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A Tracer-Based Method for Classifying Groundwater Dependence in Boreal Headwater Streams

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1 *Manuscript Title:*

2 A Tracer-Based Method for Classifying Groundwater Dependence in Boreal Headwater Streams

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Abstract

Ecosystem protection requires a better definition of groundwater (GW) dependence and tools to measure this dependence. In this study, a classification method for the GW dependence of headwater streams was devised based on the fact that GW affects discharge, thermal regime, and water quality. The method was tested in three boreal headwater streams discharging from two esker aquifers. Spatial and temporal variability of GW dependence were studied in the stream continuum at several locations, by combining continuous measurements of temperature, electrical conductivity, and discharge with discrete sampling of environmental tracers (e.g., stable water isotopes, silica, chloride). The stream tracer index method developed was used to classify stream sections into GW-dominated, GW-surface water (SW) transition, and SW-dominated zones. We found that, spatially, GW dependence along the stream varied widely, with calculated stream tracer index values ranging from 33 to 94 %. The GW-dominated areas extended at least 745, 1682, and 4202 m downstream from the main GW discharge points in the three streams studied. A stream located in a pristine peatland-dominated catchment was more prone to rapid change from GW- to SW-dominated than two streams located in catchments dominated by peatland forestry. These results suggest that to evaluate the GW dependence of streams, it may be sufficient to sample stream sections only once, during summer low-flow conditions. The proposed method can serve as a water management tool, especially for streams of exceptional ecological importance or in places where anthropogenic activities are expected to change local hydrology and ecology.

Keywords: stable water isotopes, environmental tracers, groundwater-dependent ecosystems, headwater streams

1 Introduction

Headwater streams have a large effect on downstream hydrological and geochemical processes and ecological functions [Freeman *et al.*, 2007; Finn *et al.*, 2011]. Groundwater (GW) is generally a major contributing factor to maintaining the baseflow of headwater streams [Sophocleous, 2002; Winter, 2007] and has specific geochemical, physical, and biological characteristics that differ from surface water (SW) [Bertrand *et al.*, 2012]. Therefore, any changes in GW discharge to headwater streams can have a major impact on stream water quality and volume, with the most pronounced effects occurring in areas that are highly influenced by GW. In order to reduce the impacts on groundwater-dependent ecosystems (GDEs), tools are needed for their classification, management, and protection [EC, 2006; Richardson *et al.*, 2011; Rohde *et al.*, 2017]. However, GDE classification of headwater streams is not straightforward because standard procedures are lacking and the GW-SW transition zones and ecotones can vary temporally and seasonally.

Dynamic environmental factors govern the healthy functioning of freshwater ecosystems and are categorized as: flow patterns, sediment and organic matter inputs, temperature and light penetration, chemical and nutrient conditions, and plant and animal assemblages [Younger, 2006]. In GW-dependent stream ecosystems, many organisms rely on conditions sustained by GW. These conditions are i) discharge volume, ii) stable thermal regime, and iii) water quality [Bertrand *et al.*, 2012]. During sensitive summer and winter low-flow periods in particular, GW input to headwater streams provides important refuges maintaining stable discharge [Younger, 2006] and thermal conditions in these streams [Dugdale *et al.*, 2013; Snyder *et al.*, 2015]. As GW-dominated streams provide more stable conditions for stream ecosystems than SW-dominated streams [Webb *et al.*, 2008], these ecosystems will become even more important in supporting thermal refuges in a changing climate. However, GW-dominated headwater streams can be sensitive to local anthropogenic actions such as agriculture, drainage for forestry, and GW abstraction [Ramchunder *et al.*, 2012; Rossi *et al.*, 2012, 2014; Saarinen *et al.*, 2013; Eskelinen *et al.*, 2016], which can lower GW levels, alter GW discharge patterns to headwater streams, and change water quality and the ecology of streams [Poff and Zimmerman, 2010]. This emphasizes the need to classify these ecosystems, in order to better protect and manage them and the connected GW systems.

Use of environmental tracers, such as stable water isotopes and water chemistry, is an efficient and flexible method to study dynamic and spatially varying GW-SW interactions in water courses and streams [Leibundgut *et al.*, 2009; Bertrand *et al.*, 2014]. However, past tracer approaches have often focused on only one location in a stream [Kendall and Coplen, 2001; Litt *et al.*, 2015; Soulsby *et al.*, 2015; Niinikoski *et al.*, 2016] or on intensive sampling for a rather short period [Klaus and McDonnell, 2013]. Thus, these studies cannot give a full spatial and temporal picture of GW dependence in the stream continuum. Recent studies highlight the importance of spatially dense sampling to determine stream water chemistry [Zimmer *et al.*, 2013] and stable water isotopes [Singh *et al.*, 2016]. The specific geochemistry of different landscape units in the catchment can alter the chemical composition of stream water [Blumstock *et al.*, 2015]. A study by Zimmer *et al.* [2013] suggests that GW contributions from distinct soil types control the spatial similarities found in stream water chemistry in varying flow conditions. The catchment structures (i.e. catchment “forms”, the hydrogeological setup of the catchment) also cause small-scale differences in baseflow stable water isotopes [Singh *et al.*, 2016]. In general, variations in stream water quality can result from changes in mixing proportions of GW and SW, and spatial or temporal changes in water quality, which can complicate interpretation of tracer data [Kirchner, 2016a, 2016b].

Recent tracer modelling approaches have focused particularly on studying the water age distributions in catchments [e.g., Birkel and Soulsby, 2015; Soulsby *et al.*, 2015; Huijgevoort *et al.*, 2016; Ala-aho *et al.*, 2017]. These modeling efforts are increasingly being supported by continuous measurement of isotope data [Tweed *et al.*, 2016], which has improved estimates of young water fractions [Stockinger *et al.*, 2016] and thus also estimates of GW fractions in streams. However, at this point high-resolution data cannot be obtained cost-effectively from several locations along the stream, which would be necessary for assessing spatial variations in GW dependence. Although low-resolution isotope data have uncertainties when estimating water

fractions during large events [Soulisby *et al.*, 2015], it can be sufficient to assess GW dependence during low flows and small events, which account for the majority of the hydrological year and sustain the ecological functions of streams. Thus, many tracer-based studies discuss GW-SW interactions in streams [e.g., Hagedorn and Whittier, 2015; Scholl *et al.*, 2015; Duvert *et al.*, 2016] but none has proposed a generalized method for water management purposes that could be used to evaluate the GW dependence in headwater streams.

In this study, we combined continuous measurements of discharge, temperature (T), and electrical conductivity (EC) with use of stable water isotopes and other environmental tracers to study the GW-SW transition zones in three boreal streams known to have high proportions of GW from esker aquifers. The esker aquifer systems studied are of a type commonly found in areas covered by the last glaciation and are of great importance in the Northern hemisphere as a source of potable water [Kløve *et al.*, 2017]. Typically, headwater streams originate from esker boundaries (esker-peatland interaction). We expected to find a transition zone within which a spring-originated stream turns into a SW-dominated system. By definition, SW is the water in surface storage units (e.g., lakes, streams, rivers, wetlands) and GW is the water underground. However, since our aim was to study the transition and mixing between these in streams, we applied the term SW to water that is already modified by surface processes, i.e., river water or water originating from surrounding peatlands. Our specific objectives were to determine the GW dependence along the stream continuum, study the spatial and temporal changes in mixing zones in the three streams, and develop a tool and guidelines for the use of different environmental tracers in evaluating the GW dependence of streams. This work addresses the following research questions: i) How can headwater stream sections be classified to GDEs? ii) What measurements should be made, and from where, to obtain a sound GDE classification for headwater streams? iii) Is it possible to evaluate the GW dependence of a stream based on a single sampling campaign?

