



Snow-rich conditions coincide with higher CO₂ saturation, while CH₄ is generally oversaturated and N₂O near equilibrium in alpine sub-Arctic headwaters

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Abstract.

Headwater streams and lakes exchange greenhouse gases with the atmosphere, but how their gas saturation varies between years with contrasting snow conditions remains poorly understood in cold regions. Groundwater discharge may contribute to this variability by transporting dissolved greenhouse gases to surface waters. At an alpine sub-Arctic site in Norway, we sampled streams, lakes, groundwater and snow in summer 2020 and 2021. We measured carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O) in surface waters and groundwater to calculate saturation relative to atmospheric equilibrium. A Bayesian mixing model estimated groundwater contributions from water chemistry, and separate regression models assessed their relationships with gas saturation. Our results show that 2020 was an extremely snow-rich year, with the longest snow-cover duration in the 21-year satellite record, whereas snow-cover duration in 2021 was close to the long-term average. CO₂ saturation was higher in 2020 than in 2021, both overall (medians 306% and 221%) and at most sites sampled in both years. Higher aquatic CO₂ saturation coincided with reduced terrestrial carbon uptake reported for 2020 in the companion study by Pirk et al. (2023). Median CH₄ saturation exceeded atmospheric equilibrium in both years (320% and 198%). CH₄ saturation differed among surface-water sources in 2021. N₂O medians were near equilibrium (109% and 110%), with no differences detected among surface-water sources. CO₂ saturation tended to increase with estimated groundwater contribution after accounting for year and surface-water source. However, after accounting for uncertainty in the groundwater estimates, no statistically signif-



icant relationship was detected for any of the three gases. Estimated groundwater contributions tended to be higher in 2021, when CO₂ saturation was lower. The clearest between-year contrast was observed for CO₂, whereas CH₄ and N₂O showed no consistent directional change. Multi-year observations linking snow conditions, hydrological pathways and direct gas fluxes are needed to distinguish transport from biological processing and atmospheric exchange.

20 1 Introduction

Headwater streams, which make up approximately 77% of the length of river networks worldwide (Downing et al., 2012), release considerable amounts of greenhouse gases (GHGs), such as carbon dioxide (CO₂; e.g., Saccardi and Winnick, 2021; Liu et al., 2022), methane (CH₄; e.g., Kuhn et al., 2017; Lupon et al., 2019) and nitrous oxide (N₂O; e.g., Marzadri et al., 2017; Yao et al., 2020). Although prior work has widely explored carbon (C) cycling in headwater catchments, some of its drivers remain elusive, particularly in understudied regions such as northern high-latitude environments, where snow and ice govern the hydrologic cycle (e.g., Verheijen et al., 2022). Moreover, in their reviews of C dynamics in inland waters, Marx et al. (2017) and Drake et al. (2018) both pointed out that the lack of knowledge on C export by groundwater limits our understanding of C cycling and associated GHG emissions in headwater catchments.

Nitrogen (N) cycling in headwater streams has generally received less attention than C cycling. Consequently, few studies have examined the mechanisms controlling N₂O emissions from headwater catchments, and emissions remain poorly constrained (Beaulieu et al., 2011; Soued et al., 2016). Yao et al. (2020) modelled riverine N₂O emissions on a global scale, concluding that up to 85% of global riverine N₂O emissions stem from headwater rivers and that subsurface water contributions to surface waters are a major source of N₂O emissions. These findings partly contrast with Jurado et al. (2017), who concluded that groundwater is likely a minor component of N₂O emissions to the atmosphere while acknowledging research gaps. There is also contrasting evidence about the role of glaciers and ice sheets in C cycling (see Discussion), which highlights the need for more data from understudied cold-region environments.

Groundwater discharge can supply dissolved CO₂ and CH₄ to streams and contribute to their subsequent release to the atmosphere (e.g., Johnson et al., 2008; Duvert et al., 2018; Horgby et al., 2019; Lupon et al., 2019). However, how groundwater inputs influence the saturation of multiple greenhouse gases remains poorly constrained in high-latitude and high-elevation headwaters, where snow, ice and frozen soils strongly shape hydrology and biogeochemical cycling.

Cryosphere-impacted environments need special attention because many characteristics influencing aquatic C and N cycling (such as soils, vegetation, temperature, microbial communities) are distinctively different from warmer environments (e.g., Evans et al., 2015). Moreover, northern cold environments are experiencing exceptionally fast warming with loss of snow and ice, and are thus subject to rapid hydrological and ecological changes (Meredith et al., 2019). Despite the critical importance of understanding the role of a changing cryosphere on GHGs, the difficulty of accessing and instrumenting remote areas has limited field-based research, a difficulty the COVID-19 pandemic further exacerbated (e.g., Pennisi, 2021). Also, most studies on GHGs focus on CO₂, while CH₄ and particularly N₂O exhibit a considerably higher Global Warming Potential (IPCC, 2023).



CH₄ transport has also been documented in glacier-associated waters (Christiansen and Jørgensen, 2018; Christiansen et al., 2021; Kleber et al., 2025). Less well resolved is whether CO₂, CH₄ and N₂O show comparable between-year patterns across both streams and lakes under contrasting snow conditions, and whether inferred groundwater contributions help explain those patterns. Addressing this gap requires comparing gases and water types within the same landscape rather than assuming a common response.

Here, we combine measurements of all three GHGs across glaciated and non-glaciated tributary catchments and the main valley at Finse with a 21-year satellite snow-cover record. Revisited sites allow a paired comparison between snow-rich 2020 and normal-snow 2021, while tracer-aided Bayesian end-member mixing estimates and regression models assess the relationship between groundwater contribution and gas saturation. Our goals were to compare saturation between years and among water-source categories, and to test whether groundwater contribution was associated with saturation in surface waters. This joint comparison adds a multi-gas, stream–lake perspective to earlier research focused on particular gas-delivery pathways.

2 Methods

2.1 Study area

Our study area is located in the northwestern part of the Hardangervidda mountain plateau in southern central Norway (Figure 1). Hardangervidda is the largest European mountain plateau, rich in water bodies and peatlands (Østbye et al., 1975). Our study area is defined as the area close to the mountain village Finse, which lies in a valley bottom at 1 222 m a.s.l. with surrounding mountains reaching an altitude of about 1 800 m a.s.l. Summer air temperatures can rise above 20 °C, whereas winter air temperatures can be as low as −30 °C. For the latest climate normal period (1991–2020), at the Finse meteorological station (60.593°N, 7.524°E; operated by the Norwegian Meteorological Institute), the Mean Annual Air Temperature (MAAT) was −1.1 °C, with an average annual precipitation of 967 mm (Pirk et al., 2023). For comparison, the average MAAT from the previous climate normal period (1961–1990) was −2.1 °C (Norwegian Centre for Climate Services).

Snow and ice, including the Hardangerjøkulen (the 6th largest glacier in mainland Norway), control the hydrology in Finse to a large degree. Generally, more than half of the annual total precipitation falls as snow, predominantly between October and June (Gisnås, 2016). Lakes and streams in the main valley (Figure 1a) are visibly hydrologically connected, while the hydrologic connectivity between streams and lakes in the tributary catchments (Figure 1b) is unknown. Sporadic permafrost also impacts the site (Lilleøren et al., 2013). Gisnås et al. (2016) showed that about 30% of the area around Finse exhibits a negative Mean Annual Ground Surface Temperature (MAGT), which presumably impacts the ecohydrological functioning of the study area, including streamflow generation processes and biogeochemical cycling.

The area surrounding Finse lies in the sub-arctic, alpine zone about 250 m above the tree line and has a thin soil cover. Coarse moraine deposits, block fields and bedrock dominate the rugged topography of the study area (Gisnås et al., 2016). Due to the cold temperatures and typically short snow-free seasons, vegetation cover is sparse, consisting mostly of moss, lichen, grass such as Arctic cottongrass, and shrubs (Buras et al., 2012). The valley consists of Precambrian basement rock, partly

covered by weathering materials and moraine deposits (Gisnås, 2016; Norwegian Geological Survey, 2022). In higher altitude regions (above 1 350 m a.s.l.), Cambro-Silurian calcium-rich phyllite overlays the basement rocks.

