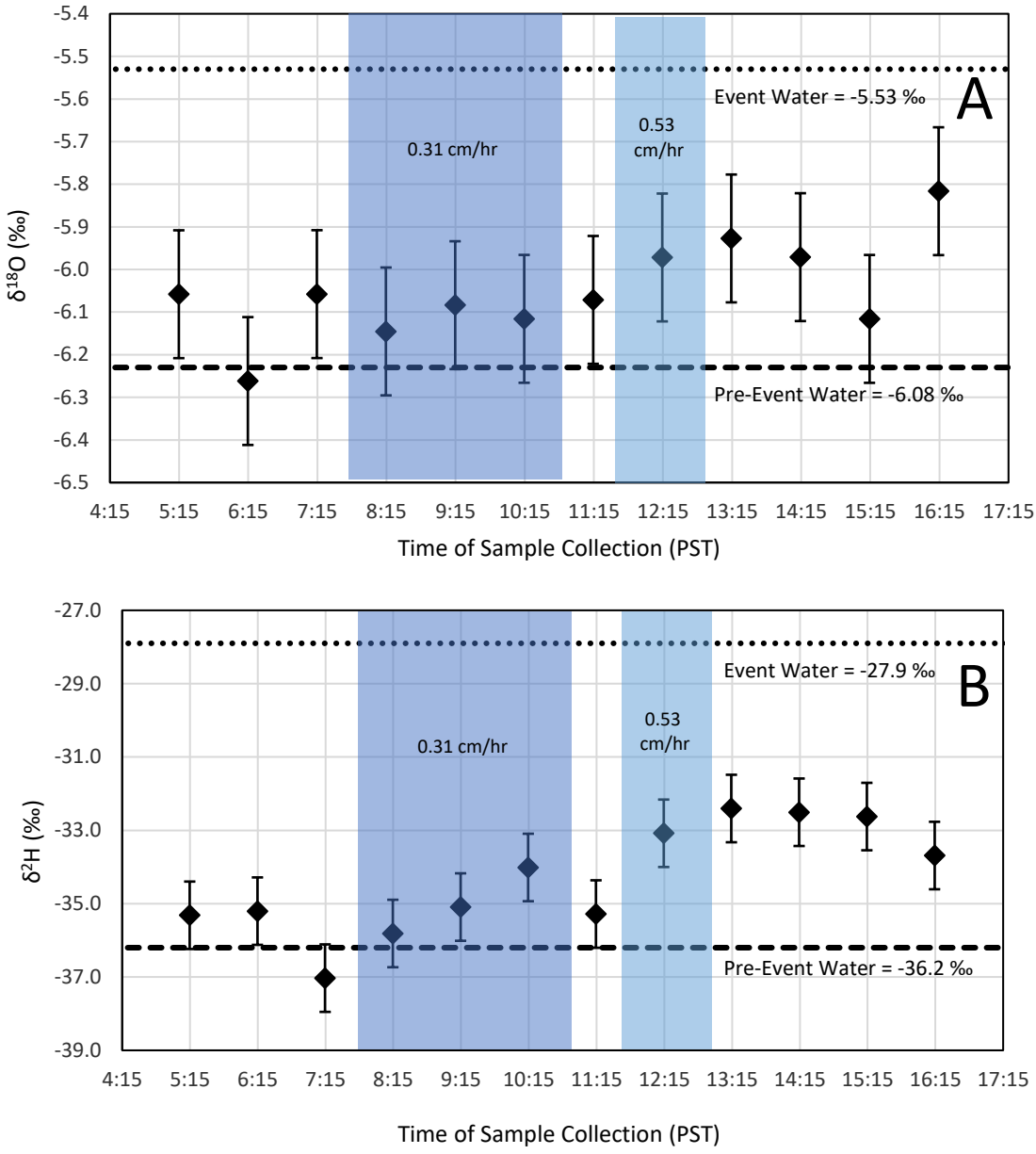


Figure 16: (A) Dissolved silica concentration of baseflow collected on Mar. 19, 2017. (B) Dissolved silica concentration for Test 3 collected on Mar. 21, 2017. Average baseflow silica concentration (dashed line) is 10.01 ± 0.08 ppm. The shaded areas represent the most intense periods of precipitation.



Figures 17: (A) $\delta^{18}O$ and (B) $\delta^{2}H$ values for Test 3 collected on Mar. 21, 2017. The storm values are shown by the horizontal dotted lines and baseflow values are shown by the horizontal dashed lines. The shaded areas represent the most intense periods of precipitation.