2 Materials and methods

2.1 Study sites

The three streams selected for the study are located in Rokua and Viinivaara esker aquifer areas and are 60 km from each other. Eskers are one of the most common aquifer types in deglaciation areas in Finland, Sweden, and Eastern Canada [Britschgi *et al.*, 2009; Nadeau *et al.*, 2015; Berthot *et al.*, 2016; Holmlund *et al.*, 2016; Quillet *et al.*, 2017]. The study sites belong to a mid-boreal coniferous forest belt. The Rokua study area represents disturbed ecosystems and Viinivaara contains nearly pristine ecosystems (Fig. 1). In the Rokua esker area, we selected two streams, Siirasoja and Lohioja, where surrounding peatlands are intensively drained for forestry. In contrast, Mesioja stream, discharging from Viinivaara esker aquifer, represents a pristine stream and flows through undisturbed peatland. The average channel widths and average maximum depths along the streams studied are presented in the Supporting Information Table S1.

2.1.1 Siirasoja and Lohioja streams in Rokua esker aquifer

Rokua esker aquifer, with a recharge area of 92 km², is a post-glacial sand and gravel deposit rising on average 30-40 m above the surrounding peatlands (max. 90 m). The aquifer itself is unconfined, but the heavily drained peatlands in the surroundings partly confine the GW [Rossi *et al.*, 2012]. On the northern side of the esker, the headwater streams Siirasoja and Lohioja discharge to the river Oulujoki. The catchments are located next to each other and the land use consists mainly of peatland forestry and some agricultural land (Table 1). Due to varying land use in the surroundings, different sections of Siirasoja and Lohioja streams show differences in channel shading, which can affect stream water temperature. Prior to this work, several studies have clarified the GW-SW interactions in the Rokua esker aquifer area [Ala-aho *et al.*, 2013, 2015; Rossi *et al.*, 2014; Eskelinen *et al.*, 2015; Isokangas *et al.*, 2015], and two have investigated the

hydrology of Siirasoja stream, revealing complex GW discharge patterns [Rossi *et al.*, 2012; Eskelinen *et al.*, 2016]. Siirasoja and Lohioja streams have tributaries that are also connected to ditches in the area (Fig. 1). Some of the ditches in Siirasoja catchment have no flow and some fully penetrate the peat layer and reach the mineral soil beneath, causing increased GW discharge to the stream. GW discharge has been found to be either diffuse seepage or point type, and is induced by high pressure underneath the peat layer (Rossi *et al.* 2012). Eskelinen *et al.* (2016) concluded that the GW discharge and thick snow pack prevent the formation of soil frost in Siirasoja catchment, which results in snowmelt water infiltration into the soil and a higher flux of weathering products than at sites with soil frost.

Fig. 1. Maps showing the location of the three study streams (Siirasoja, Lohioja, Mesioja) discharging from Viinivaara and Rokua esker aquifers, their catchment area, and the sub-catchments of the measurement points. Measurement points with no identifiers represent “dense sampling points” and points with identifiers (with a letter indicating the stream, followed by a sample number) represent “detailed sampling points”. The letter Q shows locations of continuous water level measurements (see section 2.2 for more details).

Table 1. Stream and watershed characteristics of the three headwater streams analyzed in this study

Stream	Length (km)	Watershed area (km ²)	Drained for forestry (%)	Agricultural land (%)	Q _{max} (m ³ s ⁻¹)	MQ (m ³ s ⁻¹)	Q _{min} (m ³ s ⁻¹)
Mesioja	3.0	2.6	0.6	0.0	0.018	0.007	0.001
Lohioja	5.4	13.6	59.9	5.8	1.186	0.177	0.051
Siirasoja	7.2	24.0	32.9	3.4	0.706	0.234	0.146

Note. Discharge values for Siirasoja and Lohioja streams are the highest annual discharge (Q_{max}), mean annual discharge (MQ), and lowest annual discharge (Q_{min}) (hourly data 2010-2015). Discharge values for Mesioja stream are from *in situ* measurements made during study periods 15.5.2013-14.10.2013 and 12.5.2014-10.11.2014, and are the highest discharge (Q_{max}), mean discharge (MQ), and lowest discharge (Q_{min}).

2.1.2 Mesioja stream in Viinivaara esker aquifer

Viinivaara esker is a smaller aquifer than Rokua esker and has a recharge area of 15 km². This sandy aquifer is also surrounded by peatlands, which have remained partly in pristine condition. Our study stream, Mesioja, discharges from a spring located at the break of slope where the sandy aquifer meets the peat formation and flows partly underground between measurement locations M2 and M3 (Table 1). The lower catchment area is mostly pristine peatland with bog-type vegetation. The GW dependence of the peatland area varies widely; spatial isotope studies by Isokangas et al. (2017) showed that the stable isotopic composition of the peatland pore water is not uniform near Mesioja stream, with $\delta^{18}\text{O}$ values ranging between approximately -8‰ and -13‰ at 10 cm depth during the period 4-11 August 2014.

2.2 Field measurements

In the three streams, two disturbed and one pristine, EC and temperature were continuously measured during 2013-2014 using Hobo loggers (EC and temperature logger U24-001, accuracy 5 $\mu\text{S}/\text{cm}$ and 0.1°C) installed at on average 1-km intervals in the stream, to study the spatial and

temporal variations in these variables along the streams (i.e., “detailed sampling points”, Fig. 1). In Mesioja stream, four Hobo loggers were installed along the stream and one (measurement point M5) was positioned at the outlet stream from Lake Sarvilampi, where Mesioja stream discharges. Hobo loggers were installed at four locations in Lohioja stream and at five locations in Siirasoja stream. An additional Hobo logger was installed at a small tributary of Siirasoja stream (measurement point S3), since this reach is protected by the Natura 2000 program because its grove area has remained in a more natural state than the rest of the upper catchment. Water level was monitored continuously at one location in each of the streams (point Q, Fig. 1). Discharge was measured with a current meter at all stream measurement points during the eight field measurement campaigns. Rating curves for the streams studied were developed using continuously measured and barometrically compensated water levels (Solinst Levellogger Gold) and the discharge measured with current meters (Mini Air 20, Schiltknecht) during the field work and in campaigns prior to this study (Siirasoja and Lohioja). As the field campaigns did not capture the highest recorded water levels, rating curves for Siirasoja and Lohioja were extrapolated using discharge rates obtained from fully integrated surface-subsurface flow modeling with HydroGeoSphere [Ala-aho *et al.*, 2014]. Rating curves were used to obtain continuous discharge values for the streams.

The streams were sampled quarterly during 2013 and 2014 for stable isotopes of water ($\delta^{18}\text{O}$, $\delta^2\text{H}$), nutrients (P, $\text{PO}_4^{3-}\text{-P}$, total inorganic carbon (TIC), dissolved organic carbon (DOC)), water quality parameters (T, pH, EC, O_2), geochemical parameters (dissolved SiO_2 , SO_4^{2-} , K^+ , Na^+ , Ca^{2+} , Mg^{2+} , Mn^{2+} , Sr^{2+} , Al^{3+} , Cl^- , S, Fe), and alkalinity. The samples were taken from four, four, and six locations in Mesioja, Lohioja, and Siirasoja stream, respectively (i.e., “detailed sampling points”, Fig. 1). For stable water isotopes and water quality parameters, additional water samples were taken from five, four, and six locations in Mesioja, Lohioja, and Siirasoja stream, respectively (i.e., “dense sampling points”, Fig. 1). Monthly cumulative samples for stable isotopes of water were also taken from local precipitation at Rokua, approximately 4 km from the studied streams, and near Viinivaara (Nuoritta site), 17 km from Mesioja stream.

Stable isotopic composition of water samples was analyzed using cavity ring-down spectroscopy with a Picarro L2120-i analyzer and the isotope ratios were expressed in δ notation relative to Vienna Standard Mean Ocean Water (VSMOW), with precision for $\delta^{18}\text{O}$ and $\delta^2\text{H}$

values of $\pm 0.1\%$ and $\pm 1.0\%$, respectively. Water quality parameters were measured using a field meter (WTW Multi 350i meter, accuracy: pH ± 0.005 , O₂ $\pm 0.5\%$ of the measured value; ± 1 mV for EC and ± 0.1 °C for T). Nutrients, alkalinity, and geochemical parameters were analyzed using Finnish national standards in an accredited (SFS-EN ISO/IEC 17025:2005) laboratory at the Finnish Environment Institute (SYKE) [*National Board of Waters*, 1981].

