Groundwater as a major source of dissolved organic matter to Arctic coastal waters

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Groundwater is projected to become an increasing source of freshwater and nutrients to the Arctic Ocean as permafrost thaws, yet few studies have quantified groundwater inputs to Arctic coastal waters under contemporary conditions. New measurements along the Alaska Beaufort Sea coast show that dissolved organic carbon and nitrogen (DOC and DON) concentrations in supra-permafrost groundwater (SPGW) near the land-sea interface are up to two orders of magnitude higher than in rivers. This dissolved organic matter (DOM) is sourced from readily leachable organic matter in surface soils and deeper centuries-to-millennia-old soils that extend into thawing permafrost. SPGW delivers approximately 400–2100 m³ of freshwater, 14–71 kg of DOC, and 1–4 kg of DON to the coastal ocean per km of shoreline per day during late summer. These substantial fluxes are expected to increase as massive stocks of frozen organic matter in permafrost are liberated in a warming Arctic.

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Groundwater is the largest active reservoir in the global hydrologic cycle and its movement from land to sea represents a major source of freshwater and nutrients for coastal ecological and biogeochemical processes. However, there is little information on direct groundwater nutrient inputs to the coastal ocean in the Arctic. This is partly because of a perception that in northern high-latitude coastal regions permafrost constrains water to flow paths on the land surface. Supra-permafrost groundwater (SPGW) does, however, flow through seasonally thawed active layer soils during the summer and early fall. Therefore SPGW has the potential to deliver appreciable quantities of terrestrially-derived nutrients to Arctic coastal waters. SPGW is the principal form of terrestrial groundwater entering nearshore coastal waters in the Arctic since sub-permafrost groundwater flow is firmly separated from the surface by several hundred meters of permafrost.

In the Arctic, SPGW flow and nutrient transport from soils are tightly coupled because soil water interactions are largely confined to the shallow (typically <1 m), but laterally extensive and highly permeable active layer. Soils in northern high-latitude permafrost landscapes contain large amounts of organic matter with a high capacity to release dissolved organic matter (DOM) to aquatic systems. Terrestrial DOM production and export is highest during the spring (May to June) when the thawed portion of the active layer is shallow and snowmelt-driven water flow is confined to near surface organic-rich soils and overlying plant litter layers. DOM production and export is lower during the summer (July to October) when active layer thaw exposes deeper soil horizons and groundwater recharged from rainfall and melting ground ice saturates higher proportions of mineral soils. Recent studies reveal that SPGW processes govern the summer transfer of DOM to streams and therefore influence riverine export to the coastal ocean.

In contrast to studies conducted on land, very few studies have focused on the role that SPGW plays in the direct transfer of DOM from land to the coastal ocean in the Arctic. Estimates of groundwater inputs to the coastal ocean are needed to support a more complete understanding of what fuels biological production and biogeochemical cycling in Arctic coastal waters. Climate change adds some urgency to this since warming is increasing groundwater discharge across circumpolar regions, enhancing organic matter decomposition in the active layer, and liberating globally significant stores of organic matter held in high-latitude northern soils and permafrost. A baseline understanding of how groundwater mobilizes organic matter held in coastal soils and permafrost is necessary for predicting responses to and feedbacks with climate change.

This study examines the leaching potential of DOM, which includes dissolved organic carbon and nitrogen (DOC and DON), from nearshore Arctic soils and quantifies inputs of SPGW DOM to coastal waters of the eastern Alaska Beaufort Sea. We first determined the relationship between soil organic carbon (SOC) and nitrogen (SON) contents in different active layer and permafrost soil horizons and the production and leaching potential of DOM from this soil organic matter (SOM). We then determined the relationship between leachable DOM sources and direct SPGW DOM inputs using radiocarbon (14C) dating. Lastly, we estimated DOM fluxes using concentrations of SPGW DOC and DON paired with groundwater discharge estimates that were derived from a steady-state excess radon (222Rn) mass balance model (Supplementary Note 1). Data from groundwater and nearby river water were used to compare SPGW and riverine inputs to the Alaska Beaufort Sea coast. To the best of our knowledge this is the first study to quantify fluxes and sources of DOM in direct SPGW inputs to Arctic coastal waters.