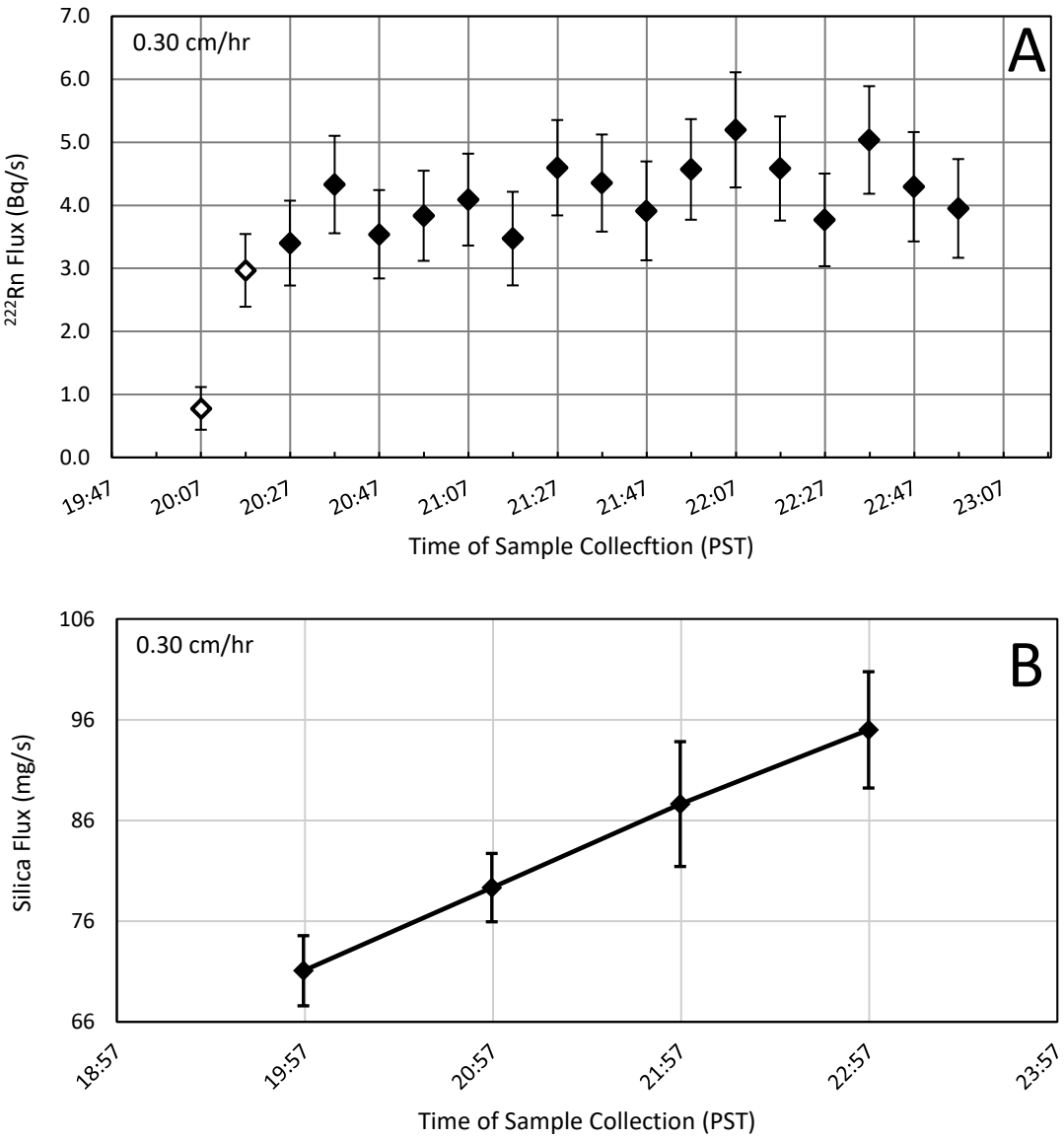
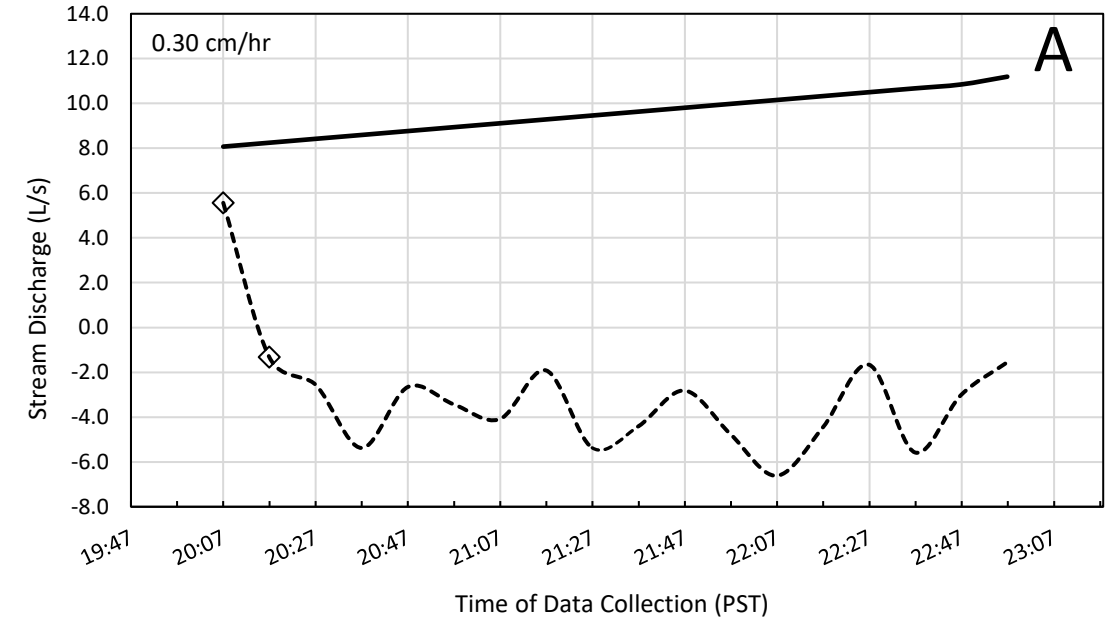
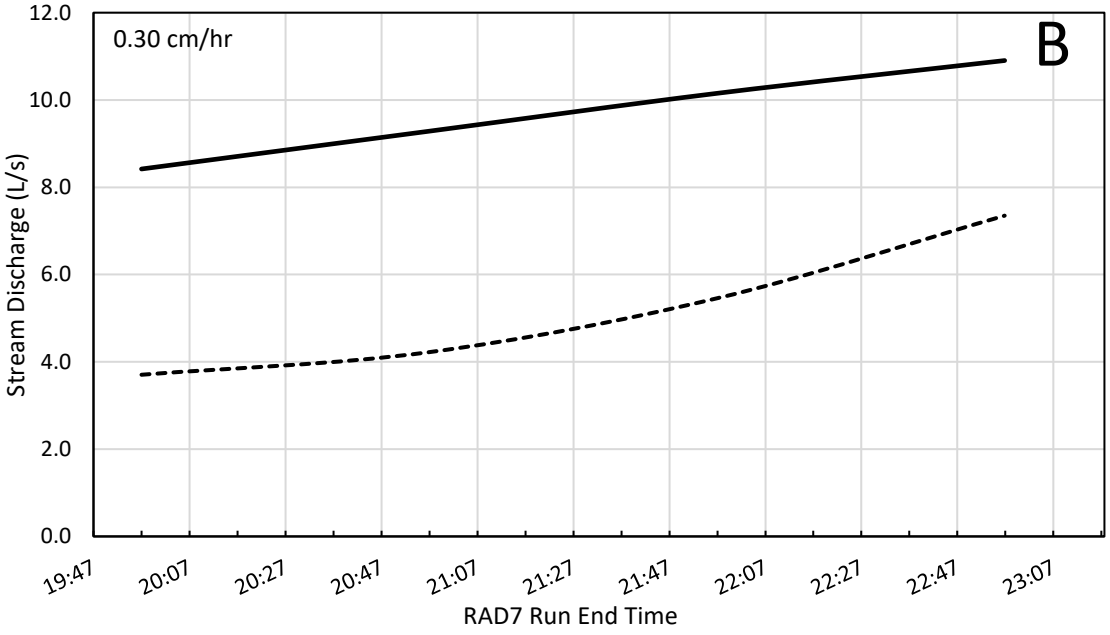