2.2.1 Local groundwater and surface water quality

Local GW and SW quality data were acquired for use as reference values to evaluate the potential of different water quality tracers to separate GW from SW (Supporting Information Table S2). The measurement locations are presented in the map in Supporting Information Fig. S1. In Viinivaara, local GW was sampled quarterly in 2014 at one location approximately 1 m below the GW level and analyzed for stable isotopes of water ($\delta^{18}\text{O}$, $\delta^2\text{H}$), nutrients (P, PO₄³⁻-P, TIC, DOC), water quality parameters (T, pH, EC, O₂), geochemical parameters (dissolved SiO₂, SO₄²⁻, K⁺, Na⁺, Ca²⁺, Mg²⁺, Mn²⁺, Sr²⁺, Al³⁺, Cl⁻, S, Fe), and alkalinity. The nearest SW sampling locations of SYKE are situated 27 km (Nuorittajoki suu station) and 9 km (Nuorittajoki Töntönkoski station) from Mesioja catchment. SW was sampled during the open water season from Nuorittajoki suu station four times per year during 2013-2014 and from Töntönkoski station one to four times per year during 2006-2011. Most of the parameters were analyzed using samples from Töntönkoski station and, although the measurements were performed before our stream sampling campaign, the data were assumed to be representative for the study period because there had not been any major changes in land use in the area. The SW sampling location of Nuorittajoki suu station is located rather far from our study stream but, as the land use is relatively similar to that in Mesioja catchment (Supporting Information Fig. S1), the data were assumed to be representative for the study area. In Rokua, local GW in the esker and also under the peat layer in the discharge zone was sampled four times a year during 2010-2012 and analyzed for stable isotopes of water, P,

PO₄³⁻-P, EC, pH, dissolved SiO₂, K⁺, Na⁺, Ca²⁺, Mg²⁺, and Cl⁻. In addition, SO₄²⁻, Mn²⁺, Fe, and alkalinity were determined by SYKE in four GW pipes (MEA 206, MEA 506, MEA 806, and MEA 1006) in Rokua esker in January 2007. In Rokua, the measurements by SYKE were also used as a reference for SW. Sampling was carried out generally once a month during 2013-2014 in the river Oulujoki, into which the studied streams discharge (at Jylhämä station, located approximately 6 km upstream from the study catchments).

2.3 Data analysis

Watersheds were delineated in an ArcGIS 10.2 environment using a 2 m resolution digital elevation model (DEM) produced by the National Land Survey of Finland. Statistical parameters (standard deviation, mean, and coefficient of variation) for continuous temperature and EC measurements were calculated with R [The R Foundation, 2019]. The data were grouped into two subgroups before analysis: warm season (June-September) and cold season (April, May, October, and November).

To graphically compare the chemistry in different water samples, piper diagrams were formed using the R package 'Hydrogeo' [English, 2017]. If the measured concentration of the substance was below the limit of detection (LOD), it was assigned a value of LOD divided by 2, which is a common procedure used to assign values for sample sets with less than 15% of the samples below the detection limit [United States Environmental Protection Agency, 2000].

To reduce the dimensionality of the dataset while retaining as much of its variation as possible, we performed principal component analysis (PCA) for the stream data (chemical and physical water quality parameters and discharge). We used the R function `prcomp` from the Stats package, which employs singular value decomposition (SVD) [R Core Team, 2019]. It is preferred over the `princomp` function because of its better numerical accuracy [Anderson, 2013]. A constant was added to isotope values to transform them to positive values (13.3‰ for δ¹⁸O and 95.8‰ for δ²H). To eliminate skewness, we log-transformed the data. We also scaled and centered the data using the `prcomp` function. We performed the analysis for two datasets; the average values of all measurements for each site and the average values for the low-flow situation (July measurements). One of the basic assumptions of PCA is that the measurements are independent [Demšar et al., 2013]. However, the measurements in this study were made at several locations along the same

streams and thus there was some spatial autocorrelation between the measurements. However, as each stream had almost the same number of sampling locations, they had similar weighting in the analysis and PCA was deemed suitable for use, although the autocorrelation between samples was borne in mind when analyzing the results. We included three PCA components, which explained 85% (all measurements) and 88% (low flow measurements) of the variation in the data set.

2.3.1 The stream tracer index method

To classify the observed GW dependence of the three streams, we developed a *stream tracer index method*. This was used to classify the stream sections into GW-dominated, GW-SW transition, and SW-dominated zones, based on three properties: i) GW volume in streams, ii) thermal properties of streams, and iii) stream water quality. GW amount in streams can be evaluated based on discharge and stable water isotopes, thermal properties based on the temporal variations in stream T, and water quality based on the GW tracers chosen to be suitable for the specific stream. The *stream tracer index* (S_i) was calculated as:

$$S_i(\%) = 100 * \frac{x_{gw} + x_{temperature} + x_{chemistry}}{3} \quad (1)$$

where x_{gw} is the classification value based on stable water isotopes and discharge (GW volume), $x_{temperature}$ the classification value based on temperature, and $x_{chemistry}$ the classification value based on water quality. Due to local variations in land use and in bedrock and soil chemistry, the same water quality tracers may not be applicable at all locations. The tracers were chosen based on the assumptions that: i) the chemical signature of GW and SW stays relatively stable within a catchment and ii) upstream locations are more GW-dominated and thus the upstream tracer values should be closer to GW than SW reference values (see section 2.2.1). In practice, the stream water tracer values (median values) also had to be between the GW and SW reference values in order to be chosen as tracers. Stream water tracer values not related to the reference values can be the

result of deviating GW and/or SW quality in the catchment area. SW tracer concentrations in particular can change markedly due to different kinds of land uses and catchment properties. However, as there is hardly any detailed information about the SW quality of different land units, in our method only tracers with behavior associated with the available reference values are used. Thus, the best suited catchment-specific tracers must be first determined for each site (see section 3.3) and then the classification value based on water quality can be calculated as:

$$x_{chemistry} = \frac{x_{variable\ 1} + x_{variable\ 2} + \dots + x_{variable\ n}}{n} \quad (2)$$

where $x_{variable}$ is the classification value based on the chosen water quality variable. The classification values are determined by evaluating whether the tracer in question indicates a clear GW signal ($x=1$), a mixture of GW and SW (transition zone, $x=0.5$), or a clear surface water signal ($x=0$). After the appropriate values are chosen, the stream tracer index values can be calculated using equations (1) and (2). Measurement locations with stream tracer index values $S_i < 50\%$ are interpreted as SW-dominated zones, those with $S_i = 50\%$ as transition zones, and those with $S_i > 50\%$ as GW-dominated zones.

3 Results

3.1 Stream discharge and its origin

The discharge in the three streams studied varied temporally and spatially, with a generally increasing trend downstream (Figs. 2 and 3). Baseflow was highest for Siirasoja stream (approximately $15 \text{ L s}^{-1} \text{ km}^{-2}$), considerably higher than for Lohioja stream ($7.5 \text{ L s}^{-1} \text{ km}^{-2}$). The base flow in Mesioja was approximately $1.3 \text{ L s}^{-1} \text{ km}^{-2}$, which was only 9% of that in Siirasoja. Siirasoja and Lohioja streams responded similarly to precipitation events and with a similar timing and magnitude of the response (Fig. 3). However, the maximum peak discharges were higher in Lohioja. In general, high flows occurred during autumn and after snowmelt in spring. During these events, the spatial variations in discharge along the stream continuum were at their highest. The coefficient of variation for discharge was greatest for Mesioja (87%) in October 2013 and for Lohioja (75%) and Siirasoja (77%) in November 2014. The lowest flows were observed during winter and occasionally during summer. The discharge at the upstream locations stayed relatively stable during all seasons.