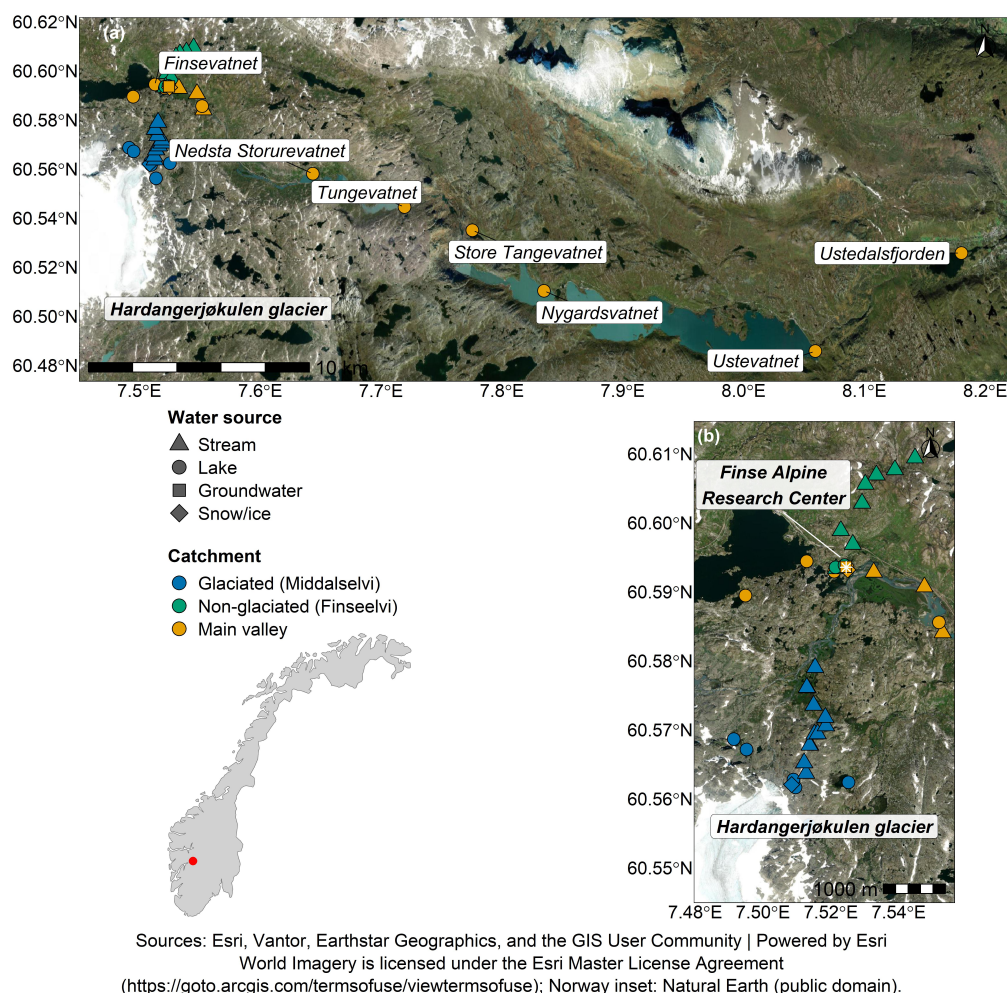


Figure 1. a) Overview of the Finse study area with the larger main-valley lakes labelled; the map (lower left) shows the location of the study area within Norway. b) Magnified view of the two contrasting tributary catchments: the glaciated southern catchment (Middalselvi) and the non-glaciated northern catchment (Finseelvi). Symbol colour denotes the catchment (glaciated, non-glaciated, or main valley) and symbol shape the water source type (stream, lake, groundwater, or snow/ice). Basemap attribution and licensing: Sources: Esri, Vantor, Earthstar Geographics, and the GIS User Community; Powered by Esri. World Imagery is used under the Esri Master License Agreement, and the Norway inset is from Natural Earth (public domain).

This work focuses on two adjacent but contrasting tributary catchments (Figure 1b): the Middalselvi catchment fed by Midtdalsbreen, a glacier arm of the Hardangerjøkulen glacier (southern catchment with an area of $\sim 12 \text{ km}^2$ and 60% glacierized) and the Finseelvi catchment (northern catchment with an area of $\sim 16 \text{ km}^2$ and 14.7% glacierized, but with stream discharge



not much impacted by glacier melt according to Eidhammer et al., 2021). The bedrock of the glaciated catchment of Middalselvi consists mostly of granite, whereas the non-glaciated catchment of Finseelvi consists primarily of phyllite (Norwegian Geological Survey, 2022).

2.2 Satellite remote sensing of snow cover phenology

90 We used satellite remote sensing to quantify the snow phenology (i.e., duration and timing) around Finse for 2020 and 2021 water years (defined from September 1 to August 31), and put this in the context of a multi-decadal snow cover climatology. For this purpose, we used imagery from the MODerate resolution Imaging Spectroradiometer (MODIS) on board Aqua (MYD10A1; Hall and Riggs, 2016a) and Terra (MOD10A1; Hall and Riggs, 2016b) satellites, providing data with a high (daily) repeat frequency for the water years 2001 through 2021. We also compiled the higher resolution imagery from the
95 Sentinel-2A, Sentinel-2B, and Landsat 8 satellites between water years 2017-2021 to acquire a more accurate and fine-grained retrieval of spatial patterns in the snow cover phenology. From both the moderate and higher resolution imagery, we retrieved daily fractional snow-covered area (FSCA) for a 9 km² area centred on the Finse flux station as described in Pirk et al. (2023). Briefly, we performed the retrieval of FSCA with established methods (see Aalstad et al., 2020 and references therein): spectral unmixing for the higher resolution (10 m) and standard linear regression on the normalized difference snow index for the moderate resolution (500 m) imagery. We also gap-filled the respective FSCA time series retrievals using interpolation techniques
100 to mitigate the effect of clouds when computing water year snow metrics. To compare the snow cover phenology in the different water years, we calculated two water year metrics at the pixel level: the snow cover duration (SCD) and the snow melt-out date (MOD; definitions in Appendix B).

2.3 Sampling and analyses of tracers and GHGs

105 We conducted two field campaigns in the study area from late August to the beginning of September 2020 and 2021. This is typically the period with least snow cover and thus offering best access to sites. During these campaigns, we took water samples ($n=97$) at various water sources, including streams, lakes, groundwater, snowpack, and glacial water (i.e., ice) in the two tributary catchments (Figure 1b) and of streams and lakes within the main catchment (Figure 1a). Weather conditions were very similar during both field campaigns with no precipitation. Gas measurements from snow and ice did not yield meaningful
110 analyses and were therefore excluded. Of the 97 samples, we analyzed dissolved gases for 79 lake, stream and groundwater samples (44 in 2020 and 35 in 2021; Table A1). 2020 had visibly more snow than the following year (Figure B1), which also impacted our sampling scheme since parts of the stream network sampled in 2020 were dry in 2021. Accordingly, we could not re-sample all sites sampled in 2020. We sampled surface waters and the snow pack by hand using a telescopic grab sampler. We sampled groundwater from an 80 m deep well installed at the Finse Alpine Research Station (Figure 1) after purging the
115 well until field parameters (electrical conductivity [EC], pH, and water temperature) reached steady values. We conducted all sampling during daylight. Note that we sampled the groundwater in the Finse valley, so it represents a mixture of water recharged from the Middalselvi and Finseelvi catchments as well as other upstream areas. We analyzed samples for common



water tracers, including various anions and cations, and dissolved gases (Ar, N₂, CO₂, CH₄, N₂O and ²²²Rn). Appendix A describes the analytical methods in detail.

120 We measured dissolved gas concentrations (i.e., Ar, N₂, CO₂, CH₄, N₂O) in duplicate using the headspace technique (Åberg and Wallin, 2014). All samples were acidified in the field with 3% HCl except some 2020 samples (samples labelled 1.1–1.14 and 2.1–2.16). Acidification converts dissolved carbonate species to CO₂ and inhibits biological activity. These non-acidified 2020 samples therefore required a post-processing correction for CO₂ (Appendix A1).

125 We calculated saturation separately for each gas relative to atmospheric equilibrium using its gas-specific solubility at the measured water temperature and barometric pressure. 100% gas saturation denotes atmospheric equilibrium. Assuming that water bodies are homogeneously mixed, values above 100% indicate potential outgassing, whereas values below 100% indicate potential atmospheric uptake. More detailed information about the sampling and analysis, and a summary of the resulting GHG saturation data by water-source category and year, are provided in Appendix A and Table A1.

2.4 Tracer-aided mixing modeling

130 To infer the contribution of groundwater to streams and lakes, we used a tracer-aided Bayesian end-member mixing model (Popp et al., 2019), which is particularly well-suited to account for tracer-related uncertainties and potentially missing end-members (Popp et al., 2021b). For a detailed model description, including its limitations and assumptions, we refer readers to Popp et al. (2019), where the code is freely available. Groundwater and snow were used as the two end-members in the mixing model, while the sampled surface waters (streams and lakes) were treated as mixtures of these end-members. These source
 135 types represent contrasting potential contributions to the headwaters: snow provides seasonal meltwater, whereas groundwater represents water that has interacted with subsurface mineral material. Their contrasting EC and major-ion chemistry provides the basis for estimating mixing proportions without using the GHG measurements themselves.

A combination of diverse tracers with different geochemical behaviour, together with explicitly accounting for tracer-related uncertainties, is generally considered the most reliable approach for tracer-aided end-member mixing modelling (Abbott et al.,
 140 2016; Moeck et al., 2017; Tetzlaff et al., 2015; Popp et al., 2025). We therefore used a diverse set of relatively conservative tracers, i.e., tracers whose potential transformation processes are considerably slower than the mixing process itself: EC, Na⁺, K⁺, Ca²⁺, Cl[−] and SO₄^{2−}. Groundwater-fraction summaries are provided in Table C1.

2.5 Statistical analyses

2.5.1 Summaries and comparisons among water sources

145 Samples were classified by water source and by location in the glaciated tributary catchment, non-glaciated tributary catchment, or main valley (Table A1 and Figure 1b). The abbreviations g-sw and g-lake denote streams and lakes in the glaciated tributary catchment, ng-sw and ng-lake denote streams and lakes in the non-glaciated tributary catchment, sw and lake denote streams and lakes in the main valley, and gw denotes groundwater. Gas saturation in each category and campaign was summarized by the median and interquartile range (25th–75th percentiles).



150 Gas saturation was skewed and the groups were small and unequal. We therefore used non-parametric Kruskal–Wallis tests to evaluate whether saturation differed among water-source categories within each campaign. Only categories represented by at least three observations for the gas being tested were included. Categories with one or two observations remained in the figures and descriptive summaries. The standard Kruskal–Wallis p -values were used. We adjusted the six p -values, one for each combination of three gases and two campaigns, using the Benjamini–Hochberg method to reduce the risk of identifying 155 differences by chance. We report the adjusted p -values in the main text and both unadjusted and adjusted values in Table D1.