Results and Discussion

Soil leaching and sources of groundwater DOM. We found that active layer and shallow permafrost soils along the eastern Alaska Beaufort Sea coast contain 5–20% OC, 0.25–1.3% ON, and produce large quantities of readily leachable DOM. Highest % OC and % ON values were observed within surface soils and plant litter. The amount of SOM decreased directly below the organic layer, but increased again in deeper active layer soils and in thawed permafrost samples. The range of soil OM contents found herein is typical of tundra active layer and upper permafrost soils. We found a similar pattern in the release of DOM from these soil layers, where surface soils and thawed permafrost tend to have the highest yield (mg DOC and DON per gram of soil) and OC and ON normalized leaching potential (mg DOC and DON per gram of soil OC and ON) (Table 1). These results demonstrate that only a small amount of coastal soil is needed to rapidly produce high concentrations of DOC and DON.

These observations are consistent with the notion that soils in northern high-latitude permafrost landscapes contain large amounts of leachable organic matter that can be exported to aquatic systems. Previous studies have demonstrated that DOM export is highest from plant litter layers and organic-rich soils.
near the surface (<5 cm) because SOM from these horizons have experienced less decomposition and fewer leaching events. Lower DOM export is expected from deeper mineral horizons (>20 cm) because these soils have undergone more leaching events and are more stable because of mineral particle interactions. We found that groundwater has a 14C-DOC age of ~1300 yBP below the permafrost boundary (Table 2). Likewise, leachable soil 14C-DOC ages increased from modern to ~3700 yBP in the shallow permafrost. Interestingly, there is a consistent offset between the 14C ages of bulk SOC and leached DOC below the surface (<5 cm), indicating that the fraction of readily leachable SOC is younger than the fraction of stable SOC in these deeper soil horizons with stronger mineral particle interactions. We found that groundwater has a 14C-DOC age of ~1300 yBP (Table 2). In comparison to our 14C-SOC and leachate DOM data, it is clear that SPGW DOC must be derived from a combination of organic-rich surface soils and deeper soil horizons.

Taking the analysis a step further, if it is assumed that SPGW DOC is received from each soil horizon in proportion to their leachability (i.e., mg DOC g soil−1; Table 1) and scale these proportions by their observed horizon thickness, we can calculate an expected 14C-DOC age for SPGW DOC to compare with our measured SPGW DOC age. Here we first calculated proportions of soil-DOC contributions to SPGW DOC (Fig. 2) by multiplying the soil-DOC yields from each of our four soil sections by their observed horizon thickness and divided by the sum of all adjusted soil-DOC yields. The contributing thickness from shallow permafrost was assumed to be 5 cm. We then multiplied each proportion by their respective Δ14C-DOC values and summed them to estimate what the 14C-DOC age of the SPGW would be. These calculations were done separately for each core and then averaged (± standard error). The predicted Δ14C-DOC value of active layer-derived SPGW is ~129 ± 30% or ~1040 yBP, which is

| Sample depth | % OC (100 × mg C mg soil−1) | % ON (100 × mg N mg soil−1) | Leachable soil DOM |
|--------------|-------------------------------|-----------------------------|-------------------|
| 0-5 cm       | 21.3 ± 4.1                    | 1.3 ± 0.24                  | 0.48 ± 0.12       |
| 15-20 cm     | 5.1 ± 1.0                     | 0.25 ± 0.09                 | 0.05 ± 0.01       |
| 30-40 cm     | 16.8 ± 8.5                    | 0.95 ± 0.45                 | 0.17 ± 0.05       |
| Permafrost   | 0.5 ± 1.7                     | 0.58 ± 0.29                 | 0.13 ± 0.05       |

Table 2 Radiocarbon and stable carbon isotopic compositions and C:N ratios in SOC, leachable soil DOC, and SPGW DOC.