Based on the stable water isotope dataset, the water origin in all three streams was mainly GW (Fig. 6 and Supporting Information Fig. S2). The average isotopic composition of GW in Viinivaara and Rokua esker areas is -13.0 and -94.3 ‰ [Isokangas *et al.*, 2017] and -13.1 and -95 ‰ [Isokangas *et al.*, 2015], respectively, for $\delta^{18}\text{O}$ and $\delta^2\text{H}$. In Siirasoja and Lohioja streams at Rokua, the isotopic composition remained relatively stable except during the rain events in November 2014 (Fig. 3), when the isotopically more enriched SW increased the delta values of the streams. Summer evaporation also slightly modified the isotopic composition of stream water. In Mesioja, the water isotope responses were more complex than in Lohioja and Siirasoja. At upstream locations, the isotopic composition resembled GW, but further downstream the delta values increased, indicating larger contributions from enriched surface runoff and soil water. However, at

the furthest downstream locations, the delta values were again more negative, indicating GW discharge into the stream also at downstream locations (Fig. S2).

Fig. 2. Stream discharge (Q) measured with a current meter at different distances from the stream start point in Mesioja, Lohioja, and Siirasoja streams during field campaigns.

Fig. 3. Continuous stream discharge obtained using water level measurements in Mesioja (MQ), Lohioja (LQ), and Siirasoja (SQ) streams and local precipitation data obtained from the Finnish Meteorological Institute weather stations Pudasjärvi Airport (Mesioja) and Pelso (Lohioja and Siirasoja). Dotted vertical lines indicate the sampling times.

3.2 Spatial and temporal variations in stream water temperature

During summer, water temperature generally increased from headwater to downstream in all streams (June-September, mean air T at Pudasjärvi airport 14.0 °C and at Vaala-Pelso station 13.3 °C). However, the streams generally had different diurnal variations (Fig. 4). During colder periods (spring and autumn), the upstream locations generally had a somewhat higher water temperature (mean 4.7 °C) than the downstream locations (mean 4.4 °C). The coefficient of variation for temperature was smallest for headwater locations in both warm (June-September) and cold (April, May, October, November) seasons. For the warm season, the values were 17.8%, 14.5%, and 13.7% for locations M1, L1, and S3, respectively, while for the cold season they were 46.1%, 39.1%, and 35.7%, respectively (Supporting Information Table S3). This shows that GW sustains stable thermal regimes in both warm and cold seasons. Although there was a clear increase in water temperature in the Mesioja stream continuum, at the last measurement location it still differed noticeably (5 °C on average in the warm season) from the SW reference, i.e., Lake Sarvilampi outlet (M5). In Lohioja and Siirasoja streams, water temperatures at different measurement points were more similar than in Mesioja. In Siirasoja, water temperature of one tributary (S3, warm season mean 6.9 °C) was mostly GW-influenced, whereas in Mesioja (M1, warm season mean 7.4°C) and Lohioja (L1, warm season mean 6.4°C), the GW impact was most pronounced at the most upstream locations (Table 2).

Fig. 4. Water temperature at different points in Mesioja, Lohioja, and Siirasoja streams, and local air temperature obtained from the Finnish Meteorological Institute weather stations Pudasjärvi Airport (Mesioja) and Pello (Lohioja and Siirasoja). Dashed grey

349 line indicates mean spring water temperature in Finland and Sweden [*Jyväsjärvi et al.*, 2015] and dotted vertical lines indicate the
350 sampling times.

3.3 Spatial and temporal variations in stream chemical properties

Stream water chemical properties varied spatially and temporally in all streams. Continuously measured EC of water reflects the total amount of ions in water and thus can be used to observe temporal changes in water chemistry. The average EC was highest in Siirasoja ($43 \mu\text{S cm}^{-1}$) and lowest in Mesioja ($19 \mu\text{S cm}^{-1}$) during both warm (June-September) and cold (April, May, October, and November) seasons (Fig. 5). The average EC of Lohioja water was $27 \mu\text{S cm}^{-1}$. In Mesioja, EC values generally decreased downstream, on average from 23 to $15 \mu\text{S cm}^{-1}$, indicating SW input to the stream (SW reference value $3 \mu\text{S cm}^{-1}$; Supporting Information Table S1). The behavior of EC in Lohioja and Siirasoja catchments was more complex. The lowest average EC values were found at upstream measurement points L1 ($20 \mu\text{S cm}^{-1}$) and S2 ($36 \mu\text{S cm}^{-1}$), and the highest at points L2 and L3 ($30 \mu\text{S cm}^{-1}$) and S1 ($50 \mu\text{S cm}^{-1}$). In general, the EC values in Lohioja and Siirasoja indicate that SW increased EC, unlike in the Mesioja catchment, although the SW reference values were the same in both areas (Supporting Information Table S2). This is supported by the relatively low GW reference values in Rokua, which ranged from 2.9 to $7.8 \mu\text{S cm}^{-1}$ depending on measurement location (Supporting Information Table S2).

Fig. 5. Electrical conductivity (EC) at different points in Mesioja, Lohioja, and Siirasoja streams. Dotted vertical lines indicate the sampling times. Some of the data were filtered out due to unreliable results (compared against field measurements) caused by biofilm growth on loggers.

Based on piper diagrams, the dominant water type was Ca-HCO_3 for Siirasoja, Ca-HCO_3 to Ca-SO_4 for Lohioja, and Na-HCO_3 to Na-SO_4 for Mesioja (Fig. 6). Finnish streams usually have Ca-HCO_3 as the dominant water type, with dark water color and high organic matter and Fe content [Lahermo *et al.*, 1996]. The piper diagrams showed that Mesioja had significantly different water chemistry than Siirasoja and Lohioja streams. However, Siirasoja and Lohioja also differed slightly from each other. Siirasoja had the most stable water chemistry, based on the piper diagram.

Fig. 6. Piper diagrams for Mesioja, Lohioja, and Siirasoja streams.

Furthermore, stream water chemistry varied spatially in Mesioja, Lohioja, and Siirasoja streams (Fig. 6). In Mesioja water, several substances decreased downstream (TIC, K, Ca, Mg, S, Sr, SO₄, and SiO₂) and only DOC increased in the Mesioja stream continuum. The chemistry of Lohioja and Siirasoja water varied less regularly. Stream water chemistry was compared against the local GW and SW composition (Supporting Information Table S2). The variables that changed along the stream continuum which could be best related to these reference values were conventionally used environmental tracers SiO₂ and Cl⁻ and,

in addition, DOC, TIC, and $\text{PO}_4^{3-}\text{-P}$. Thus, these variables were chosen for use as GW tracers in this study (see section 3.4). However, not all these variables could be used for tracing GW in all streams. In general, the change in GW dominance was more easily associated with the tracer concentrations in Mesioja stream than in other streams.

In the Mesioja stream continuum (from M1 to M4), the DOC values rose from the GW reference value (1.0 mg L^{-1}) to the SW reference level (23 mg L^{-1}) (Fig. 7). Therefore, the DOC values indicated that the first measurement location (M1) had a clear GW signal, the next two (M2 and M3) belonged to the transition zone, and the last measurement location (M4) had a clear SW signal. In Lohioja stream, all DOC values were higher than the GW and SW reference values and DOC could not be used to indicate GW dependency. In Siirasoja stream, most of the measured DOC values fell between the reference values and those of all other measurement locations, except for S2, which was in the GW-SW transition zone.

TIC decreased by approximately half in the Mesioja stream continuum, from near its GW reference value to near its SW reference value. However, the transition occurred earlier than for DOC and already at the M3 location the stream had a clear SW signal. There was no available information about TIC in GW in the Rokua esker, so the Viinivaara esker reference value was used as an estimate. Based on TIC, all the locations in Lohioja stream were in the GW-SW transition zone. Furthermore, in Siirasoja only the first measurement location S1 had a clear GW signal and the others fell between GW and SW reference values to the transition zone.