2.5.2 Comparisons between campaigns

Between-year comparisons used only sites sampled in both 2020 and 2021. For each gas, an exact two-sided paired sign test assessed whether saturation tended to be higher in one year. We report the median difference between years, the proportion of paired sites with higher saturation in 2020, and the 95% confidence interval for that proportion. The three gas-specific p -values 160 were adjusted together using the Benjamini–Hochberg method. The main text reports adjusted p -values, with both unadjusted and adjusted values given in Table D2.

2.5.3 Relationships with groundwater contribution

Regression models tested groundwater relationships across all surface-water samples ($n=74$ for CO_2 and N_2O , and $n=72$ for CH_4 because two measurements were missing). Gas saturation was $\log_{10}$ -transformed because the values covered a wide 165 range and a few very high measurements could otherwise have had too much influence. For each gas, the first model tested the overall relationship with groundwater fraction while accounting for year. A second model included a groundwater fraction $\times$ year interaction to test whether the relationship differed between years.

The model results describe proportional changes in gas saturation. To present these changes on an interpretable scale, we report the estimated change associated with an 8.2-percentage-point increase in groundwater contribution, for example from 170 5.0% to 13.2%. This interval equals one standard deviation of the groundwater-fraction estimates across all samples and is only a reporting unit. It does not represent the uncertainty of individual estimates.

We incorporated the uncertainty of each groundwater estimate by creating 1,000 alternative datasets. In each dataset, every sample was assigned a plausible groundwater fraction from a beta distribution matching its mixing-model estimate and uncertainty. We fitted the gas models to all datasets and combined their results using Rubin’s rules (Rubin, 1987). Two-sided Wald 175 tests evaluated the overall groundwater relationship and its interaction with year (Table D3). The p -values for the three groundwater effects and three groundwater-by-year interactions are reported without correction for multiple testing. This procedure accounts for the uncertainty of individual groundwater estimates but not for uncertainty shared among samples through the common mixing-model end-members.

The initial regression models also accounted for similarities among observations from the same water-source category or 180 site. A grouping term was removed if it explained no variation. The final CO_2 model retained a category grouping term, and the CH_4 model retained category and site grouping terms. N_2O required neither and was therefore fitted with standard linear



regression. All models fitted successfully to all 1,000 datasets. Mixed-effects models were fitted with the lme4 package (Bates et al., 2015).

3 Results

185 3.1 Snow conditions

The time series analysis of the SCD (Figure 2) shows that 2020 had the longest spatial average SCD for the grid cell containing the Finse flux station in the last 21 years, with around 300 days. The spatial average SCD in 2021 was 250 days which is around the climatological average. Based on the maximum likelihood beta distribution fit (Pirk et al., 2023) to the 21-year spatial mean MOD climatology from the MODIS retrievals, the MOD in late July 2020 was in the 92nd percentile, whereas the
 190 MOD in mid-June 2021 was in the 11th percentile. Our analysis with higher-resolution satellite imagery also supported these findings (Appendix B and Figure B2). Accordingly, we classify 2020 as a "snow-rich" year and 2021 as a "normal snow" year. Although the average SCD appeared relatively stable over the past decade, the record appeared more variable after 2010. The consequences of the extreme 2020 snow conditions for local carbon and water budgets are examined by Pirk et al. (2023).

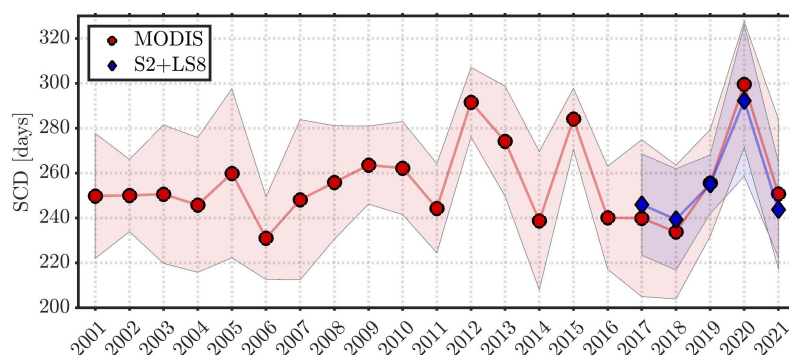


Figure 2. Snow cover duration (SCD) time series for the area around the Finse flux station retrieved from moderate resolution MODIS imagery (red; water years 2001-2021) and higher resolution Sentinel-2 and Landsat 8 imagery (blue; water years 2017-2021). The solid lines and shading show the spatial mean and variability ($\pm 3\sigma$) in SCD, respectively.

3.2 Greenhouse gas saturation

195 GHG saturation varied across sites and between years with both over- and undersaturation relative to atmospheric equilibrium (Table A1 and Figure 3). Measurements across all water sources showed that CO₂ oversaturation was considerably higher in the extreme snow-rich year (2020) than in 2021, the normal snow year: in 2020, the median was 306% [25th–75th percentiles: 210–398%]; in 2021, the median was 221% [74–331%]. Among the 34 sites sampled in both years, CO₂ saturation was higher in 2020 at 25 sites (73.5%, exact 95% CI: 55.6–87.1%; adjusted $p=0.027$). The paired medians were 301% in 2020 and 220% in
 200 2021, and the median paired difference was +107 percentage points. The paired-site comparison supports a between-year CO₂



difference that cannot be explained solely by the different sets of sites sampled. Median CH₄ saturation was 320% [135–777%] in 2020 and 198% [93–1,665%] in 2021. Median N₂O saturation was 109% [100–119%] in 2020 and 110% [107–114%] in 2021. Exact sign tests did not detect a consistent directional between-year change in CH₄ (18 of 32 sites higher in 2020; adjusted $p=0.608$) or N₂O (15 of 34; adjusted $p=0.608$).

205 Beyond these between-year patterns, GHG saturation also varied strongly among water sources. Kruskal–Wallis tests of categories represented by at least three observations showed differences in CO₂ saturation in both years (2020: adjusted $p=0.023$; 2021: adjusted $p=0.0078$). CH₄ saturation differed among categories in 2021 (adjusted $p=0.023$), but not in 2020 (adjusted $p=0.247$). N₂O saturation did not differ among categories in either year (2020: adjusted $p=0.912$; 2021: adjusted $p=0.143$). Full test statistics, degrees of freedom, and unadjusted p -values are reported in Table D1. Categories with fewer than three ob-

210 servations remain visible in Figure 3 and Table A1 but were not included in these tests. Lake samples were CO₂ oversaturated in both campaigns, except for the single non-glaciated lake sampled in 2021. Median lake CH₄ saturation exceeded 100% in each category and year, although four individual lake observations were undersaturated in 2021. Lake N₂O medians were close to atmospheric equilibrium, with individual observations both above and below 100% (Table A1; Figure 3). Glaciated-stream medians exceeded 100% for all three GHGs in both campaigns, but individual observations did not always do so. In particu-

215 lar, four of the eight glaciated-stream CO₂ observations were below equilibrium in 2021. All sampled non-glaciated streams were CO₂ oversaturated in 2020 and undersaturated in 2021. In the main valley, two of the three stream observations were CO₂ oversaturated in 2020, whereas the single observation in 2021 was undersaturated. Stream CH₄ medians exceeded 100% except in the non-glaciated catchment in 2021, although individual undersaturated samples occurred in both years. Stream N₂O medians were slightly above equilibrium in every category and year (Table A1). Meanwhile, groundwater held several of

220 the most extreme values recorded in this study: it was the most oversaturated sample for CO₂ (2,651%, in 2020) and for CH₄ (474,038%, in 2021), and the most undersaturated for N₂O (27%, in 2021); the only comparable extreme in a surface water was the very high CH₄ of a non-glaciated lake in 2020. Figure 4a–c summarises median GHG saturation by water-source category and year. CO₂ saturation generally decreased from the snow-rich 2020 campaign to the normal-snow 2021 campaign, with several stream categories shifting below atmospheric equilibrium (Figure 4a). CH₄ category medians were generally above

225 equilibrium, with particularly high values in groundwater and the non-glaciated lakes (Figure 4b), whereas N₂O was generally near equilibrium except for a pronounced decline in groundwater N₂O saturation in 2021 (Figure 4c).

3.3 Groundwater contribution to surface waters

The Bayesian end-member mixing modelling approach allowed us to estimate the groundwater contribution of the lakes and streams we sampled. Figure 5 shows that the contribution of groundwater to lakes and streams varies depending on the catch-

230 ment and year (summarized in Appendix C and Table C1).