Figure 18: (A) ^{222}Rn activity and (B) silica flux during Test 1 collecte on Mar. 5, 2016. Discharge rates were determined using the channel geometry and a flow velocity measurement. Open diamonds show values measured before the RAD7 device warm-up time (Fig. 5B). Average precipitation during Test 1 was 0.3 cm/hr.


0.30 cm/hr
A
14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
-2.0
-4.0
-6.0
-8.0
Stream Discharge (L/s)
19:47
20:07
20:27
20:47
21:07
21:27
21:47
22:07
22:27
22:47
23:07
Time of Data Collection (PST)


0.30 cm/hr
B
12.0
10.0
8.0
6.0
4.0
2.0
0.0
Stream Discharge (L/s)
19:47
20:07
20:27
20:47
21:07
21:27
21:47
22:07
22:27
22:47
23:07
RAD7 Run End Time

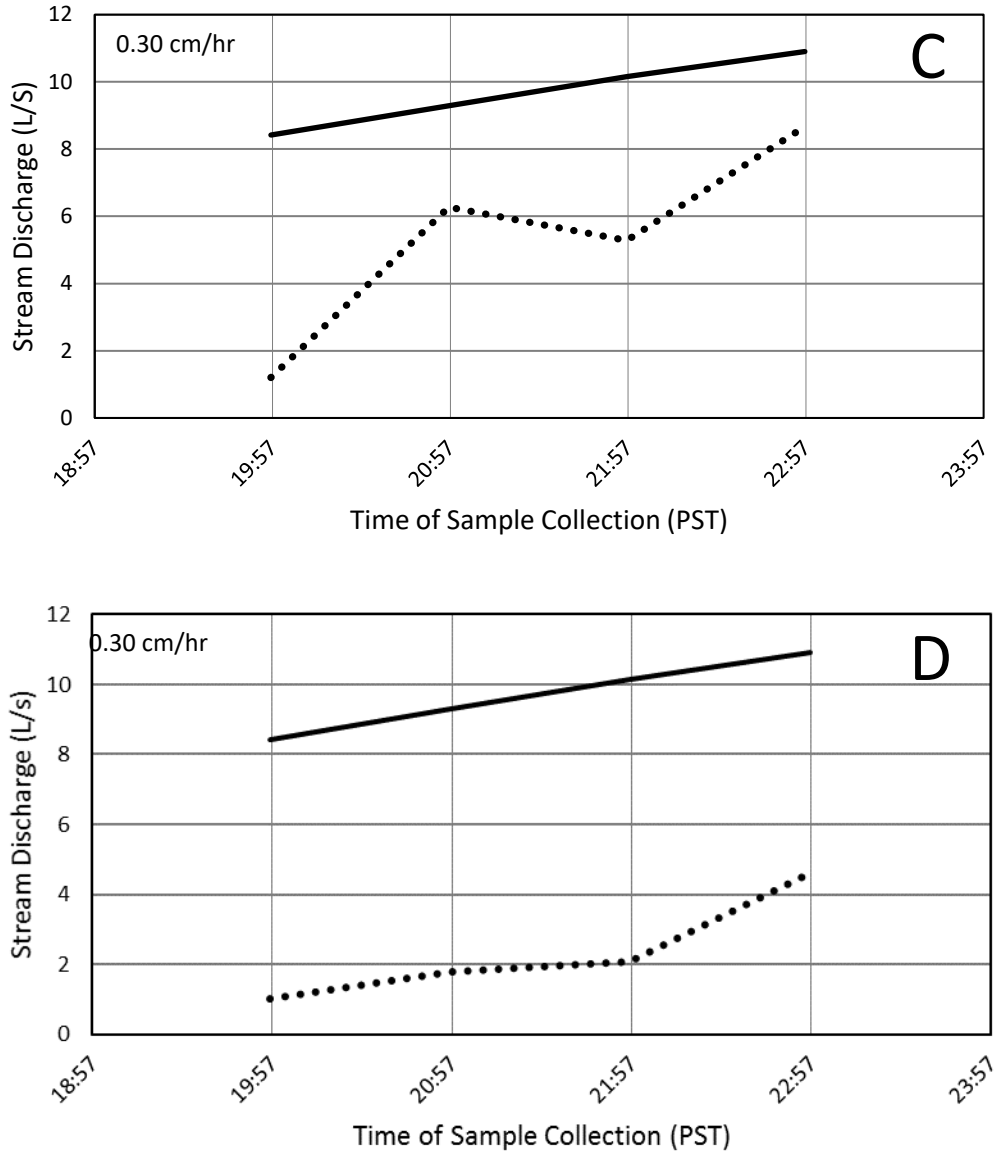