| Sample   | Fraction of modern | Δ14C (% ε) | 14C age (year BP) | Δ13C (% ε) | C:N (molar ratio) |
|----------|--------------------|------------|-------------------|------------|-------------------|
| SOC      | 0-5 cm             | 1.046 ± 0.035 | 38 ± 35 | >Modern | −27.8 ± 0.4 | 16.2 ± 0.94 |
| 15-20 cm | 0.622 ± 0.060      | −383 ± 59  | 3895 ± 799       | −28.9 ± 0.5 | 24.2 ± 5.1  |
| 30-40 cm | 0.53 ± 0.053       | −474 ± 53  | 5177 ± 774       | −28.5 ± 0.1 | 17.4 ± 0.87  |
| Permafrost | 0.515 ± 0.515  | −490 ± 57  | 5383 ± 581       | −28.1 ± 0.3 | 17.1 ± 1.4   |
| Leachate DOC | 0-5 cm | 1.042 ± 0.003 | 33 ± 2.5 | >Modern | −27.3 ± 0.5 | 517 ± 15.8  |
| 15-20 cm | 0.747 ± 0.048      | −257 ± 47  | 2350 ± 526       | −27.3 ± 0.1 | 101.5 ± 40.7 |
| 30-40 cm | 0.652 ± 0.023      | −353 ± 23  | 3447 ± 279       | −27.2 ± 0.3 | 44.4 ± 20.0  |
| Permafrost | 0.631 ± 0.022  | −374 ± 21  | 3710 ± 274       | −26.8 ± 0.2 | 26.4 ± 4.51  |
| SPGW DOC  | 0.853 ± 0.046      | −154 ± 45  | 1298 ± 421       | −28.2 ± 0.2 | 20 ± 1.2      |

The permafrost category represents soils at approximately 5-10 cm below the ice table. Values are ±1 standard error, n = 3 for all samples.
Fig. 2 Schematic of SPGW flow to Arctic coastal lagoons during late summer summarizing several key results of this study. (left) Estimates of the percent contributions of soil-DOM from active layer and thawing permafrost soils to SPGW DOM. Percent soil-DOM contributions were made by multiplying soil-DOC yield values of the four indicated soil sections by their horizon thickness and then divided by the sum of the adjusted soil-DOC yields. (right) Average concentrations of DOC and DON found in SPGW and maximum freshwater, DOC, and DON flux values calculated from $^{222}$Rn measurements. Values in the schematic are ±1 standard error.

Results from a $^{222}$Rn mass-balance model demonstrate that total groundwater discharge to Arctic lagoons is significant during the late summer (Fig. 2). A caveat of this approach is that submarine groundwater discharge estimates do not differentiate terrestrial and marine inputs (i.e., porewater circulating through and discharged from benthic sediments). We found that $^{222}$Rn concentrations in Kaktovik Lagoon were 32.4 ± 3.9 Bq m$^{-3}$ (Supplementary Fig. 1), and that the average SPGW $^{222}$Rn concentration is 223 ± 20 Bq m$^{-3}$. Total groundwater inputs (from land and benthic circulation) to Kaktovik Lagoon is an estimated $8.6 \times 10^5$ m$^3$ day$^{-1}$ or $42.6$ m$^3$ day$^{-1}$ m$^{-1}$. These values are similar in magnitude to previously reported values of $18 \pm 10$ Bq m$^{-3}$ $^{222}$Rn concentration and discharge of $12 \pm 4$ m$^3$ day$^{-1}$ m$^{-1}$ in Elson Lagoon$^2$.

While the role of groundwater in the coastal ocean has gained marked attention over the past two decades, it has proven challenging to determine how much of this groundwater is terrestrial versus marine derived$^1$. Terrestrial-derived groundwater is typically a minor component of total groundwater contributions in the coastal ocean (1–10%), but much higher percentages (e.g., 20–35%) have been observed in coastal systems with strong topographic gradients at the land-sea interface and/or low wave and tidal-driven marine groundwater recirculation$^{28,45}$. We expect that the percentage of terrestrial SPGW discharge in our lagoon system is in the lower range of previous estimates (<10%) because Kaktovik Lagoon is surrounded by flat tundra terrain in a region of continuous permafrost. However, terrestrial SPGW discharge is likely greater than 1% because tidal amplitudes and wave activity are very small. Therefore, assuming that 1 to 5% of the groundwater discharge that we measured with $^{222}$Rn in Kaktovik Lagoon is terrestrially-derived, we estimate that SPGW delivers roughly $8.6 \times 10^3$ to $4.3 \times 10^4$ m$^3$ of freshwater day$^{-1}$, $284$ kg to $1420$ kg of DOC day$^{-1}$, and $17$ to $86$ kg of DON day$^{-1}$ to Kaktovik Lagoon in late summer. This equates to approximately $400–210$ m$^3$ freshwater, $14–71$ kg DOC, and $1–4$ kg DON per km of shoreline per day in late summer (Fig. 2). Minimum and maximum values associated with these flux estimates range from
piezometers and one from a small groundwater-fed stream. Lagoon water \( ^{222}\text{Rn} \) samples were collected from the interior and perimeter areas of Kaktovik Lagoon. A possible pump discharge near the lagoon before 21 August 2017 (Supplementary Data 1). The water was directly pumped into a degassing chamber connected to three radon-in-air gas analyzers (Durrle Rad7 connected to the RAD-AQUA module) which analyzed the samples in sequence every 10 min over a 30 min cycle, i.e., each RAD7 measured \( ^{222}\text{Rn} \) every 30 min. This work was conducted over two consecutive days in order to sample the entire lagoon.