Across all surface waters, the mean estimated groundwater contribution was 7.0% in 2020 and 8.7% in 2021; the corresponding mean posterior SDs of the individual estimates were 3.3 and 4.0 percentage points, respectively (Table C1). Descriptively, groundwater fractions were higher in 2021 for most water-source categories, except for the non-glaciated lakes. Glaciated lakes showed the largest increase, from 7.6% in 2020 (mean posterior SD: 3.8 percentage points) to 12.2% in 2021 (6.1 percentage

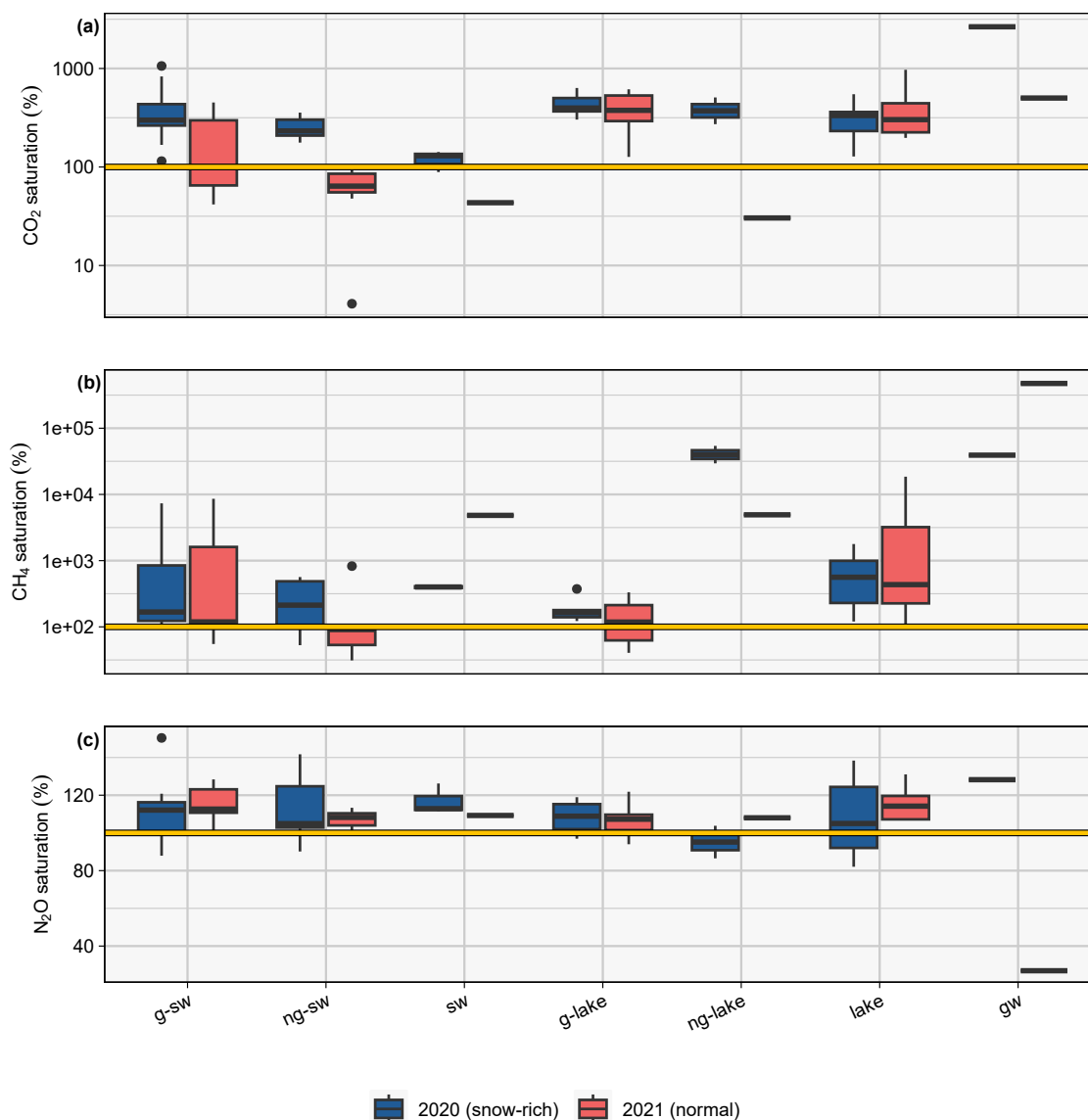


Figure 3. Greenhouse-gas saturation relative to atmospheric equilibrium for the different water sources (defined in Table A1) of (a) CO₂ (log-scale), (b) CH₄ (log-scale) and (c) N₂O for the two years (2020 and 2021) and water-source categories as defined in Table A1. The centre line in the box represents the median, the extent of the boxes the 25th and 75th percentiles, the whiskers extend to the most extreme observations within 1.5 times the interquartile range, and points beyond the whiskers are outliers. Values above 100% indicate a relative gas oversaturation, whereas values below 100% indicate an undersaturation of the respective gases. The yellow horizontal lines in each plot highlight the 100% gas saturation (i.e., no over- or undersaturation).

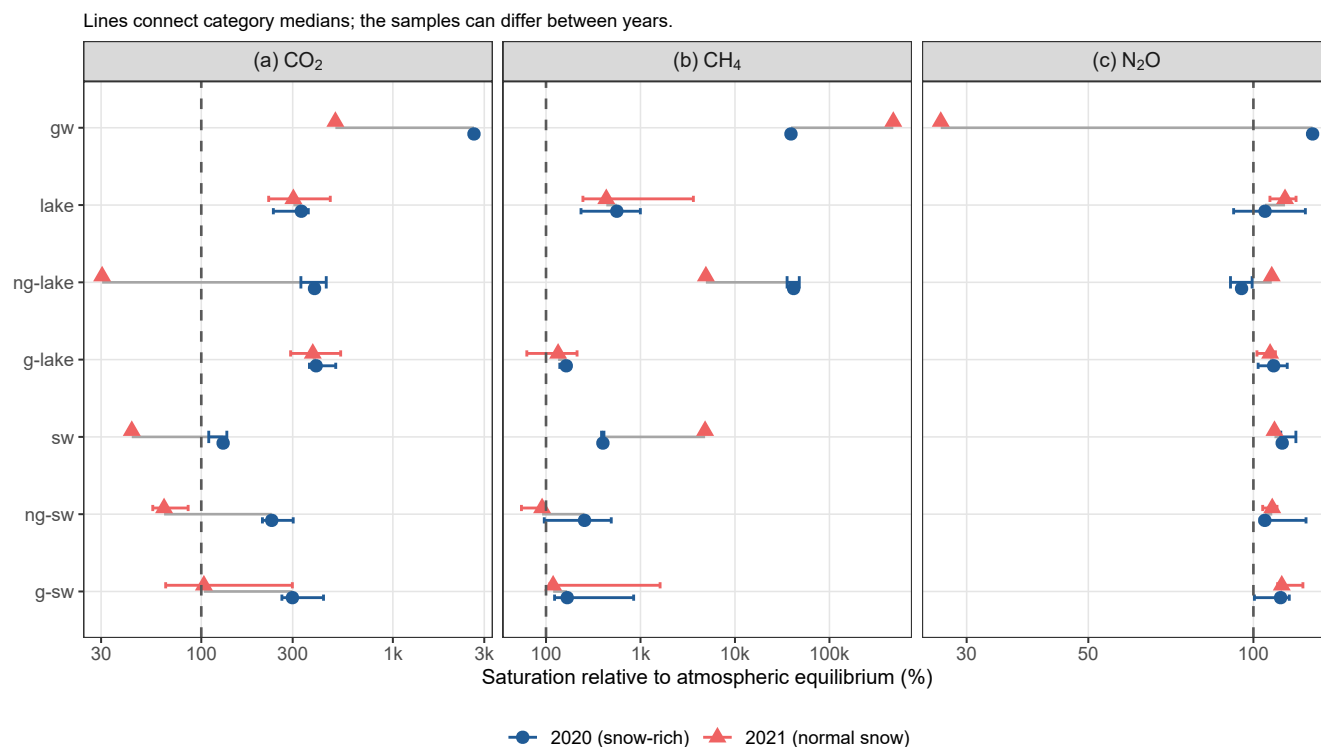


Figure 4. GHG saturation by water-source category for (a) CO₂, (b) CH₄ and (c) N₂O in 2020 (blue) and 2021 (red). Points show medians and horizontal bars the interquartile range. Grey lines connect category medians from potentially different sets of samples, not changes at paired sites. Paired-site changes are shown separately in Figure D1. The dashed line marks atmospheric equilibrium (100%). Each gas has its own logarithmic horizontal scale. Categories and sample sizes are given in Table A1. Category–year combinations with a single observation have no interquartile bar.

points). Across both years and catchment categories, most surface waters received less than 10% of their water from groundwater. However, glaciated streams consistently received larger fractions: 14.8% in 2020 (mean posterior SD: 6.3 percentage points) and 17.9% in 2021 (7.0 percentage points). The posterior SDs quantify mixing-model uncertainty, whereas the boxplots in Figure 5 describe variation among samples.

3.4 Linkage between groundwater contribution and GHG saturation

To test groundwater relationships across all surface-water observations, we fitted a regression model of CO₂ saturation with groundwater fraction and year as fixed effects and a random intercept for water-source category (Appendix D and Table D3). After propagating the mixing-model uncertainty, the model estimated a 1.18-fold change in CO₂ saturation per one-standard-deviation (8.2 percentage-point) increase in groundwater fraction. However, the 95% confidence interval ranged from a 0.95-fold to a 1.46-fold change, allowing for either a small decrease or an increase in CO₂ saturation (unadjusted $p = 0.134$; Figure 6).

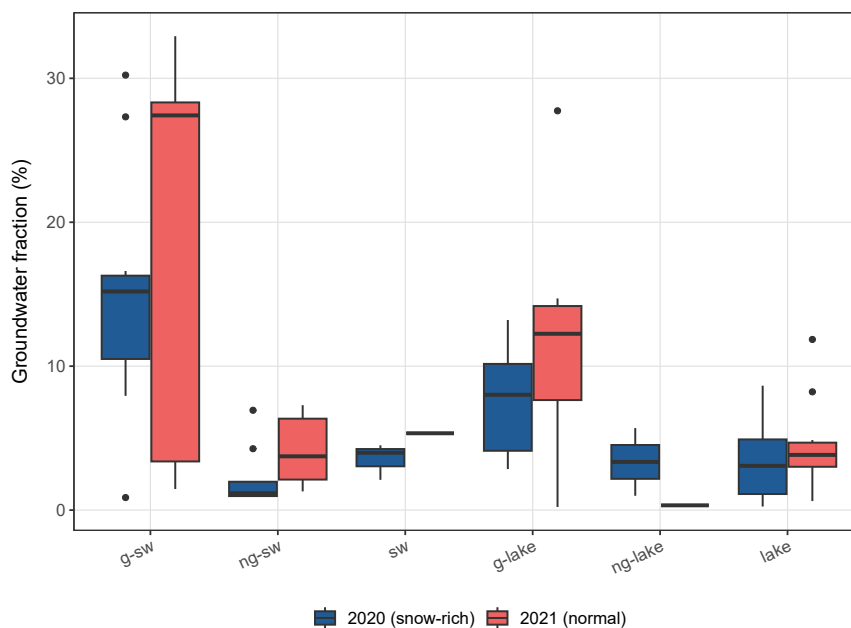


Figure 5. Posterior mean groundwater fraction (%) contributing to surface waters in 2020 (snow-rich year) and 2021 (normal snow year). The centre line in each box represents the median among samples, the box the 25th–75th percentiles, the whiskers extend to the most extreme observations within 1.5 times the interquartile range, and points beyond the whiskers are outliers. Sample-specific uncertainty is summarised separately by the mean posterior SDs in Table C1. Table A1 defines the water-source categories.