416 In Mesioja stream, SiO_2 concentrations decreased downstream, indicating
417 gradual SW input to the stream. The first three measurement points were located
418 in the GW-SW transition zone, with gradually increased SW downstream, and the
419 last point had a clear SW signal. In Lohioja, the SiO_2 concentration stayed
420 relatively stable throughout the stream continuum and indicated a mixture of GW
421 and SW. In Siirasoja, the second measurement location S2 belonged to a GW-SW
422 transition zone, whereas the other measurement locations had a clear GW signal.

423 In Lohioja, Cl^- concentrations indicated that the first measurement location
424 (L1) had a clear GW signal and the other locations were in the GW-SW transition
425 zone. In Siirasoja, the first three locations had Cl^- concentrations near to the GW
426 reference value, the next two belonged to the GW-SW transition zone, and the
427 last measurement location had a clear SW signal. In Mesioja, Cl^- concentrations
428 showed no consistent variation and could not be used to trace GW.

429 $\text{PO}_4^{3-}\text{-P}$ was not useful as a tracer in Mesioja, as the reference values of GW
430 and SW were very close to each other in the Viinivaara area. However, in the
431 Rokua area the reference values showed a clear distinction from each other. Due
432 to the high phosphate content of the aquifer sand, the GW had a high phosphate
433 content and all the measurement locations in both Lohioja and Siirasoja streams
434 belonged to the GW-SW transition zone. The behavior of total P was similar to
435 that of $\text{PO}_4^{3-}\text{-P}$.

436

Fig. 7. Stream water chemical variables represented as box plots for each measurement point, where M is Mesioja, L is Lohioja, and S is Siirasoja. Vertical axes for SiO_2 , $\text{PO}_4^{3-}\text{-P}$, and P are rescaled and the plots do not show all outliers. Continuous lines indicate local groundwater (average of esker groundwater and groundwater

441 under the peat layer at discharge zone in Rokua), dotted lines represent surface water
442 (see Table 2), and dashed lines represent summer precipitation.

443 PCA was applied to average values of all measurements and to average values of
444 low-flow measurements (July samples). We observed no notable dissimilarities
445 between the PCA results of these two sampling seasons (Table 2). For all
446 measurements, 75% of the variation in the data was explained by the first two
447 principal components (PCs), while for low-flow measurements these two PCs
448 explained 79% of the variation. In both cases, all three streams were distinctly
449 separated from each other when plotted along the first two PCs (Fig. 8). Mesioja
450 had the greatest variance between measurement locations, while in Lohioja and
451 Siirasoja the variance along the first two PCs was much smaller. On examining
452 the component loadings of different variables, it was possible to find physical
453 interpretations for different PCs. The first PC could be connected with GW, since
454 many of the variables known to be associated with GW, e.g., pH, alkalinity, PO_4^{3-}
455 -P, P, and SiO_2 (see section 4.3), had high negative PC1 loadings. Thus, generally
456 low PC1 loadings indicated high GW influence. The second PC could be
457 associated with peatland water, since DOC in particular is correlated with
458 increased peatland surface water contribution. Therefore, negative PC2 loading
459 could indicate a high amount of peatland SW in a stream. The third PC was
460 associated with discharge and temperature and was therefore related to the GW
461 amount and the thermal regime of the streams.

Table 2. Summary of principal component (PC) results for the stream data showing the eigenvalues, percentages and cumulative percentages of explained variances, and component loadings for different parameters.

	All measurements			Low-flow conditions		
	PC1	PC2	PC3	PC1	PC2	PC3
Eigenvalue	12.97	6.50	2.70	13.55	7.09	2.20
% explained	49.90	25.00	10.38	52.12	27.26	8.45
Cumulative % explained	49.90	74.90	85.28	52.12	79.38	87.83
EC	-0.259	0.047	0.048	-0.249	0.071	-0.012
pH	-0.248	0.102	-0.150	-0.231	-0.062	-0.194
Alkalinity	-0.256	0.072	-0.103	-0.254	0.067	-0.142
SiO ₂	-0.200	0.130	-0.020	-0.259	0.009	0.099
P	-0.243	-0.150	0.048	-0.234	-0.150	0.033
PO ₄ ^{3--P}	-0.249	-0.151	0.093	-0.235	-0.159	0.056
SO ₄ ²⁻	-0.254	0.100	0.064	-0.247	0.122	0.092
Ba ²⁺	-0.248	-0.154	0.086	-0.249	-0.130	0.071
Ca ²⁺	-0.271	-0.074	-0.034	-0.263	-0.067	-0.093
Mg ²⁺	-0.251	0.145	-0.103	-0.230	0.158	-0.175
Mn ²⁺	-0.265	-0.053	0.030	-0.242	-0.095	0.065
S	-0.253	0.077	0.081	-0.244	0.117	0.114
Sr ²⁺	-0.195	-0.156	-0.024	-0.194	-0.205	-0.082
Al ³⁺	-0.020	-0.370	0.106	-0.016	-0.352	0.142
TIC	-0.131	0.246	0.218	-0.036	0.339	0.126
DOC	0.173	-0.247	0.041	0.176	-0.220	-0.041
Fe	-0.157	-0.255	0.237	-0.153	-0.251	0.203
Ti	-0.027	-0.361	0.120	-0.048	-0.330	0.195
δ ¹⁸ O	0.111	-0.127	-0.401	0.137	-0.219	-0.218
δ ² H	0.119	-0.165	-0.382	0.198	-0.219	-0.159
K ⁺	-0.180	0.187	-0.232	-0.140	0.305	-0.096
Na ⁺	-0.121	0.317	-0.214	-0.044	0.302	-0.357
Cl ⁻	-0.129	-0.207	-0.344	-0.115	-0.180	-0.473
Q	-0.117	-0.244	-0.304	-0.141	-0.178	-0.304
T	0.097	0.188	-0.312	0.146	-0.064	-0.448
Dissolved O ₂	-0.154	-0.236	-0.276	-0.222	-0.074	-0.089

Note. The highest loadings for each PC are shown in bold.

Fig. 8. Principal component analysis results for low-flow measurements (July samples) in Mesioja, Lohioja, and Siirasoja streams, plotted against the first two principal components (PC1, PC2).

3.4 Groundwater and surface water dominance of streams

The stream tracer index method was developed to combine the various types of information obtained during this study (see section 2.3.1.). The transition between the GW-dominated and SW-dominated sections occurred in the middle of

475 Mesioja stream, between locations M2 and M3, and at the end of Lohioja and
 476 Siirasoja streams. The upper parts of the streams were classified as zones with a
 477 clear GW signal (Table 3). Thermal properties (warm and cold seasons) were
 478 used to give T-based classification values (see section 3.2). The set of water
 479 quality variables used to obtain the water quality classification values were
 480 specifically customized for each stream (see section 3.3).

481 The calculated stream tracer index value S_i ranged from 33 to 94% for
 482 Mesioja, 50 to 88% for Lohioja, and 50 to 90% for Siirasoja. High S_i values
 483 indicate strong GW dependence, which was expected as the streams discharge
 484 from esker aquifers. Based on the index values, Lohioja and Siirasoja streams
 485 were more affected by GW than Mesioja stream. Mesioja was also the only
 486 stream where SW dominated in part of the stream. However, both in Lohioja and
 487 Siirasoja there was a clear shift from a GW-dominated to a SW-dominated system
 488 and the downstream locations were classified as GW-SW transition zones
 489 ($S_i=50\%$).

490 As the results of PCA for the whole dataset and for the low-flow situation
 491 resembled each other, the classification was reproduced using only the low-flow
 492 measurements (Supporting Information Table S4). The final classification results
 493 were almost identical except for location M3 in Mesioja, which belonged to a
 494 transition zone, not a SW-dominated zone, in the classification with low-flow
 495 measurements. On average, S_i values determined from the low-flow
 496 measurements were only 3.6% higher than the values determined from all
 497 measurements.

