In the Tuxertal (Tux Valley, Austria), like in other Alpine regions, drinking water supply is predominantly organised privately or in cooperatives from nearby springs. Currently used springs may become unsuitable in future due to increasingly strict legal limits and changes in the water balance caused by climate change. In this study, the Tuxbach catchment area (135 km²) is examined by a reference-date measurement. Within 11 days, 153 springs and creeks were sampled to evaluate their appropriateness. All results of critical parameters for the drinking water supply are summarized and displayed in a hydrochemical map. Locally the groundwater composition differs due to various changes of petrographic units. Analysis results are statistically evaluated and characteristic values derived from six rock types. It becomes evident that apart from ammonium and arsenic, legal limits are mostly met. Low discharge rates present the major challenge for drinking water supply in future.

In addition, the importance of glaciers as water storage is decreasing continuously (Vanham, 2012). Probstl et al. (2009) state that in the Tuxertal (Tux Valley), glacier area reduced from 20.6 km² to 7.1 km² between 1850 and 2004 (confer data for the whole Zillertal in Lambrecht and Kuhn (2007) and Fischer et al. (2015)). In the Tuxertal, glacier area was 5.2 km² in 2016 (Schäffer et al., 2020a) and has decreased significantly since then. Active and inactive/fossil rock glaciers present an area of 2.2 and 9.1 km², respectively (Krainer & Ribis, 2012). Active rock glaciers can influence discharge rates, chemical composition including heavy metal concentrations as well as physical properties of undercurrent streams and springs on a daily basis (Krainer & Mostler, 2002; Nickus et al., 2015; Thies et al., 2013). Permafrost and dead ice melt may influence discharge rates and water composition as well (Brighenti et al., 2019; Colombo et al., 2018; Winkler et al., 2016).

In the Tuxertal, small cooperatives organise drinking water supply and operate nearby springs with small catchments. As groundwater quality can differ on a small scale due to numerous variations of petrographic units, it is important to compile hydrochemical data. A regional overview is crucial to identify the most suitable springs to replace springs with elevated metal concentrations or inconstant discharge. In this study, the whole Tuxertal was examined using the
method of a reference date measurement (Schäffer et al., 2020b). The applied concept is suitable to create a local map of the groundwater characteristics giving decision-makers adequate information to ensure a reliable drinking water supply based on local springs.

2. Study area

2.1 Topography

The study area, shown in Figure 1, is located in the state of Tyrol within the Austrian Alps and comprises 135 km², the entire catchment area of the Tuxbach (Tux Creek). Olperer (3,476 m) is the highest peak; the lowest point is the confluence of the Tuxbach into the Zemmbach at Gstan (645 m). The densely populated Tuxertal, a tributary valley of the Zillertal, is glacially shaped with a 16-km-long trough floor, several smoothed high elevation flat areas and arêtes (Wirsig et al., 2016). Tuxer Ferner, Friesenbergkees, Schwarzbrunnenkees and Federbettekees are the remaining glaciers today, but, as visualised in Figure 1, the largest glacier area belongs predominantly to the Tuxer Ferner. Impressive lateral moraines and other remnants of the Little Ice Age exist especially below the Tuxer Ferner (Zasadni, 2007), which is still used as an all year-round ski resort. In general, the Tuxertal is strongly developed for tourism offering a good coverage by footpaths and trails, which was crucial for this study.

2.2 Geology

As Figure 1 shows, the Tuxertal is situated in the Eastern Alps in the north-western edge of the Tauern Window and features a complex geological setting (Kurz et al., 1998; Schiavo et al., 2015; Schmid et al., 2013). The Tauern Window is an elongated structure with about 170 km E–W axis and 50 km wide N–S direction. With European basement in its core and Penninic nappe stacks in its rim, the Tauern Window is enclosed by Austroalpine units (Castellarin et al., 2006; Lüschen et al., 2004). The rim is composed by meta-sediments containing meta-ophiolites; the core consists of gneisses, which underwent eclogite and blueschist facies metamorphism (Bousquet et al., 2008; Morteani & Raase, 1974; Selverstone et al., 1984; Schulz et al., 1995). Many other studies describe different aspects of the evolution of the Tauern Window (Veselá et al., 2011) like uplift (Grundmann & Morteani, 1985; Lammerer & Weger, 1998), exhumation (Bertrand et al., 2015; Neubauer et al., 1999), small or large scale foldings (Lammerer, 1988; Ledoux, 1984, respectively) or fault zones (Bertrand et al., 2015; Töchterle et al., 2011). Following nomenclature of the Geological Survey of Austria (GBA, 2005), lithological units displayed in Figure 1 are classified from northwest to southeast:

- Innsbruck Quartzphyllite Nappe
- Radstadt Nappe System
- Gerlos Zone
- Glockner Nappe System
- Seidlwinkel-Moderreck Nappe
- Wolfendorn Nappe
- Ahorn Core Complex
- Schönach Depression
- Tux Core Complex

They are described thoroughly in the literature (Beil-Grzegorczyk, 1988; Frisch, 1968, 1973, 1975, 1980; Häusler, 1988; Häusler et al., 1993; Höck, 1969; Kießling & Zeiss, 1992; Köhne & Miller, 1980; Kupka, 1956; Sengl, 1991; Thiele, 1976; Veselá et al., 2011). Various quaternary deposits are present in the Tuxertal, mainly valley fills, slope debris, alluvial fans, rock falls, landslides and moraines. The most prominent ones are the landslides between Finkenberg and Lanersbach (Kossendey, 1992), glacial deposits below the Tuxer Ferner (Zasadni, 2007) and several rock glaciers between Höllenstein and Grinbergspitze (Kogler, 2018; Krainer & Ribis, 2012; Schäffer et al., 2020a).

2.3 Hydrogeology

A nearly 7-km-long water management tunnel, also drawn in Figure 1, deviates the uppermost part of the catchment area to feed a water reservoir in a neighbouring valley (Zamser Grund, Austria). Since its construction in the late 1960s, the Tuxbach does not present the natural runoff conditions. A persistent positive thermal anomaly was identified within this tunnel (Heldmann, 2020a). Remarkably, hot springs are located 2 km further north of the tunnel in Hintertux. The thermal springs of Hintertux consists of 22 outlets with an average discharge of 17–26 l/s, enabling temperatures up to 22.5 °C (Czurda & Zötl, 1993; Elster, 2018; Heldmann, 2020b). Located at an altitude of 1500 m, they are probably Europe’s highest thermal springs (Carlé, 1975). Another recently constructed 8.5-km-long diversion tunnel in the lower part of the Tuxbach catchment area (Blauhut et al., 2019) will lead to additional distortions of the natural flow regime.

As the karstified Hochstegen Formation occurs only at the southern valley floor, the northern side features a significantly denser drainage network, clearly visible in Figure 1. The Hochstegen Formation is the only major aquifer in the Tuxertal and drains large parts of the southern valley slope subterraneously (Sass et al., 2016a). Two supposed effluents are the karst springs Tuxbachquelle and Goldbründl nearby
Finkenberg, with a discharge of up to 1.5 m³/s (Schäffer et al., 2020a). Apparently, the karstification is not distributed randomly, but strikes SW-NE, following the direction of several thrust faults shown in Figure 1 (cf. Bauer et al., 2016). Karstified zones have a permeability in the range of 1.2 × 10⁻¹ to 1.6 × 10⁻⁴ m/s (Lehr & Sass, 2014; Schäffer et al., 2020a). Other rocks offer orders of magnitude lower formation permeability from 10⁻⁶ to 10⁻⁹ m/s. Higher permeabilities are only achieved locally at the Olperer Shear Zone with 2.5 × 10⁻⁵ m/s and at valley slopes, where extension strain fractures enhance permeability up to 10⁻⁴ m/s (Heldmann, 2020a). Approximately 40 caves are known in the Tuxertal and the ongoing glacier retreat enabled new discoveries (Spötl, 2009; Spötl et al., 2016b). Spannagel Cave south of Hintertux is the most prominent one with circa 11 km of explored passages (Spötl & Mangini, 2010).

In Finkenberg, nine 400-m-deep borehole heat exchangers exploit the Hochstegen Formation geothermally. Constructed in 2013 it was the first medium deep borehole heat exchanger system in an alpine karst aquifer, designed for 1 GWh/a extraction and 400 MWh/a induction (Lehr & Sass, 2014; Sass et al., 2016b). Based on the positive experience in the first years of operation (Lehr et al., 2020), expansion is planned in future.

3. Material and methods
3.1 Field campaign

Sampling took place within a few days in order to achieve the best possible comparability of measured parameters over the whole catchment area of the Tuxbach. A list of tapped springs was compiled from the Tyrolean Geographic Information System (Tiris, 2020) and supplemented, if untapped springs were found in the field. Most of the springs had to be reached on foot via tracks or pathways, sometimes across country. The study area was subdivided into eight zones: the numbering of the measuring points is chosen accordingly in the hydrochemical map.