Figure 19: (A) ^{222}Rn activity hydrograph for Test 1 created using the baseflow measurement (Feb. 28, 2016) as a proxy for pre-event water. (B) Dissolved silica chemical hydrograph separation for Test 1. Stable Isotope (C) $\delta^{18}O$ and (D) $\delta^{2}H$ hydrograph separation for Test 1. Test 1 was conducted on Mar. 5, 2016. The solid line is total stream discharge and the dashed line is the calculated storm water discharge. Open diamonds show values measured before the RAD7 device warm-up time (Fig. 5B). Average precipitation during Test 1 was 0.3 cm/hr.

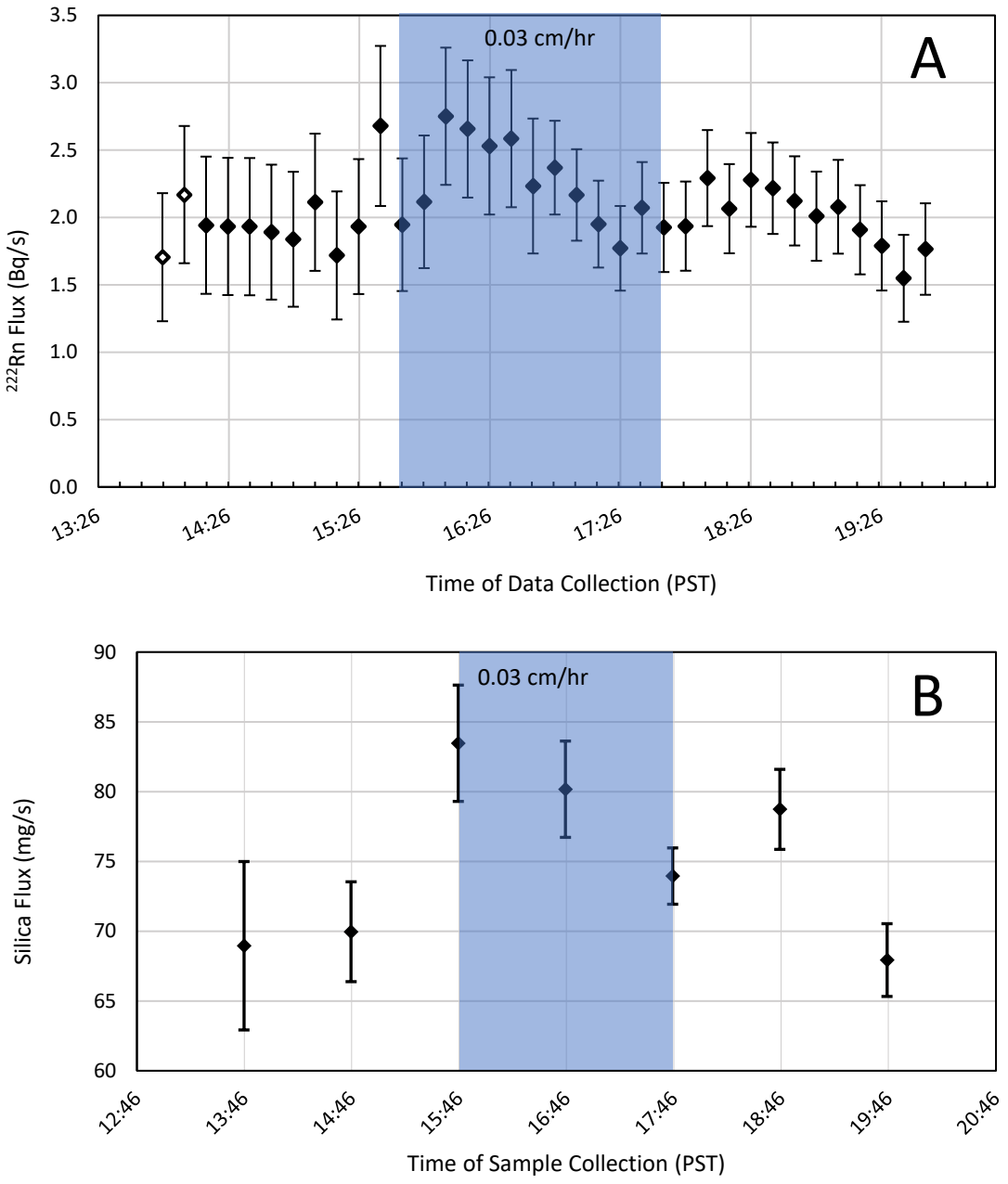


Figure 20: (A) ^{222}Rn flux for Test 2 and (B) silica flux during Test 2. Test 2 was conducted on Apr. 10, 2016. Open diamonds show values measured before the RAD7 device warm-up time (Fig. 5B). The shaded area represents the most intense precipitation period.