245 We found no evidence that the groundwater–CO₂ slope differed between years (groundwater × year interaction, unadjusted $p = 0.518$). In the same framework, we found no evidence of an association between groundwater fraction and CH₄ saturation (unadjusted $p = 0.850$) or N₂O saturation (unadjusted $p = 0.778$).

4 Discussion

250 The three gases showed distinct patterns rather than a common response across the stream–lake network. The clearest between-year signal was higher CO₂ saturation in the snow-rich 2020 campaign at most sites sampled in both years, especially in tributary streams. Across both campaigns, most waters were CO₂ oversaturated and CH₄ was generally oversaturated but highly variable among water sources, whereas N₂O medians were close to atmospheric equilibrium. These contrasts point to different balances among terrestrial and subsurface inputs, processing within streams and lakes, and exchange with the atmosphere. We therefore first consider the overall distribution of each gas before discussing the between-year contrast and the
 255 inferred groundwater contributions.

CO₂ in streams and lakes can be supplied by aquatic respiration and by the transport of soil- and subsurface-respired CO₂, whereas photosynthesis and gas exchange can lower its saturation. Groundwater can provide an additional pathway connecting

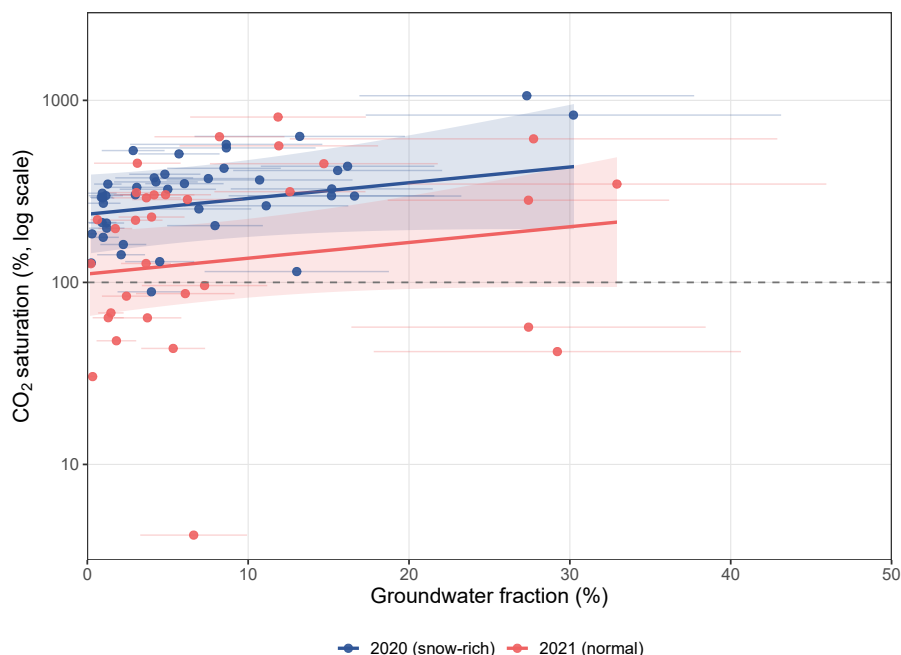


Figure 6. Relationship between groundwater fraction and CO₂ saturation from the uncertainty-propagated model (Table D3). Points and horizontal bars show sample estimates and one posterior SD; lines and bands show fixed-effect predictions and 95% confidence intervals for 2020 and 2021. Lines and bands are restricted to the range of posterior mean groundwater fractions in each year. The dashed line denotes atmospheric equilibrium; the y-axis is logarithmic. All 74 matched surface-water observations are shown.

terrestrial CO₂ production to surface waters (Lupon et al., 2019; Horgby et al., 2019), and carbonate buffering also influences dissolved CO₂ concentrations (Stets et al., 2017). Most sampled waters were CO₂ oversaturated, although some were under-
 260 saturated (Table A1; Figure 3, CO₂ panel). The predominance of oversaturation agrees with earlier work in (sub)arctic streams and lakes (Cole et al., 2007; Lundin et al., 2013; Valiente et al., 2022). At the same time, photosynthetic uptake can lower dissolved CO₂ concentrations (Alleson et al., 2022), and CO₂ undersaturation in proglacial waters can also result from chemical weathering (St. Pierre et al., 2019). Because we did not measure aquatic metabolism or gas-exchange rates, the relative importance of these processes cannot be separated.

265 The glaciated setting introduces additional carbon pathways. Meltwater can export organic carbon from glaciers (Colombo et al., 2019), which may subsequently be mineralized, while subglacial processes can supply dissolved CO₂ and CH₄ (Christiansen and Jørgensen, 2018; Christiansen et al., 2021). At Finse, Hågvær and Ohlson (2013) showed that ancient carbon released from Midtdalsbreen enters aquatic and terrestrial food webs in its foreland. These findings make glacier-derived carbon a plausible local contribution, but the saturation measurements alone cannot identify or quantify that contribution.

270 CH₄ showed a different spatial pattern from CO₂. It was oversaturated in most sampled waters, with particularly high values in groundwater and the non-glaciated lakes, although several surface-water observations were undersaturated in 2021 (Figure 3,



CH₄ panel; Table A1). The predominance of oversaturation is consistent with observations from sub-Arctic and alpine streams (Crawford et al., 2013; Flury and Ulseth, 2019). Although methanogenesis is usually associated with organic-rich, anoxic environments, oxygenated headwaters can contain anoxic streambed microzones and can receive CH₄-rich groundwater. Field experiments identify CO₂ reduction in streambed sediments and groundwater delivery as plausible CH₄ sources (Flury and Ulseth, 2019), consistent with simulated hyporheic redox microzones (Briggs et al., 2015). These mechanisms could explain the high CH₄ saturation observed here, but our data cannot resolve their relative contributions. Geological context also matters. Kleber et al. (2025) identified thermogenic CH₄ transported by groundwater and meltwater in a Svalbard catchment underlain by organic-rich sedimentary rocks. That source attribution cannot be transferred directly to the predominantly granitic and phyllitic catchments at Finse, where we did not measure CH₄ isotopic composition.

N₂O exhibited a third pattern. N₂O is produced mainly through nitrification and denitrification in the soil–water continuum (e.g., Gil et al., 2022). Surface-water category medians were close to atmospheric equilibrium or slightly above it, whereas the single groundwater observation was oversaturated in 2020 and markedly undersaturated in 2021 (Figure 3, N₂O panel; Table A1). Values close to equilibrium imply only a small instantaneous concentration gradient with the atmosphere, but do not demonstrate an absence of nitrogen cycling. The small departures from equilibrium, spatial variability, and short sampling windows do not support classifying these waters as persistent N₂O sources or sinks or identifying the dominant nitrogen-cycling process.

4.1 GHG saturation across the two contrasting snow campaigns

Against these overall saturation patterns, the contrast between campaigns was clearest for CO₂. The paired-site comparison supported higher CO₂ saturation in snow-rich 2020 than in 2021 (Table D2). No consistent directional change between years was detected for CH₄ or N₂O. The CO₂ contrast was particularly clear at revisited tributary-stream sites, most of which had higher saturation in 2020. Main-valley lakes showed mixed directions of change at paired sites (Figure D1). The overall contrast therefore does not imply a uniform response across the stream–lake network. Longer water residence and opportunities for biological processing in lakes could contribute to this heterogeneity, but neither residence times nor metabolic rates were measured here.

The terrestrial observations provide a plausible context for the CO₂ contrast. During 2020, annual evapotranspiration was approximately 50% lower than in 2019 and 2021, and reduced growing-season carbon uptake shifted the terrestrial ecosystem from a moderate annual carbon sink to a net source (Pirk et al., 2023). This independent evidence indicates that terrestrial carbon cycling differed substantially in 2020 and coincided with higher aquatic CO₂ saturation. The larger snowpack, lower evapotranspiration, and more extensive flowing stream network may have maintained hydrological connectivity and enhanced the lateral transport of soil-respired CO₂ and organic carbon to surface waters. Conversely, the drier stream network and longer snow-free period in 2021 may have reduced terrestrial carbon delivery and allowed greater biological CO₂ uptake. These mechanisms remain hypotheses because we did not measure discharge, terrestrial-to-aquatic carbon export, aquatic metabolism, or gas exchange, and the two campaigns cannot separate snow effects from other year-specific differences.