498

499

500 **Table 3. Use of the stream tracer index (S_i) method and classification values (x) to**
 501 **spatially classify the different parts of Mesioja, Lohioja, and Siirasoja headwater**
 502 **streams into groundwater-dominated (GW, $S_i > 50\%$) or surface water-dominated (SW,**
 503 **$S_i < 50\%$)**

Location	GW	Thermal	Water quality					S _i (%)	Classification
	amount	properties							
	X _{gw}	X _{temperature}	X _{DOC}	X _{TIC}	X _{SiO2}	X _{Cl}	X _{PO4-P}		
Mesioja									
M1	1	1	1	1	0.5			94	GW-dominated
M2	1	0.5	0.5	0.5	0.5			67	GW-dominated
M3	0.5	0.5	0.5	0	0.5			44	SW-dominated
M4	0.5	0.5	0	0	0			33	SW-dominated
Lohioja									
L1	1	1		0.5	0.5	1	0.5	88	GW-dominated
L2	1	0.5		0.5	0.5	0.5	0.5	67	GW-dominated
L3	0.5	0.5		0.5	0.5	0.5	0.5	50	Transition zone
L4	0.5	0.5		0.5	0.5	0.5	0.5	50	Transition zone
Siirasoja									
S1	1	0.5	0.5	1	1	1	0.5	77	GW-dominated
S2	1	0.5	0	0.5	0.5	1	0.5	67	GW-dominated
S3	1	1	0.5	0.5	1	1	0.5	90	GW-dominated
S4	1	0.5	0.5	0.5	1	0.5	0.5	70	GW-dominated
S5	0.5	0.5	0.5	0.5	1	0.5	0.5	53	GW-dominated
S6	0.5	0.5	0.5	0.5	1	0	0.5	50	Transition zone

504 Classification values: 1 - Clear groundwater signal, 0.5 - Transition zone, 0 - Clear surface water signal.

505 **4 Discussion**

506 **4.1 The role of groundwater in boreal streams**

507 Groundwater plays an important role in boreal headwater systems as the main
 508 source of base flow, providing unique biodiversity due to its cool and stable
 509 temperature and supply of good-quality water [*Ilmonen et al.*, 2012; *Jyväsjärvi et*
 510 *al.*, 2015; *Lehosmaa et al.*, 2017]. Classification of streams and aquifers is needed
 511 to protect these systems and manage water abstraction and land use activities that
 512 influence the GW source [*Laini et al.*, 2012; *Nadeau et al.*, 2015; *Rossi et al.*,
 513 2015] or the stream continuum itself [*Jyväsjärvi et al.*, 2014]. In this study,
 514 discharge, continuous measurements of EC and temperature, and tracer
 515 measurements (e.g., stable water isotopes, ions) were successfully used to trace
 516 the amount of GW in a stream continuum and classify the GW dependence of
 517 boreal headwater streams.

518 As expected for gaining streams, discharge increased towards downstream
 519 reaches due to increased GW exfiltration and/or SW input. GW maintained the
 520 flow in the small streams also during the dry season, when a constant isotopic
 521 composition was observed. During high flows in autumn and spring, surface
 522 water runoff from peatlands was observed and indicated by stable water isotopes,
 523 especially at downstream measurement points. The discharge at upstream
 524 locations close to the eskers stayed relatively stable throughout the year.

525 While GW dominated the first stream sections, differences among sites were
526 noted in downstream reaches. In Mesioja, stable water isotope data showed more
527 variations throughout the year than in Lohioja and Siirasoja streams. This
528 variation can be the result of fractionation by evaporation from the stream channel
529 or significant SW flow to the stream. However, based on the discharge and stable
530 water isotopes, all the streams are first GW-dominated, and then SW starts to
531 contribute more and the downstream locations are classified into GW-SW
532 transition or SW-dominated zones (Table 2).

533 Our results show that boreal headwater streams can be highly GW-dependent.
534 Changes in GW discharge would particularly affect the position and length of the
535 GW-SW transition zone in the stream continuum and could thus alter stream
536 ecosystems. As GW supports stream flow, especially at upstream measurement
537 locations, our study streams would most probably dry out without GW input at
538 least occasionally. In future, stream discharge in the Viinivaara study area will
539 probably decrease considerably due to planned GW abstraction for the city of
540 Oulu, as a large proportion of the annual recharge will be extracted [Rantala *et al.*,
541 2014]. Earlier snowmelt due to climate change may also lower GW levels in the
542 region during summer months, exacerbating the impacts of drought [Okkonen *et*
543 *al.*, 2010; Okkonen and Kløve, 2011]. These potential changes in stream discharge
544 pose a threat to the viability of aquatic ecosystems [Mustonen, 2016] and
545 highlight the importance of GW-dominated streams in boreal landscapes for
546 supporting ecological biodiversity.

547 4.2 Thermal properties change radically in the stream continuum

548 Water temperature can be a simple and affordable indicator of GW exfiltration. In
549 the streams studied here, stream temperature generally changed rapidly from
550 upstream to downstream sections. During summer, the measurements revealed
551 drastic changes in stream water temperature from cold (3 °C) to warm (up to 19
552 °C) occurring within a few kilometers in the boreal stream continuum. In general,
553 the temperature provided an approximation of GW amount, except during autumn
554 and spring seasons when GW and air temperature were similar.

555 The variations in stream water temperature were smallest at upstream
556 locations M1, L1, and S3 (classified as having a clear GW signal), where GW
557 sustained stable thermal regimes in both warm and cold seasons. Water
558 temperature at downstream locations still deviated from that in a local surface
559 water body (Lake Sarvilampi). The average temperature increase during the warm
560 season was 4.3, 3.7, and 2.6 °C in Mesioja, Lohioja, and Siirasoja, respectively.
561 The low values in Siirasoja stream were most likely due to higher discharge rate
562 and greater GW volume than in the other streams. The temperature-based GW-
563 SW transition zone started before 745 m and 1682 m distance from the beginning
564 of the stream in Mesioja and Lohioja, respectively, while in Siirasoja even the
565 first measurement location belonged to the transition zone and only the small
566 tributary (S3) had a GW-influenced thermal regime. Although we did not have a
567 complete set of winter temperature measurements, the cold season results provide
568 an indication of the conditions in winter. They show that the stream sections

569 which were most GW-influenced during the warm season were also the most
570 GW-influenced in winter. A GW influence on streams was also clearly visible
571 during winter, as the highly GW-dependent locations did not freeze due to the
572 stable GW temperature (approximately 4-6 °C). This provides specific conditions
573 for aquatic biota and can be vital for their survival. Unreported winter-time
574 observations (2010-2012) in Siirasoja stream supported our conclusion that the
575 GW-influenced section stays the same in winter, as the upper part of Siirasoja
576 was mostly unfrozen.

577 Our results showed that GW plays a major role in the thermal sensitivity of
578 the streams studied, such that GW-dependent areas were less sensitive to changes
579 in air temperature, although still responded to it. For example, the water
580 temperature at these locations still showed diurnal variations and during
581 exceptionally warm days the water temperature increased. Fortunately, these
582 events were relatively short (some days) and the highest temperatures were only
583 short-term mid-day events (e.g., on 1 July 2013, T in Siirasoja stream, location S3,
584 increased to 10 °C for 45 minutes). Changes in water temperature can be critical
585 for highly sensitive freshwater ecosystems [Yvon-Durocher *et al.*, 2011]. For
586 example, Jyväsjärvi *et al.* (2015) showed that even a 1 °C increase in mean water
587 temperature of springs can affect the species present in water and alter bryophyte
588 and macroinvertebrate communities in streams discharging from springs. In
589 addition, salmonid fish in particular have been found to be extremely sensitive to
590 the current warming trend and thermal refuges are becoming even more important
591 for preserving their populations [Isaak *et al.*, 2015]. However, stream biota can

592 have very different responses to temperature changes and therefore it is difficult
593 to give an overall estimate of a critical temperature limit. In addition, increasing
594 stream temperatures may not only reduce the amount of thermally suitable areas
595 available, but may also increase stream network fragmentation through thermal
596 barriers that reduce local ecological viability [Isaak *et al.*, 2012, 2015; Orr *et al.*,
597 2015; Snyder *et al.*, 2015].