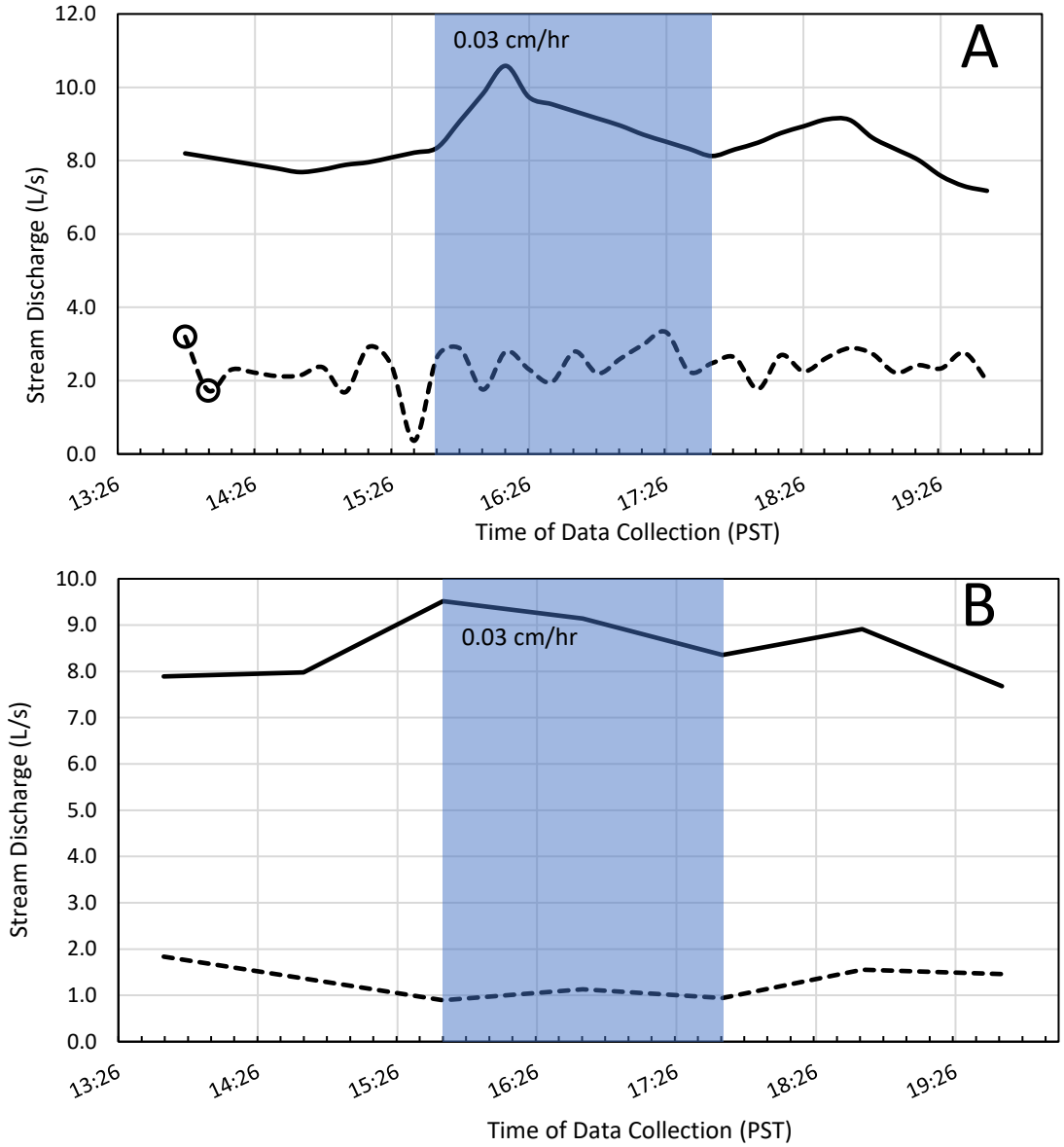


Figure 21: (A) ^{222}Rn activity and (B) silica chemical hydrograph separations for Test 2 on April 10, 2016. The solid lines are the total stream discharge while the dashed lines are the calculated storm water discharge. Open circles show values measured before the RAD7 device warm-up time (Fig. 5B). The shaded area represents the most intense precipitation period.