### Soil and lagoon sediment sampling

Three soil cores that include the seasonally thawed active layer and shallow permafrost were collected within high-centered polygons (the primary surface type) on the landward sides of Kaktovik Lagoon on 9 August 2015 and Jago Lagoon on 8–9 August 2016 for bulk SOM measurements (red circles in Fig. 1). Three distinct soil layers were evident at all three sites. These soil layers had relatively uniform organic matter content from 20 cm to the top of the ice table. Soil samples were collected at four depths: surface–5 cm, 15–20 cm, 30–40 cm, and 5–10 cm below the frozen boundary. Thaw depths (the depth of the ice table) at the soil collection sites were 0, 24, 54 cm, and 54 cm, meaning the permanganate at respective depths of approximately 40–50 cm, 58–63 cm, and 59–64 cm. These soil increments were chosen specifically in order to gain a wide range of soil types and depths within the active layer and shallow permafrost where changes in organic matter content and age are anticipated. The first two samples soil sections (surface–5 cm and 5–10 cm) had an observed horizon thickness of 10 cm, while the next sample soil section (30–40 cm) had observed horizon thicknesses of 20, 33, and 34 cm. Bulk soils were placed into individual whirl-packs, stored frozen at the ANWR facility, and taken back to the University of Texas at Austin, Marine Science Institute (UTMSI) for soil water leaching experiments and chemical analysis. Seven benthic sediment samples were collected from the interior and perimeter areas of Kaktovik Lagoon on 23 August 2017 for \( ^{222}\text{Rn} \) activity measurements. Bulk sediments were placed in plastic Ziploc bags, dried, and stored at the University of Texas at Austin until \( ^{222}\text{Rn} \) analysis.

### Soil water leaching experiments

Soil samples (>300 g frozen) were allowed to thaw in a refrigerator (4 °C) until the soils appeared moist, but not dripping with water (at most 24 h). Soils of the same type were then placed on a composted aluminum foil (550 °C for 1 h) and gently homogenized. Care was taken to maintain common soil features and to ensure the sample remained close to its natural condition. This also included removing large roots and anomalous material not representative of the soil horizon. Three subsamples were collected to obtain an average wet weight: dry weight ratio. Subsamples were dried in an oven at 60 °C for 48 h. Thawed soils were kept in the refrigerator for a total of 48 h before leaching. Sample wet weight: dry weight ratios were used to calculate the equivalent of 35 g of dry soil. Field-moist soils were then placed in a composted glass beaker with 500 mL of a 0.001 N NaHCO₃ Nanopure solution (\( >18.5 \text{Ω cm} \)), which was used to buffer changes in pH and mimic the natural iconic strength of water in natural systems. The wet soil: solution volume ratio of the leaching solutions was maintained between \( >1:1 \) and \( 1:1 \). The volatilization efficiency at \( 1:1 \) was found to be close to 100%, with loss in precision to \( 1:1 \) and \( 1:2 \). The sample size was 24 h incubation period to simulate groundwater flow through the soil profile. Following, the soil water was filtered through a composted glass filtration system holding a 0.7 μm glass fiber filter (precombusted at 450 °C \( >5 \) h). The filtrate was then dispensed into acid washed and Milli-Q rinsed poly-carbonate bottles and stored frozen until DON and DOM concentrations were measured.