598 **4.3 The applicability of local groundwater and surface water** 599 **reference values**

600 The water quality of the three streams studied showed clear differences, despite a
601 similar geological formation being the main water source. Therefore different
602 water quality tracers were chosen for each of the streams (see sections 3.3. and
603 3.4). Changes in stream water quality can result from changes in mixing
604 proportions of GW and SW, or changes in GW and/or SW water quality spatially
605 or temporally. These kinds of variations can complicate interpretation of tracer
606 data [Kirchner, 2016a, 2016b]. In general, GW is assumed to have more stable
607 water quality than SW, but seasonal variations in GW quality can stem from
608 snowmelt or storm events [James and Roulet, 2006]. Furthermore, the hyporheic
609 processes and interchanges between GW and SW can increase the contact time
610 between stream water and subsurface material and intensify biochemical activity,
611 which can be seen in changes in water quality [Sophocleous, 2002].

612 In the present case, some of the GW and SW reference water quality
613 variables, mostly the SW variables, were not suitable and did not represent the
614 actual GW and/or SW observed in the catchment area. SW quality is dependent
615 on several factors, including local geology, soil properties, and land use. For
616 example, even within the same catchment, peat porewaters can have differing
617 geochemical signals caused by e.g., substance accumulation in peat, vegetation
618 uptake, variations in water source and GW level and its fluctuations, temperature,
619 and matrix diffusion [Tahvanainen *et al.*, 2002; Levy *et al.*, 2016; Isokangas *et al.*,
620 2017; Menberu *et al.*, 2017]. Isokangas *et al.*, [2017] showed that peatland
621 surface water quality in the Viinivaara area is variable, e.g., near Mesioja stream,
622 $\delta^{18}\text{O}$ values were found to range between approximately -8‰ and -13‰ and SiO_2
623 values between 0 and 30 mg L⁻¹ during the period 4-11 August 2014. This large
624 range in values results mainly from differences in peatland water source, as some
625 parts of the peatland are GW-dependent and some are rainwater-dominated. In the
626 present study, we opted to use a nearby river water as a local SW reference,
627 instead of studying and determining the small-scale variations and features of the
628 immediate, actual peatland water surrounding the stream. Thus, the water quality
629 signal was a mixture of the deviating SW quality found in the area. Furthermore,
630 although it is still possible that the SW reference value does not fully represent
631 the SW of the studied catchment, at the moment this is the best available option
632 for management purposes.

633 Moreover, GW quality reflects the local geology. In geologically
634 homogeneous settings, as in Viinivaara and Rokua esker aquifer areas, GW

quality is often assumed to be spatially variable rather uniform. However, our results from Rokua show that there are some variations in GW quality, as the quality of esker GW deviates from the quality of GW under the peat layer (Supporting Information Table S2). Spatial variations in GW quality in Rokua esker aquifer area were investigated more closely using data from 13 piezometers sampled for three of the water quality tracers used in this study (SiO_2 , Cl^- and $\text{PO}_4^{3-}\text{-P}$) during previous studies in the area [Ala-aho *et al.*, 2013, 2015]. The piezometers were sampled quarterly during 2010-2012. In general, SiO_2 and Cl^- were more stable spatially and temporally than $\text{PO}_4^{3-}\text{-P}$ (Supporting Information Fig. S3). The average coefficient of variation for Cl^- , SiO_2 , and $\text{PO}_4^{3-}\text{-P}$ measured in the different piezometers was 17.6, 12.5, and 68.6 %. This suggests that SiO_2 and Cl^- are more reliable tracers in this area. In addition, temporal variations in GW and SW quality were detected in both the Rokua and Viinivaara areas. However, the chosen catchment-specific tracers for the areas showed generally reasonably steady behavior. The average coefficient of variation for the GW reference variables used (excluding $\text{PO}_4^{3-}\text{-P}$) was 7.5% and that for the SW reference variables was 17.4%.

4.4 Surface water input causes changes in water quality in the stream continuum

As the processes affecting stream water quality are catchment-specific, relatively conservative tracers for a certain catchment can be challenging to distinguish. In

656 this study, we handled this problem by developing a method that overcomes the
657 uncertainty of using a single tracer by applying multiple tracers. The selected
658 catchment-specific GW tracers in this study were: DOC, TIC, SiO₂, Cl⁻, and PO₄³⁻
659 -P. Although selection of these variables was not governed by their reputation as
660 GW tracers, many of them have been used previously to study GW-SW
661 interactions [e.g., Kalbus *et al.*, 2006; Ala-aho *et al.*, 2013; Bertrand *et al.*, 2014].

662 A clear effect of peatland water sources was shown by elevated DOC in
663 stream water. Soils, especially riparian and organic-rich soils like peatlands,
664 together with forested areas, are generally the main source of DOC to headwater
665 streams [Laudon *et al.*, 2011; Marx *et al.*, 2017]. The typical brownish waters of
666 boreal streams and rivers are the result of high DOC concentrations, which also
667 affect the physio-ecological conditions in streams [de Witt *et al.*, 2016]. In this
668 study, the peatlands surrounding the stream in Mesioja catchment released high
669 amounts of DOC along the stream continuum. In Siirasoja stream, higher DOC
670 concentrations at measurement point S2 could again be explained by a relatively
671 higher proportion of peatlands in this upstream subcatchment. In addition, the
672 decreasing amount of TIC downstream observed in all streams studied can be
673 related to atmospheric outgassing of carbon dioxide or SW input, as in headwater
674 streams TIC mostly originates from GW [Marx *et al.*, 2017].

675 Fertilizers and manure from agriculture can raise Cl⁻ concentrations in surface
676 waters [Granato *et al.*, 2015]. This is the most probable reason for the increased
677 chloride concentrations observed downstream in Lohioja and Siirasoja streams,
678 where the proportion of agricultural land in the catchment is higher than at

upstream locations. The impact of the esker aquifers could also be seen in the tracer dataset. The high concentrations of dissolved SiO_2 found in all streams resulted from leaching of SiO_2 from the sandy soils of the eskers and the relatively long flow paths to the discharge zone, enabling long contact time with soil. For example, in the Rokua area the average SiO_2 concentration of the esker GW increased towards the discharge zone (Table 2). In the Rokua area, phosphate also leaches from the soil and GW acts as a phosphate source for lakes and streams [Ala-aho *et al.*, 2013]. Interestingly, however, the first measurement location in Lohioja had relatively low phosphate concentrations. This might be due to uptake of phosphate by biological processes, which could be more pronounced at this upstream location with relatively low discharge.

Most of the other water quality parameters tested (alkalinity, SO_4^{2-} , K^+ , Ca^{2+} , Mg^{2+} , and Na^+) decreased downstream in Mesioja due to SW dilution. Alkalinity values dropped downstream from an ecologically good ($>0.2 \text{ mmol L}^{-1}$) to a poor level ($<0.01 \text{ mmol L}^{-1}$) [Oravainen, 1999]. In Lohioja and Siirasoja, this drastic drop in alkalinity was not observed and therefore it is likely that the pristine peatland area surrounding Mesioja affected the SW and caused alkalinity to decrease. These results suggest that GW sustains high alkalinity at the study sites, which make the streams less sensitive to changes in pH and thus protects the aquatic biota.

Although temporal variations in water quality are important for aquatic biota and habitats, the results from our PCA analysis indicated that snapshot sampling during low-flow periods was sufficient to reveal GW dominance in the streams.