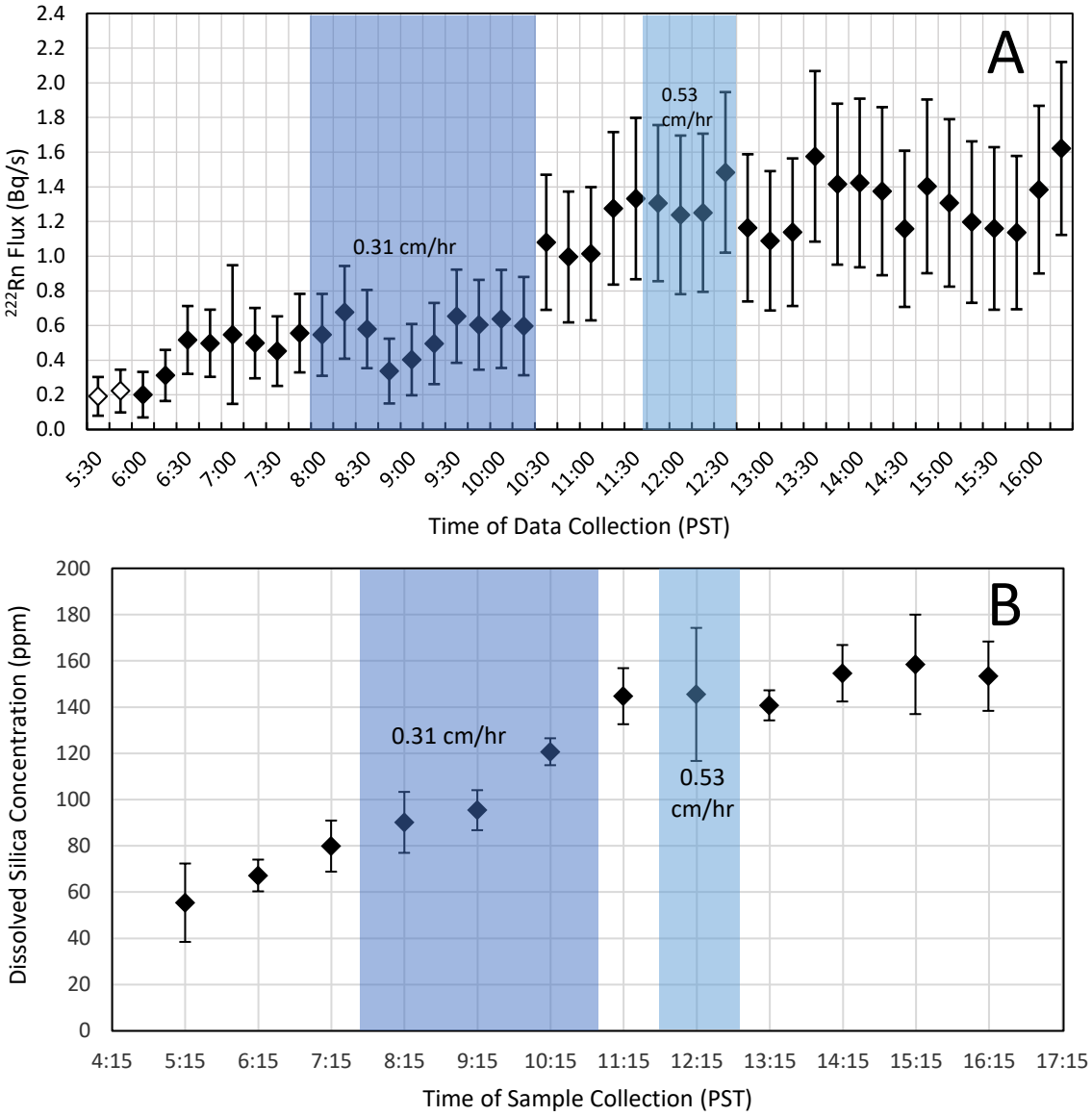
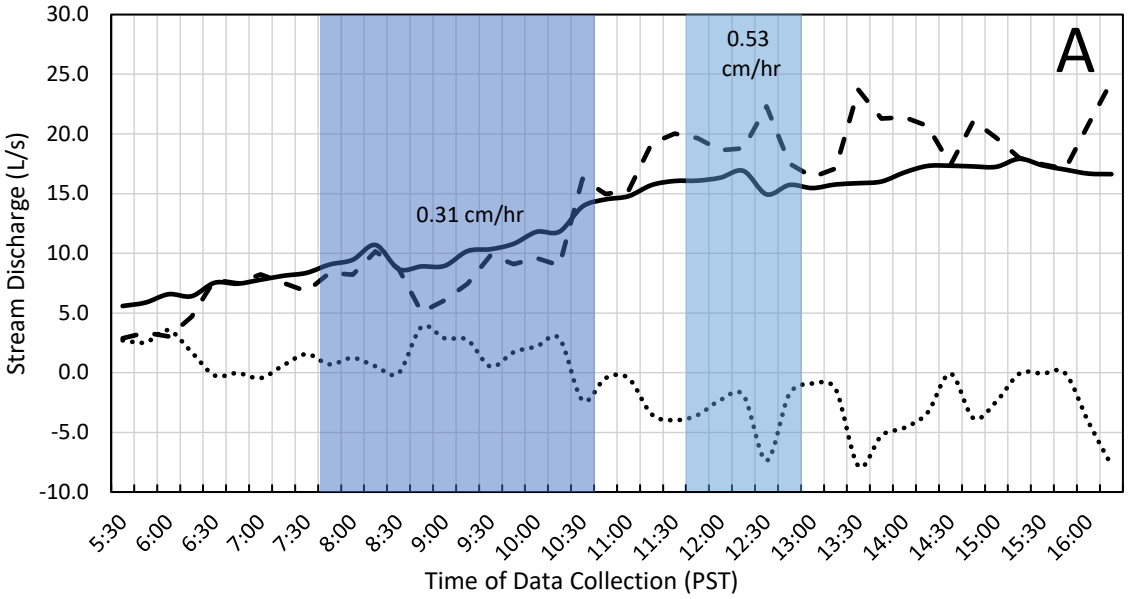
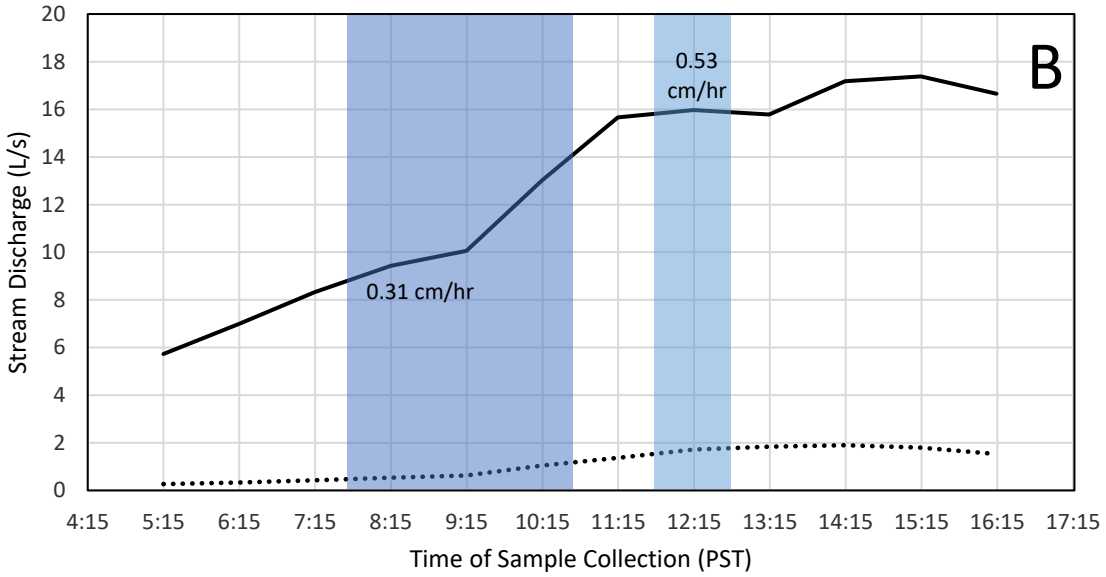