305 CH_4 did not mirror the CO_2 contrast between campaigns. Its overall median exceeded atmospheric equilibrium in both campaigns, although some observations were undersaturated. Differences were detected among water-source categories represented by at least three observations in 2021, but not in 2020 (Table D1). No consistent directional change between campaigns was detected (Table D2). Spatially variable production, transport, and gas exchange may therefore have been more important for CH_4 than a uniform response to the contrasting snow conditions. However, the two summer campaigns cannot exclude
 310 snow-related effects at other times of the year.

N_2O likewise showed no consistent between-campaign change. Its medians were close to atmospheric equilibrium in both years, and the paired comparison did not detect a consistent between-year change (Table D2). Snow insulation can affect microbial N cycling (Brooks et al., 1998), and wet-year N_2O undersaturation has been reported elsewhere in the Arctic (Harms et al., 2020); however, our two campaigns and lack of residence-time information do not allow attribution to snow conditions
 315 rather than other interannual drivers (Figure 3c and Figure 4c).

4.2 What role does the contribution of groundwater to surface waters play for GHG saturation in cold-region environments?

Snow and freeze–thaw processes strongly affect groundwater recharge and discharge in cold mountain catchments (van Tiel et al., 2024). At Finse, the inferred groundwater contributions varied among locations and were descriptively higher in 2021,
 320 opposite to the overall CO_2 pattern (Figure 5; Table C1). The higher estimates in 2021 could reflect lagged recharge from the extreme 2020 snowpack (McDonnell et al., 2010), although two campaigns cannot establish that mechanism. Groundwater fraction alone also does not represent groundwater-derived CO_2 delivery, which depends on both the water contribution and its CO_2 concentration. The available groundwater gas observation was more CO_2 -supersaturated in 2020 than in 2021, but one observation per campaign and the absence of groundwater-flux measurements preclude evaluating whether this contributed to
 325 the surface-water difference.

EC and major-ion patterns accompanied this difference, but these tracers were inputs to the mixing model and therefore do not provide independent validation; radon provides only qualitative evidence of contact with radon-producing mineral material (Appendix E and Figure E1). Groundwater delivery is a plausible CO_2 source, as demonstrated elsewhere (Duvert et al., 2018; Horgby et al., 2019), but our estimated groundwater fractions did not establish a clear relationship with surface-water CO_2
 330 after their uncertainty was propagated (Table D3; Figure 6). The confidence interval allows a substantial positive relationship, so this result is not evidence that groundwater delivery is unimportant. Differences in gas exchange, metabolism, lithology, and subsurface carbon concentrations may modify or obscure any groundwater signal.

Because EC and major ions were used to estimate groundwater fractions, any lithological influence on these tracers may partly be reflected in the inferred groundwater contributions. CO_2 was not included in the mixing model, so the groundwater–
 335 CO_2 relationship is not mathematically predetermined. However, lithology can also influence carbonate chemistry, meaning that our data cannot fully distinguish hydrological mixing from lithological effects.



4.3 General limitations and ways forward

The two sampling campaigns resolve spatial contrasts but not diel, seasonal, or annual variability. Previous-season conditions can also influence aquatic CO₂ cycling (Finlay et al., 2019). Our source–sink classifications therefore describe potential exchange at the time of sampling rather than annual GHG budgets; establishing the latter requires longer, higher-frequency records. Mechanistic attribution is further limited by gas exchange. The steeper, higher-velocity tributary streams likely exchange gases faster than the valley stream and lakes (Horgby et al., 2019), complicating comparisons among water types. Moreover, GHGs are non-conservative, and different subsurface flow paths, in-stream metabolism, and turbulence can alter saturation between groundwater entry and sampling (Duvert et al., 2018; Marx et al., 2017). CH₄ is especially uncertain because ebullition can dominate its release (Katsman et al., 2022). Saturation patterns should therefore not be interpreted as direct estimates of flux or of groundwater-derived GHG loads.

Longitudinal tracer sampling improved spatial coverage, but the grab-sampling design remained temporally limited. Future studies should combine spatial sampling with simultaneous, high-frequency measurements of gases and conservative tracers (von Freyberg et al., 2017; Popp et al., 2020, 2021a), together with direct flux measurements.

Finally, subglacial weathering and chemosynthetic production can supply C and nutrients (Christiansen and Jørgensen, 2018; Christiansen et al., 2021; Dunham et al., 2021; Wadham et al., 2019). Targeted process measurements are needed to separate these glacier effects from groundwater recharge and terrestrial C cycling.

5 Conclusions

This study compared late-summer greenhouse gas saturation and inferred groundwater contributions across streams and lakes during the snow-rich 2020 and normal-snow 2021 campaigns in an alpine sub-Arctic system. The main findings are:

- CO₂ saturation was higher in the snow-rich year 2020 than in 2021 at most sites sampled in both years. Sampled non-glaciated-catchment streams were potential CO₂ sources in 2020 but potential sinks in 2021. Lakes were generally CO₂ oversaturated, whereas glaciated streams included both over- and undersaturated observations in 2021 (Figure 3a, Figure 4a, and Figure D1; Tables A1 and D2).
- Estimated groundwater contributions tended to be higher during the normal-snow 2021 campaign, opposite to the CO₂ pattern. Their relationship with CO₂ saturation remained uncertain after accounting for mixing-model uncertainty. Groundwater fraction alone therefore did not explain the between-year CO₂ pattern (Figures 5 and 6; Tables C1 and D3).
- CH₄ was generally oversaturated, although some observations were undersaturated, and its saturation varied among water sources in 2021. N₂O category medians in surface waters were close to atmospheric equilibrium or slightly above it. No clear increase or decrease between 2020 and 2021 was detected for CH₄ or N₂O. Neither gas showed a clear relationship with groundwater fraction (Figures 3b–c and 4b–c; Tables A1 and D1–D3).



Together, these results show that the between-year contrast was expressed primarily in CO₂, whereas CH₄ remained spatially heterogeneous and N₂O stayed close to atmospheric equilibrium. Estimated groundwater fractions alone did not account for these gas patterns, emphasizing that the three gases respond differently across alpine headwater environments.

370 **Appendix A: Analytical methods and greenhouse-gas saturation data**

We collected water samples for anion analysis (chloride [Cl⁻], limit of quantification [LOQ] = 0.1 mg L⁻¹; nitrate [NO₃⁻], LOQ = 0.2 mg L⁻¹; sulfate [SO₄²⁻], LOQ = 0.1 mg L⁻¹) and cation analysis (sodium [Na⁺], LOQ = 0.1 mg L⁻¹; potassium [K⁺], LOQ = 0.1 mg L⁻¹; magnesium [Mg²⁺], LOQ = 0.1 mg L⁻¹; calcium [Ca²⁺], LOQ = 0.15 mg L⁻¹). Anion samples were collected in 20 mL Falcon tubes. Cation samples were collected in 20 mL Falcon tubes acidified with one drop of
 375 nitric acid (65% AnalaR NORMAPUR, VWR). We analysed both on a Dionex ICS-1000 Ion Chromatography System at the University of Oslo water chemistry laboratory. Phosphate, ammonium, nitrate, lithium, fluoride and bromide were below their LOQ in more than 90% of samples and were excluded from further analysis.

We collected water for radon (²²²Rn) analysis in 40 and 250 mL glass bottles and analysed it within a few hours in the field with a calibrated DurrIDGE RAD7 instrument, following the grab-sampling method in the instrument manual (DURRIDGE
 380 Company Inc., 2019, Section 4.4). Atmospheric radon activities are very low, so elevated activities in surface water indicate recent contact with radon-producing mineral material. This can occur through groundwater discharge, sediment contact or hyporheic exchange (Cook and Herczeg, 2000; Gleeson et al., 2018; Hoehn et al., 1992).

For greenhouse-gas analysis, we collected either 20 or 30 mL of lake, stream or groundwater into a 60 mL syringe and created a 20 mL headspace with ambient air. The sample-specific water volume was used in the gas calculations. We added 3%
 385 HCl (~1 M) in the field to all samples except the 2020 samples with field codes 1.1–1.14 and 2.1–2.16. We shook the syringes for approximately 30 s at ambient temperature and transferred 15 mL of headspace gas into 12 mL evacuated vials.

We analysed the gases at the Norwegian University of Life Sciences by automated gas chromatography following Yang et al. (2015). An Agilent 7890A gas chromatograph with a 20 m wide-bore Poraplot Q column separated CO₂, CH₄, N₂O, Ar, N₂ and O₂. CH₄ and N₂O were measured with flame-ionization and electron-capture detectors, respectively, and the other gases
 390 with a thermal-conductivity detector. Certified CO₂/CH₄/N₂O standards in helium and ambient air were used for calibration. Analytical precision was below 1%. Saturation was calculated separately for each gas using its gas-specific solubility, measured water temperature and barometric pressure. A value of 100% denotes atmospheric equilibrium.

A1 Post-processing correction for non-acidified CO₂ samples

For the non-acidified 2020 samples, CO₂^{*} (dissolved CO₂ plus H₂CO₃) at headspace equilibrium was calculated from mea-
 395 sured headspace CO₂ using a temperature-corrected Henry's law constant derived according to Wilhelm et al. (1977). Assuming carbonate equilibrium and using measured field pH, HCO₃⁻ and CO₃²⁻ were calculated from the temperature-dependent dissociation constants *K*₁ and *K*₂. DIC was calculated as the sum of CO₂^{*}, HCO₃⁻ and CO₃²⁻. A water-headspace mass bal-



ance following Åberg and Wallin (2014) was then used to reconstruct the DIC initially present in each sample. No alkalinity measurement was used in this calculation.

400 All water samples except those used for radon analysis were filtered through nylon membrane filters (0.2 μm where possible, otherwise 0.45 μm), chilled immediately and stored cool until analysis. Table A1 gives the gas-saturation summaries used in the main text.