702 The PCA results for the whole dataset and for the low-flow situation resembled
 703 each other, which suggests that it could be sufficient to sample streams only in
 704 summer during low-flow conditions, which would make field studies more cost-
 705 effective. Furthermore, the classification and S_i values were similar, irrespective
 706 of whether the summer temperature measurements or the whole temperature
 707 dataset were used. In fact, mid-summer can be considered the optimum time to
 708 detect the GW impact on water temperature, because at that time the deviation
 709 between upstream and downstream water temperatures was found to be most
 710 pronounced. Overall, these results answer our research question (iii), by
 711 confirming that it is possible to obtain a reliable GDE classification based on a
 712 single sampling campaign conducted under low-flow conditions during a rainless
 713 period.

714 **4.5 Using the stream tracer index method to determine GW-SW** 715 **transition zones – Implications for practical management**

716 When the GW dependence of a stream is studied, it is also important to consider
 717 aspects other than the actual amount of GW in the stream, which is determined
 718 using stable water isotopes in many cases. From an ecological perspective, water
 719 temperature, water quality, and water amount are important. Therefore, we
 720 developed our stream tracer index method to combine the information we
 721 considered most important for evaluating GW dominance and transition zones
 722 towards SW-dominated sections in streams (Fig. 9). The method answers our

research question (i), by showing how headwater stream sections can be classified to GDEs. Method development was guided by the recommendation to use a combination of different tracers to understand ecosystem GW-SW interactions and to estimate the anthropogenic influence on these systems [Bertrand *et al.*, 2014]. In this study, we determined the stream tracer index value (S_i) for Mesioja, Lohioja, and Siirasoja streams, and found that it ranged between 33 and 94%, 50 and 88%, and 50 and 90%, respectively. As high S_i index values indicate strong GW dependence, we concluded that Lohioja and Siirasoja streams are more GW-dependent than Mesioja. The transition zones between GW and SW occurred at the end of Lohioja and Siirasoja streams and approximately in the middle of Mesioja. This suggests that streams discharging from esker aquifers located in pristine peatland-dominated catchments may be more prone to rapid change from GW to SW systems than streams located in catchments dominated by peatland forestry.

This study shows that the combined use of environmental tracers can serve as a general water management tool. The method is especially suitable when there is a clear temperature difference between local GW and SW. During the warm season, GW temperature is lower than SW temperature, which can be used to trace GW (Fig. 9). Furthermore, the method is particularly suitable for sites where there is a well-defined, rather homogeneous aquifer as a source of GW (Fig. 9). This set-up increases the probability of stable GW quality and isotopic composition and reduces the uncertainty of the classification. One of the assumptions for the method is that the chemical signature of GW and SW stays

746 relatively stable within a catchment. However, our case study showed that the
747 method can still be applied even when water quality displays some variation
748 (Supporting Information Table S2 and Fig. S3). We analyzed a number of water
749 quality parameters, instead of just a few, increasing the likelihood of some of the
750 tracers analyzed having rather uniform and stable behavior, and thus being
751 suitable for further evaluation.

752 Based on our results and findings in the literature, we recommend use of SiO_2 ,
753 DOC (especially in peatland-dominated catchments), TIC, and Cl^- (in catchments
754 with agricultural land) as tracers, although bearing in mind that their applicability
755 has to be decided case-by-case. In addition, as the classification is not based
756 solely on water quality, but also on water quantity and temperature, deviating
757 results can be spotted and further analyzed, providing more credible classification.
758 For example, in a case with an additional major GW source from a different
759 geological formation affecting the stream further downstream, this would be
760 evident in changing water temperature. In that case, it would be possible to
761 analyze the chemistry of this other GW formation and adapt the classification as
762 indicated. Finally, we must emphasize that our method is developed for
763 headwater streams, for which we believe it is reliable enough to produce sensible
764 estimates of the GW dependence.

765 A clear benefit of the proposed method is its simplicity, which makes it easy
766 to use in water management. A disadvantage is that expert knowledge is needed
767 to choose appropriate tracers for a selected area and the classification values for
768 those tracers. However, the method resembles other management tools, such as

analytic hierarchy process [Subramanian and Ramanathan, 2012], so in that regard it should be rather easy to adopt in decision making. Furthermore, the stream tracer index method could be especially helpful in the intense monitoring programs required in areas of exceptional ecological importance [Bertrand et al., 2014]. The method could also be applied in places where anthropogenic actions are expected to change the local hydrology and affect stream ecosystems. In addition, available historical data could be applied in some cases if there have not been any major changes in the catchment area.

Fig. 9. Conceptual illustration of the stream tracer index method (see section 2.3.1 for more details).

779 5 Conclusions

780 Spatial and temporal aspects of the groundwater dependence of three boreal
781 headwater streams were studied using environmental tracers and a novel tool for
782 classification and management of groundwater-dependent stream ecosystems was
783 developed. Our stream tracer index method combines the ecohydrologically
784 important characteristics dominated by groundwater, namely groundwater volume
785 in streams, thermal properties of streams, and stream water quality. As water
786 quality tracers are site-specific, they need to be specifically chosen for each
787 stream, using reference measurements of local groundwater and surface water.

788 We found that spatially, the groundwater dependence in the three streams
789 studied varied widely, with groundwater-dominated areas reaching at least 745,
790 1682, and 4202 m from the main groundwater discharge points located at the
791 stream head. Groundwater sustained flow in the streams during the whole
792 hydrological year and the groundwater dependence was similar during summer
793 and winter seasons. Generally, stream temperatures changed rapidly from
794 upstream to downstream and the most pronounced effects of groundwater on
795 stream water temperatures were observed during summer. Furthermore, water
796 quality analyses revealed that, even though the boreal headwater streams studied
797 all discharge from esker aquifers, they have very different characteristics.
798 Therefore different water quality tracers were chosen for each of the streams.

799 It is important to classify boreal headwater streams, owing to their ability to
800 act as refuges, supporting stable conditions vital for specific aquatic biota in a

801 changing climate The results of this study suggest that it might be sufficient to
802 sample stream sections only once, during summer low-flow conditions, when
803 evaluating the groundwater dependence of streams. The stream tracer index
804 method could serve as a useful management tool, especially at sites of exceptional
805 ecological importance or at sites where anthropogenic measures are expected to
806 change the local hydrology.

807

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Abstract:

Ecosystem protection requires a better definition of groundwater (GW) dependence and tools to measure this dependence. In this study, a classification method for the GW dependence of headwater streams was devised based on the fact that GW affects discharge, thermal regime, and water quality. The method

was tested in three boreal headwater streams discharging from two esker aquifers. Spatial and temporal variability of GW dependence were studied in the stream continuum at several locations, by combining continuous measurements of temperature, electrical conductivity, and discharge with discrete sampling of environmental tracers (e.g., stable water isotopes, silica, chloride). The stream tracer index method developed was used to classify stream sections into GW-dominated, GW-surface water (SW) transition, and SW-dominated zones. We found that, spatially, GW dependence along the stream varied widely, with calculated stream tracer index values ranging from 33 to 94 %. The GW-dominated areas extended at least 745, 1682, and 4202 m downstream from the main GW discharge points in the three streams studied. A stream located in a pristine peatland-dominated catchment was more prone to rapid change from GW- to SW-dominated than two streams located in catchments dominated by peatland forestry. These results suggest that to evaluate the GW dependence of streams, it may be sufficient to sample stream sections only once, during summer low-flow conditions. The proposed method can serve as a water management tool, especially for streams of exceptional ecological importance or in places where anthropogenic activities are expected to change local hydrology and ecology.

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Highlights:

- A novel index method was developed to classify stream sections

- 1114 • The classification was based on water quantity, quality, and
1115 stable isotopes
1116 • As a result the groundwater dependence of stream sections
1117 can be determined
1118 • Groundwater dependence in studied headwater streams
1119 varied spatially and temporally
1120 • The proposed method improves monitoring and impact
1121 assessment in headwater streams
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1126 **Declaration of interests**
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1128 ☒ The authors declare that they have no known competing financial interests or
1129 personal relationships that could have appeared to influence the work reported in
1130 this paper.
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1132 ☐ The authors declare the following financial interests/personal relationships
1133 which may be considered as potential competing interests:
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