Figure 22: (A) ^{222}Rn flux and (B) silica flux for Test 3 collected on Mar. 21, 2017. Open diamonds show values measured before the RAD7 device warm-up time (Fig. 5B). The shaded areas represent the two most intense precipitation periods.


A
0.53
cm/hr
0.31 cm/hr
Stream Discharge (L/s)
30.0
25.0
20.0
15.0
10.0
5.0
0.0
-5.0
-10.0
5:30
6:00
6:30
7:00
7:30
8:00
8:30
9:00
9:30
10:00
10:30
11:00
11:30
12:00
12:30
13:00
13:30
14:00
14:30
15:00
15:30
16:00
Time of Data Collection (PST)


B
0.53
cm/hr
0.31 cm/hr
Stream Discharge (L/s)
20
18
16
14
12
10
8
6
4
2
0
4:15
5:15
6:15
7:15
8:15
9:15
10:15
11:15
12:15
13:15
14:15
15:15
16:15
17:15
Time of Sample Collection (PST)

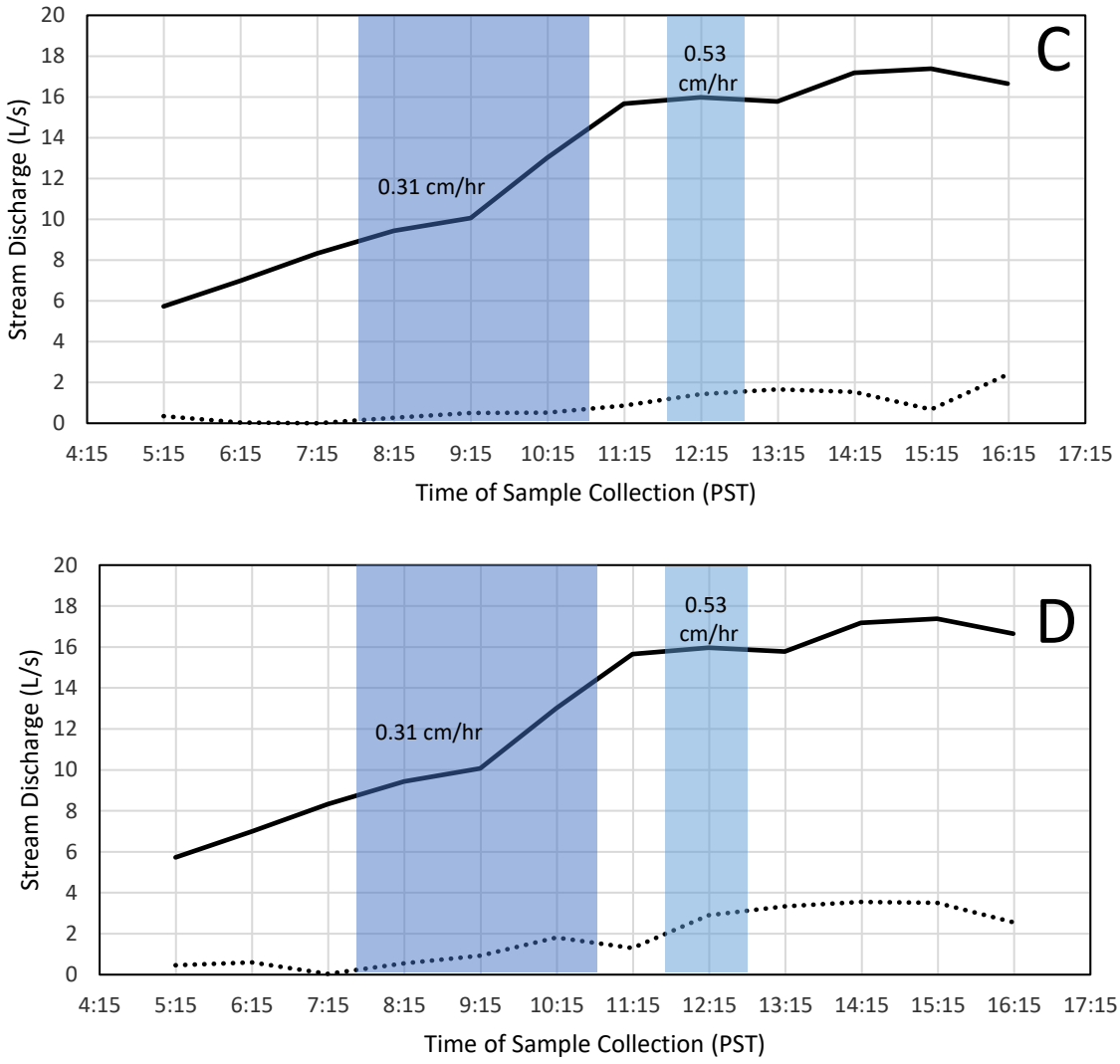


Figure 23: (A) ^{222}Rn activity chemical hydrograph separation for Test 3 using the baseflow activity determined on Mar. 19, 2017 (0.067 Bq/L). (B) Dissolved silica, (C) $\delta^{18}O$, and (D) $\delta^{2}H$ hydrograph separations for Test 3. Test 3 was conducted on Mar. 21, 2017. The shaded areas represent the two most intense precipitation periods. The solid line is the total stream discharge, the dotted line is the calculated storm water discharge, and the dashed line (on A) is the calculated groundwater discharge.

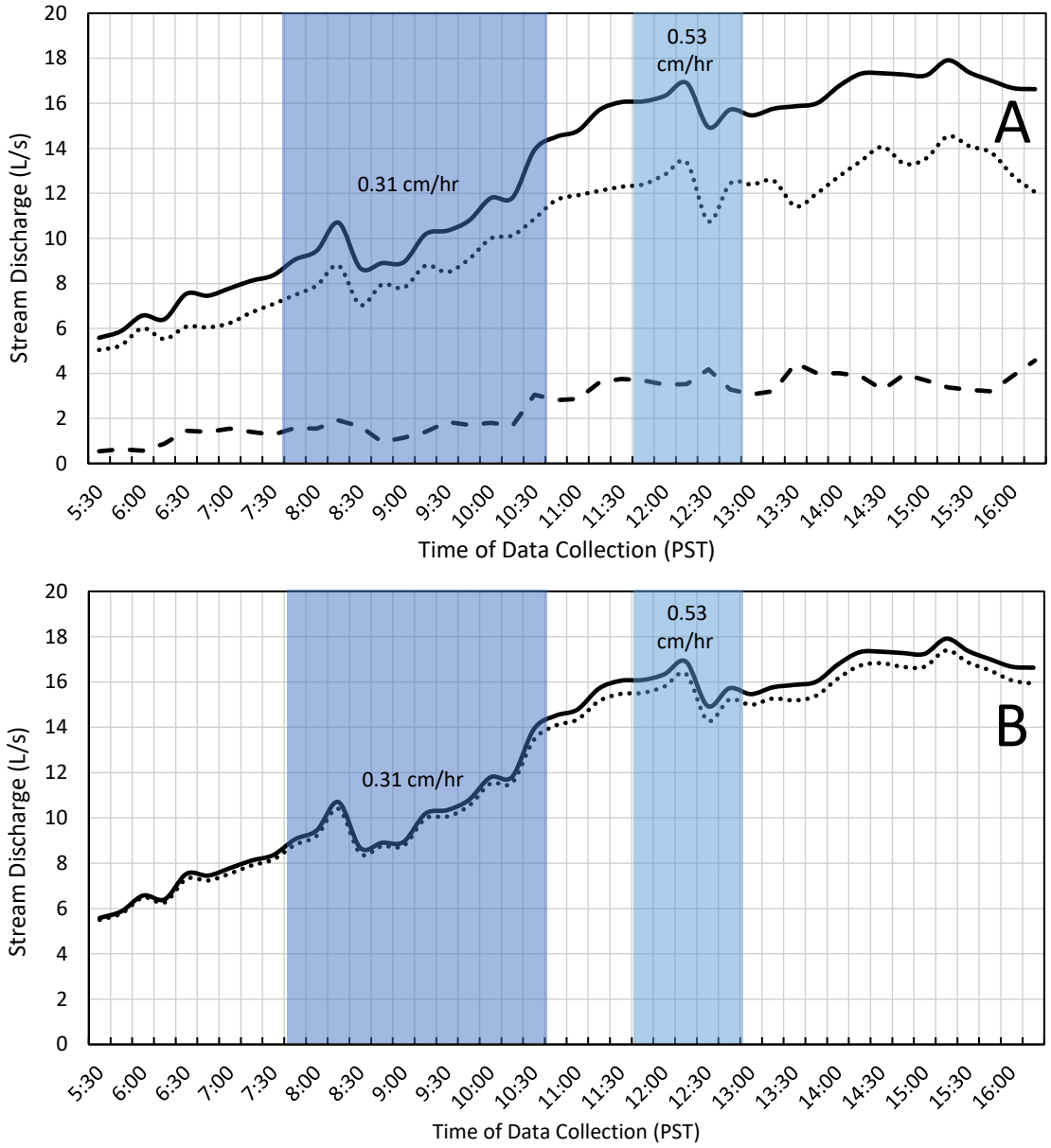


Figure 24: ^{222}Rn activity chemical hydrograph separations for Test 3 (Mar. 21, 2017) using (A) the groundwater activity measured from the deep groundwater pool near site 1 (0.354 ± 0.065 Bq/L) and (B) the groundwater activity provided by the 2008 MWD Water Quality Report (2.294 Bq/L). The shaded areas represent the two most intense precipitation periods. The solid line is the total stream discharge, the dotted line is the calculated storm water discharge, and the dashed line is the calculated groundwater discharge.