### Methods

#### Water sampling

SPGW DOM samples were collected along the landward sides of Kaktovik Lagoon on 16–17 August 2014 (\( n = 10 \)) and 8–12 August 2015 (\( n = 10 \)), and then along Jago Lagoon on 17 August 2017 (\( n = 15 \)) (yellow stars in Fig. 1). In total, 35 groundwater DOM samples were collected during the study period (Supplementary Data 1). SPGW was extracted using piezometer wells that were installed to the depth of frozen ground (\( >1 \text{m} \)) running parallel to the shoreline. Samples from these piezometers capture groundwater that has moved through the active layer to the lagoons without becoming channeled surface water flow. Some samples were also collected along a transect running from the beach to ~50 m inland, as well as from groundwater springs that emerge on the beach as small surface water streams in order to capture SPGW in transit to the coast. Groundwater samples were collected using peristaltic pumps attached with an acid washed and Milli-Q rinsed Master-Flex tubing. Groundwater was pumped until clear water was flowing and then filtered through a 0.45 μm GeoTech membrane capsule directly into acid washed and Milli-Q rinsed high-density polyethylene (HDPE) or poly-carbonate bottles. Sample bottles were transported in a cooler to the U.S. Fish and Wildlife Arctic National Wildlife Refuge (ANWR) facilities in Kaktovik, Alaska where they were stored frozen until analysis. River water DOM samples were collected previously in August 2011 and 2012 with a similar sampling procedure. SPGW and lagoon water \( ^{222}\text{Rn} \) samples were collected using widely used procedures\(^ {22–28} \). Four discrete groundwater \( ^{222}\text{Rn} \) samples were collected along a transect from the beach to the tundra surface at the Kaktovik Lagoon site on 12 August 2015 (Supplementary Data 1). These included three SPGW samples from
Data 1). Riverine DOC and DON concentrations near Kaktovik Lagoon were estimated using the average of samples collected in August 2011 from the Halulaha (n = 1), Okpilak (n = 2) rivers near the Beaufort Sea. Total groundwater discharge was calculated using a steady-state excess soil/sediments and serves a useful tool for quantifying submarine groundwater discharge.

We analyzed 14C-DOC on SPGW samples collected at three individual locations in August 2015 (Supplementary Data 1). DOC samples were prepared for 14C analysis using the UV-oxidation method at the Woods Hole Oceanographic Institution, National Ocean Sciences Accelerator Mass Spectrometry facility (WHOI/NOSAMS).53. Sample water was diluted with pre-treated UV-oxidized nanopure water (to bring the total volume up to 1 L) and placed in a quartz reactor. The combined sample water plus treated nanopure water solution was acidified with 35 g of ultra-high purity (UHP), UV-treated strong phosphoric acid and then purged with UHP nitrogen gas to remove any inorganic carbon. Pure UHP O2 was subsequently sparged through the system to provide an oxidant for the UV-oxidation of DOC. The sample was then oxidized with UV and the resulting CO2 was transferred to a vacuum line and cryogenically purified during this step. The resulting CO2 was transferred to a vacuum line and cryogenically purified. The purified CO2 gas samples (salt C) were converted to graphite targets using a closed-tube Zn reduction CO2 graphitization method.54. Targeted graphite samples were subsequently analyzed for stable and radiocarbon isotopes (δ13C and 14C as fraction modern carbon). All δ14C values (in ‰) were corrected for isotopic fraction using measured δ13C values that were quantified during the 14C-AMS procedure. We measured δ13C in these samples separately on a VG Prism Stable Mass Spectrometer at NOSAMS. Δ14C and radiocarbon age were determined from percent modern carbon using the year of sample analysis according to ref. 55.

We also analyzed 14C-DOC on a composite SPGW sample that was made from ten individual sample collections on the beach of Jago Lagoon in August 2017. The composite sample collected in 2017 had a 14C-DOC age of 1060 yBP, which is within error of the measured age of 226Ra. This result was not used along with the individual measurements described in the previous paragraph to calculate an average SPGW age because it was determined using different methodology, but it does confirm that the average 14C-DOC age estimate used in this study is representative of August SPGW more generally. The groundwater composite collected in August 2017 was solid-phase extracted (SPE-DOM) using modified styrene divinyl benzene polymer PPL cartridges.56 The SPE-DOM was high-temperature combusted using an Elementar vario EL Cube CN analyzer. Bulk soil % OC and % ON were quantified during this step. The resulting CO2 was transferred to a vacuum line and cryogenically purified. The purified CO2 gas samples (salt C) were converted to graphite targets using a closed-tube Zn reduction CO2 graphitization method.54. Targeted graphite samples were subsequently analyzed for stable and radiocarbon isotopes (δ13C and 14C as fraction modern carbon). All δ14C values (in ‰) were corrected for isotopic fraction using measured δ13C values that were quantified during the 14C-AMS procedure. We measured δ13C in these samples separately on a VG Prism Stable Mass Spectrometer at NOSAMS. Δ14C and radiocarbon age were determined from percent modern carbon using the year of sample analysis according to ref. 55.