Table A1. Median greenhouse-gas saturation (%) relative to atmospheric equilibrium by water-source category and year. Brackets give the interquartile range for $n \geq 4$ and the observed range for $n = 2-3$; single observations are shown without brackets. A value of 100% denotes atmospheric equilibrium. Category abbreviations are defined below.

Category	Year	n	CO ₂	CH ₄	N ₂ O
g-lake	2020	6	398 [367–503]	164 [140–179]	109 [102–115]
g-lake	2021	6	382 [293–534]	134 [63–213]	107 [101–110]
g-sw	2020	13	299 [263–435]	168 [123–847]	112 [100–116]
g-sw	2021	8	103 [65–299]	119 [110–1,612]	113 [111–123]
gw	2020	1	2,651	39,150	128
gw	2021	1	501	474,038	27
lake	2020	11	333 [238–362]	561 [235–996]	105 [92–124]
lake	2021	11	302 [225–471]	435 [246–3,628]	114 [107–120]
ng-lake	2020	2	390 [272–508]	41,780 [29,462–54,098]	95 [87–104]
ng-lake	2021	1	30	4,922	108
ng-sw	2020	8	233 [209–302]	256 [96–490] ^a	105 [103–125]
ng-sw	2021	7	64 [56–85]	91 [55–96]	108 [104–110]
sw	2020	3	130 [89–142]	400 [374–421]	113 [112–126]
sw	2021	1	43	4,828	109

The n column gives the number of CO₂ observations. ^a Based on $n = 6$ because two ng-sw CH₄ measurements were below detection. Quartiles use R's default type-7 sample quantiles. Categories: g-lake and g-sw, lakes and streams in the glaciated tributary catchment; ng-lake and ng-sw, lakes and streams in the non-glaciated tributary catchment; lake and sw, lakes and streams in the main valley; gw, groundwater.



Appendix B: Snow-cover evidence

Field photographs show the visibly greater late-summer snow cover in 2020 relative to 2021 (Figure B1). Snow-cover duration (SCD) is the number of days with fractional snow cover above 0.25 in a water year. Snow melt-out date is the final non-ephemeral snow-cover day belonging to a period of at least five consecutive snow-cover days. Figure B2 shows 10 m SCD retrievals from Sentinel-2 and Landsat 8 for the 9 km² area surrounding the Finse flux station. Relative to the 2017–2021 mean, SCD was approximately one month longer in 2020 and approximately 10 days shorter in 2021. These higher-resolution observations support the classification of 2020 as snow-rich and 2021 as close to the climatological average based on the longer
 405
 410 MODIS record in the main text.

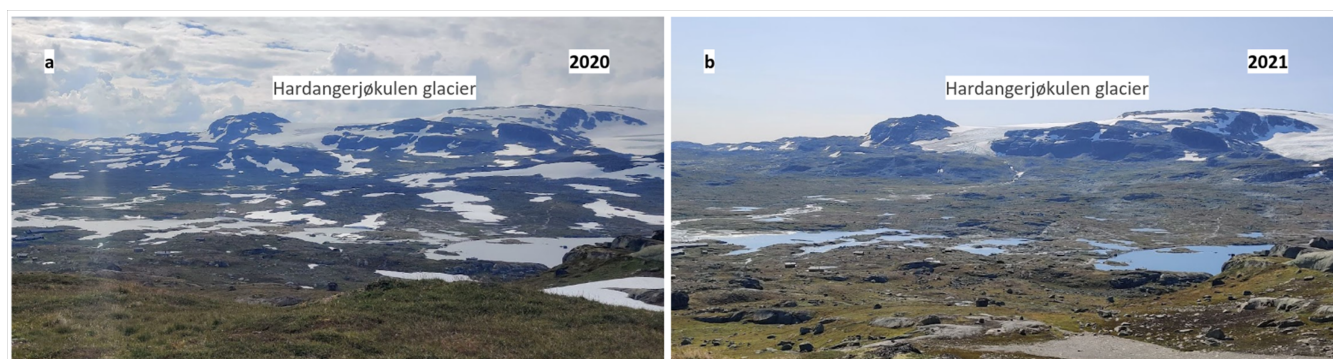
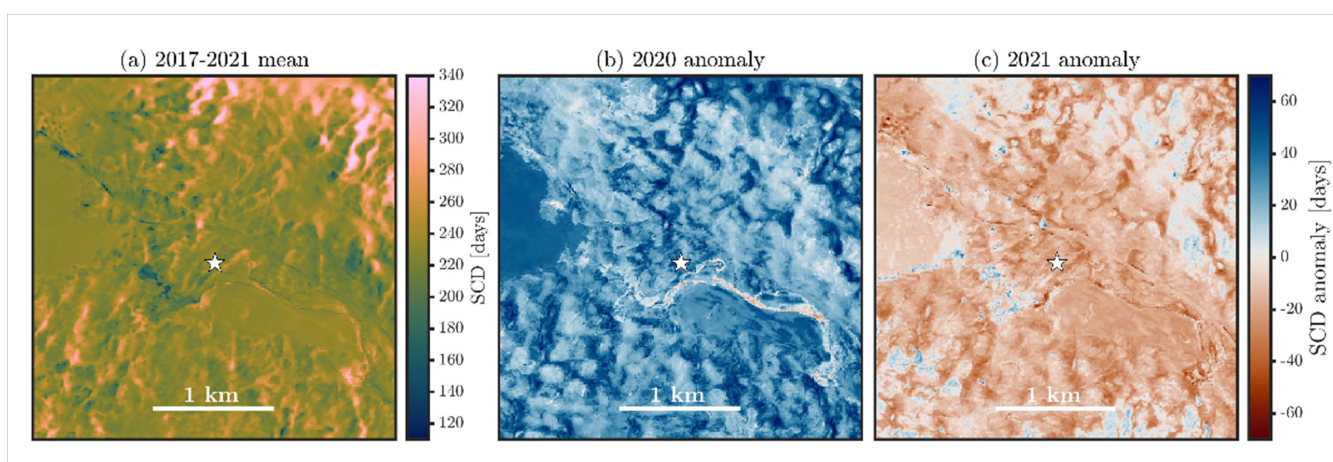


Figure B1. Contrasting late-summer snow conditions at Finse. Panel (a) shows the view south towards the Middalselvi glaciated catchment at the end of August 2020. Panel (b) shows the same view at the end of August 2021. Photographs: A. L. Popp.



Contains modified Copernicus Sentinel data (2017–2021), used under the Copernicus Sentinel Data Legal Notice. Landsat 8 data courtesy of the U.S. Geological Survey (public domain).

Figure B2. High-resolution (10 m) snow-cover duration (SCD, days) retrievals for the 9 km² area around the Finse flux station (star). Panel (a) shows mean SCD for the 2017–2021 water years. Panels (b) and (c) show the pixel-wise anomalies in 2020 and 2021.

Appendix C: Groundwater fractions

Table C1 summarises the groundwater fractions estimated with the tracer-aided Bayesian end-member mixing model. Gas and mixing-model data were linked by validated sample identifiers rather than coordinates. The category means summarise the sample-specific posterior means. Mean posterior SD describes uncertainty in the individual estimates, not variation among sites or uncertainty in the category mean. Mixing modelling and subsequent statistical analyses were performed in R.

Table C1. Groundwater fraction estimates (%) by surface-water category and year from the tracer-aided Bayesian end-member mixing model. Values are the mean across observations and the mean of their sample-specific marginal posterior standard deviations (SDs); n is the number of observations.

Category	Year	n	Mean groundwater fraction (%)	Mean posterior SD (%)
<i>All categories combined</i>				
all	2020	42	7.0	3.3
all	2021	32	8.7	4.0
<i>Classified by water-source category</i>				
g-sw	2020	12	14.8	6.3
g-sw	2021	7	17.9	7.0
ng-sw	2020	8	2.2	1.5
ng-sw	2021	7	4.2	2.3
sw	2020	3	3.5	1.9
sw	2021	1	5.3	2.0
g-lake	2020	6	7.6	3.8
g-lake	2021	6	12.2	6.1
ng-lake	2020	2	3.3	1.8
ng-lake	2021	1	0.3	0.2
lake	2020	11	3.3	1.9
lake	2021	10	4.5	2.4



Appendix D: Statistical results

D1 Comparisons among water-source categories

Table D1 gives the Kruskal–Wallis tests reported in the main text. Categories represented by fewer than three observations were not included in these tests.

Table D1. Kruskal–Wallis tests comparing gas saturation among water-source categories represented by at least three observations, conducted separately for each gas and campaign. Adjusted p -values use the Benjamini–Hochberg method across the six gas-by-campaign tests.

Gas	Year	n	Categories	H	df	Unadjusted p	Adjusted p
CO ₂	2020	41	5	13.00	4	0.0113	0.0226
CO ₂	2021	32	4	15.72	3	0.00129	0.00776
CH ₄	2020	39	5	5.91	4	0.206	0.247
CH ₄	2021	32	4	11.36	3	0.00995	0.0226
N ₂ O	2020	41	5	0.99	4	0.912	0.912
N ₂ O	2021	32	4	6.36	3	0.0955	0.143

420 D2 Paired comparisons between years

Table D2 gives the paired sign tests. These three tests form a separate multiple-testing family from the six Kruskal–Wallis tests.

Table D2. Exact two-sided paired sign tests for sites sampled in both years, including the groundwater well. The median difference is 2020 minus 2021 in saturation percentage points. Adjusted p -values use the Benjamini–Hochberg method across the three gases. All paired differences were nonzero.

Gas	Pairs	Higher in 2020	Median difference	Unadjusted p	Adjusted p
CO ₂	34	25	+106.92	0.0090	0.0271
CH ₄	32	18	+18.59	0.5966	0.6076
N ₂ O	34	15	−4.64	0.6076	0.6076

D3 Uncertainty-propagated groundwater regressions

Table D3 gives the groundwater regressions described in the main Methods. The models used 74 surface-water observations for CO₂ and N₂O and 72 for CH₄. Groundwater-fraction uncertainty was propagated through 1,000 beta-distributed realizations
 425 matched to each sample’s posterior mean and standard deviation. Estimates and covariance matrices were combined using Rubin’s rules (Rubin, 1987). Regression p -values were not adjusted for multiple testing. Models containing random effects were fitted with lme4 version 1.1-35.1 (Bates et al., 2015).

Table D3. Groundwater effects from uncertainty-propagated regressions of $\log_{10}$ -transformed GHG saturation. Slopes and 95% confidence intervals are per 8.2-percentage-point increase in groundwater fraction. Regression p -values are unadjusted for multiple testing.

Response	GW-fraction slope [95% CI]	p (GW effect) ^a	p (GW $\times$ year) ^b
CO ₂	+0.071 [−0.022, 0.164]	0.134	0.518
CH ₄ ^c	−0.015 [−0.170, 0.140]	0.850	0.879
N ₂ O	+0.002 [−0.010, 0.014]	0.778	0.494

^a Two-sided Wald test of the groundwater effect after combining estimates across uncertainty realizations. ^b Corresponding test of the groundwater $\times$ year interaction. ^c $n = 72$ for CH₄ and $n = 74$ for CO₂ and N₂O. Two samples lacked a CH₄ saturation measurement.

D4 Paired-site changes in gas saturation

Figure D1 shows the between-year differences at sites sampled in both years. Unlike the category-median connections in
430 Figure 4, every point compares the same physical site.

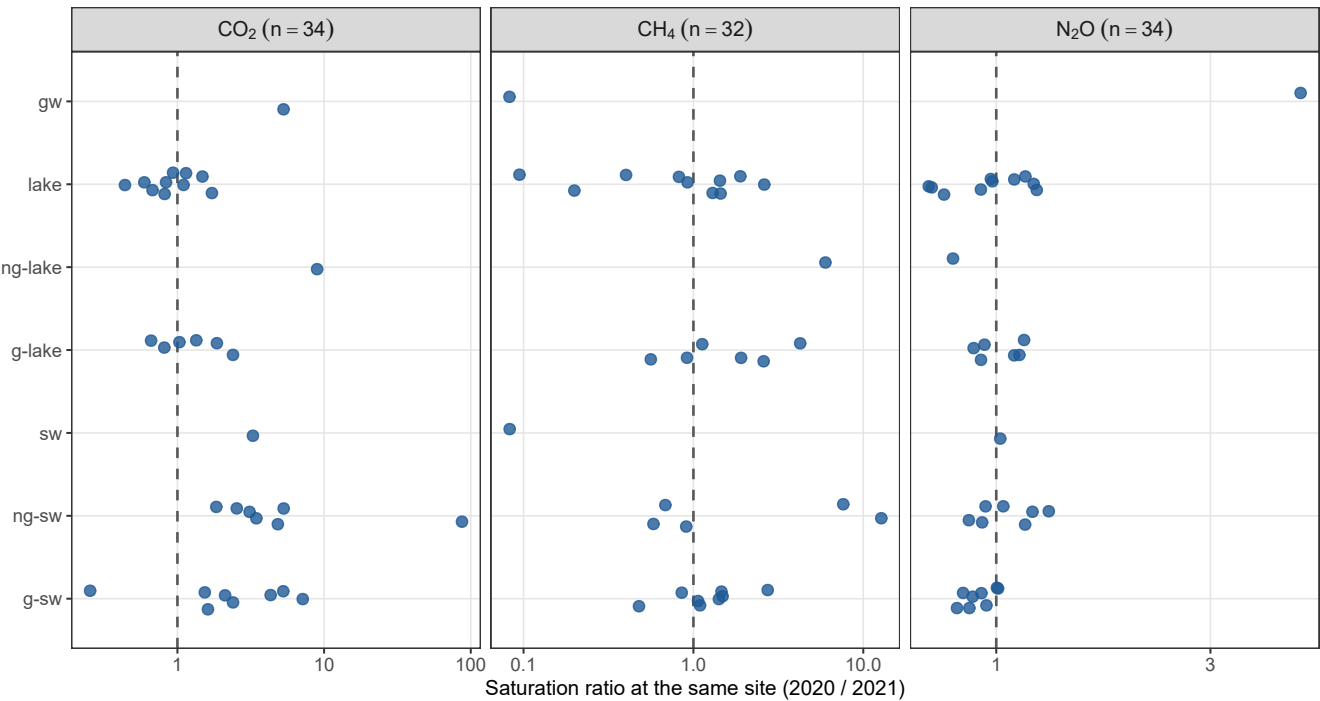


Figure D1. Paired-site contrasts in CO₂, CH₄ and N₂O saturation. Each point shows saturation in 2020 divided by saturation in 2021 at the same site. The dashed line marks no change. Values left of 1 indicate higher saturation in 2021, and values right of 1 indicate higher saturation in 2020. Each gas has its own logarithmic horizontal scale. Points are offset vertically only to reduce overlap. There are 34 paired sites for CO₂ and N₂O and 32 for CH₄, including the groundwater well. Category abbreviations are defined in Table A1.

Appendix E: Radon and tracer concentrations

Radon activities in surface waters were low relative to groundwater (Figure E1d). Measurable surface-water activities indicate recent contact with radon-producing mineral material but cannot distinguish groundwater discharge from sediment contact or hyporheic exchange. Figure E1a–c shows EC, chloride and calcium by water-source category and year. These variables were
 435 mixing-model inputs and therefore show the chemical patterns underlying the groundwater estimates rather than providing independent validation.

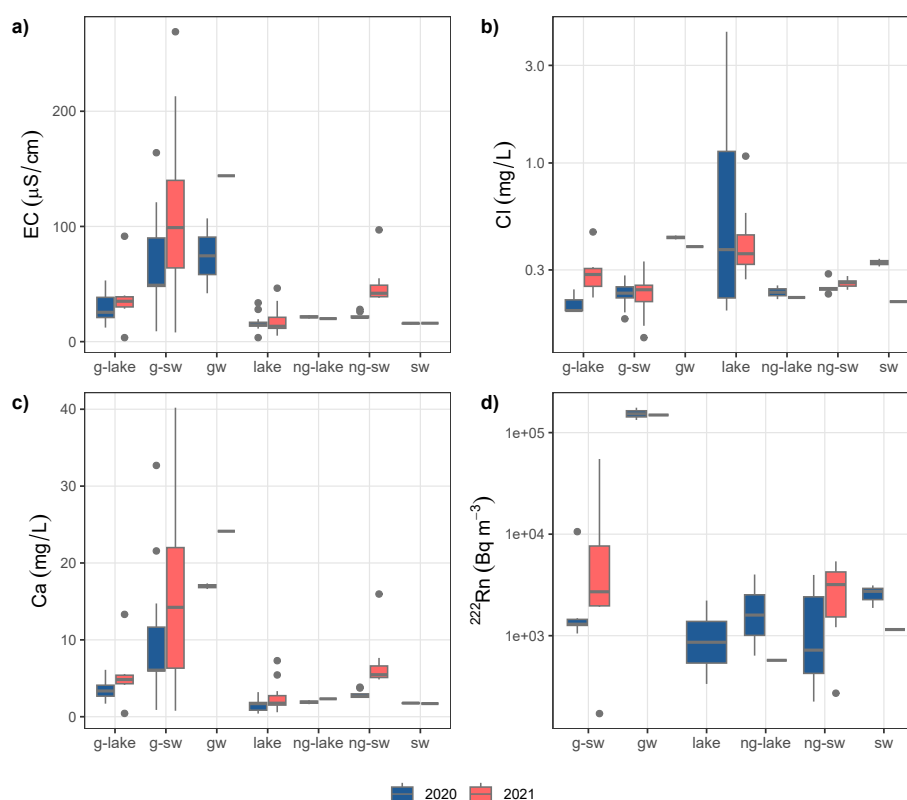


Figure E1. Water-chemistry and tracer measurements by water-source category in 2020 (blue) and 2021 (red): (a) electrical conductivity (EC), (b) chloride, (c) calcium and (d) radon (^{222}Rn) activity. No radon measurements were available for the g-lake category.



Code and data availability. The greenhouse-gas, radon and hydrochemical tracer data, together with the groundwater-fraction estimates from the Bayesian mixing model, are deposited at Zenodo under <https://doi.org/10.5281/zenodo.22847435>. The record is restricted during peer review and will be made publicly available following review. Access is provided to the editor and reviewers. The Bayesian end-member
440 mixing-model code is freely available through Popp et al. (2019).

Author contributions. We describe author contributions following the CRediT taxonomy. **Conceptualization:** A.L.P. **Methodology:** A.L.P., N.V., K.A., P.D. **Software:** A.L.P., K.A. **Formal analysis:** A.L.P., N.V., K.A., Y.A.Y. **Investigation (field sampling):** A.L.P., N.V., S.T.K., A.E., D.O.H. **Resources:** A.L.P., P.D., D.O.H., L.M.T. **Data curation:** A.L.P., N.P. **Writing (original draft):** A.L.P., N.V., K.A. **Writing (review & editing):** all authors. **Visualization:** A.L.P., K.A. **Supervision:** D.O.H., L.M.T., L.G.L. **Project administration:** A.L.P. **Funding acquisition:** A.L.P., K.A., D.O.H., L.M.T., L.G.L.
445

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