Boat-based 222Rn measurements were made around Kaktovik Lagoon using a circuit of three RAD7 Radon-in-air monitors (Durridge Co., Inc.) connected to a RAD Alert device following procedures detailed in ref. 26. The outer circuit was installed after the system reached full gas/radioactive equilibrium. Measurements at ~1 m depth from the lagoon bottom were made in survey mode while driving a small inflatable boat around the lagoon. To optimize spatial resolution, the three RAD7 units analyzed samples staggered with 15-min intervals with water pumping at flow rates >6 L min−1. 222Rn concentrations shown at each location in Supplementary Figure 1 represent an average of a continuous measurement made along some distance traveled before the average was calculated by each RAD7 instrument. 222Rn concentrations in discrete SPGW samples were collected using the Wat-250 ml protocol in the Durridge RAD7 user manual. 222Rn production measurements were conducted with dry lagoon sediments (ranging from 328 to 546 g) using a Durridge RAD7 bulk emissions chamber and methods outlined in the user manual.

Estimation of groundwater fluxes using 222Rn. Naturally occurring 222Rn (t1/2 = 3.8 d) is a widely-used geochronal tracer of water flow through rocks and soil/sediments and thus serves a useful tool for quantifying submarine groundwater discharge. Total groundwater discharge was calculated using a steady-state excess 222Rn mass balance model as described in ref. 26,27. We used a steady-state model because our lagoon system has no direct connections with the Beaufort Sea and has only low to very low (2–3 mm) and narrow (~12 m across) passes that connect with adjacent lagoons. It is important to note that there are several primary assumptions of the model: (1) lagoon 222Rn used for the calculation reflects the lagoon average concentrations over days to weeks; (2) the only significant 222Rn source is from the tundra active layer and lagoon benthic sediments, and does not include water that enters the lagoon via rivers and lakes; and (3) the only losses of 222Rn are due to decay and atmospheric evasion. In addition, we assume marine inputs do not affect the 222Rn inventory in Kaktovik Lagoon since there is very little water exchange with the Beaufort Sea and lagoon water residence time is long during the summer (weeks to months) in comparison to the decay rate of 222Rn. The mass-balance equation for 222Rn is given by

\[ \text{{}^{222}Rn}_{\text{in}} - \text{{}^{222}Rn}_{\text{out}} = \text{{}^{222}Rn}_{\text{production}} - \text{{}^{222}Rn}_{\text{decay}} - \text{{}^{222}Rn}_{\text{atmospheric}} - \text{{}^{222}Rn}_{\text{marine}} \]

Calculations regarding this conversion can be found in Supplementary Note 1. Standard errors in these values reflect variability in concentrations between samples as opposed to analytical uncertainty. A description of the uncertainty in our groundwater discharge estimate can be found in Supplementary Note 2. We did not measure 226Ra in this study, but rather used estimates from Elson Lagoon in ref. 28. Therefore we also assume that the 226Ra concentration between these lagoons is the same. Total groundwater 222Rn input was estimated using an iterative approach that accounts for the 226Ra flux from lagoon benthic sediments, atmospheric evasion, and marine inputs. We estimated a 226Ra groundwater age estimate that increases by 0.2 y when the 226Ra concentration in the lagoon is increased by a factor of 2. The uncertainty in our groundwater discharge estimate is calculated using the uncertainty in the 226Ra concentration and the iterative approach that accounts for the 226Ra flux from lagoon benthic sediments, atmospheric evasion, and marine inputs.

Data availability

New data reported herein is made available in the Supplementary Data 1 file.

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Author contributions

C.T.C., G.A.B., M.B.C., and J.W.M. collected data, contributed to study design, and helped with analysis of groundwater constituents and discharge. C.T.C. collected data and designed the soil sampling, soil water extractions, and isotopic analysis with gui-

Competing interests

The authors declare no competing interests.