In an extended field campaign, a team with 37 members sampled and examined a total of 146 springs and 7 creeks – including one glacier and one rock glacier runoff, sampled for comparison – between 981 and 2692 m above sea level from 21 to 31 August 2018.
According to the Central Institution for Meteorology and Geodynamics (ZAMG, 2019), 2018 was the warmest year in the 250-year lasting weather measurement history of Austria and also set new records for sunshine hours and summer days. 2018 was characterized by recurring, long-lasting phases of warm, dry and sunny weather. Nationwide, 95% of the usual precipitation height and an accumulation of heavy precipitation events were observed. In the Tuxertal, June, July and August were 2.3 °C warmer on average, with 10% less precipitation compared to the reference period of 1971–2000. However, a long period of warm and dry weather ended abruptly on August 23rd during the field campaign. By the end of the month, two-thirds of the precipitation (108 mm) fell, the temperatures dropped significantly and snow fell at higher altitudes.

Water temperature, pH, electrical conductivity and oxygen content were measured in-situ (pocket meter Multi 340i by WTW, and HQd portable meter by Hach). Bicarbonate was determined via titration up to pH 4.3 using sulfuric acid (digital titrator, Hach). Wherever possible, discharge was measured, partly by channelling the flow, digging the streambed or improvising weirs. Coordinates and altitudes of the sampling points were determined with GPS and subsequently checked in Tiris (Tiris, 2020). Two 100 ml PE bottles were filled at each sampling point. Samples for laboratory analysis of cations were filtered with a 0.45-μm PVDF membrane filter and acidified to pH < 2 with nitric acid.

3.2 Lab measurements

Sodium, potassium, magnesium, calcium, strontium, ammonium, nitrate, nitrite, sulphate, fluoride and chloride concentrations were determined by ion exchange chromatography (Compact IC plus, Metrohm). A total of 21 trace elements (Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Mo, Ag, Cd, Sn, Sb, Ba, Tl, Pb, U) was analysed by inductively coupled plasma mass spectrometry (ICP-MS, PlasmaQuant MS Elite®, AnalytikJena). Instrumental conditions were optimized utilizing a tuning solution resulting in sensitivities of In and Th of 1.4 • 10⁶ c/s and 1 • 10⁶ c/s respectively, and an oxide ratio (CeO/Ce) and doubly charged ion ratio (Ba⁺⁺/Ba⁺) below 2%. Helium served as collision gas in the integrated collision-reaction cell (iCRC), minimizing potential interferences. A peristaltic pump added four internal replicates was 1.6 ± 1.5%.

4. Results

4.1 Hydrochemical map

The hydrochemical map summarizes and displays all relevant parameters for the drinking water supply. Despite a lot of complex information, the design provides a quick and intuitive overview and a comparison on the suitability of springs. Design, signatures and colours are a further development of the map in Schäffer et al. (2020b) and should appeal to both, experts and laymen like the local population. Since one focus is on arsenic and uranium, these concentrations are divided into five classes, shown prominently in different colour in the measuring point symbols. Limit exceedances of other trace elements or ions – namely antimony, nickel, manganese, nitrite or ammonium – appear as coloured rings around the measuring point symbols.

All measured electrical conductivities fulfil the requirements of the Drinking Water Ordinance (BMSG, 2001) and are displayed in three classes as coloured numbers of the sample-ID in order to distinguish low, normal and higher mineralized waters, easily in the hydrochemical map. Normal tap water is assumed to range typically between 75 and 500 μS/cm, shown as black sample-ID. Red measurement point numbers mark low mineralized waters, here defined by values below 75 μS/cm. These waters are suitable for drinking water supply from a legal perspective, but from a nutritional point of view long-term consumption of low mineralized water impacts negatively human health (Kozisek, 2005). Blue sample-IDs indicate electrical conductivity above 500 μS/cm. A red framework of the sample-ID mark values outside the permitted pH range of 6.5–9.5. Shape and size of measuring points visualize discharge, the larger the discharge, the bigger the symbol.

All 153 investigated waters fulfil the requirements for sodium, chloride, fluoride, nitrate, sulphate, aluminium, chrome, iron, copper, selenium, cadmium and lead. Hence, these parameters do not appear on the map. Nevertheless, it is important to notice that in 6–4 the aluminium concentration is 199 μg/l and thus close to the limit value of 200 μg/l. The next highest concentrations are observed in 4–9 and 6–4 with 37.4 μg/l each. In 5–1 the fluoride concentration of 1.49 mg/l is close to the limit of 1.5 mg/l. The second highest concentration is found in 5–3 with 0.57 mg/l.

The electrical balance of all analyses was controlled (formula after Appelo & Postma, 2007), and 14 analyses exceeded an error of 5%, namely 1–19, 4–4, 4–8, 4–10, 5–9, 5–11, 5–12, 5–16, 6–4, 6–6, 7–6, 7–7, 7–8 and 8–9. Concentrations of single ions were corrected by using the electrical conductivity (Rossum, 1975). This allowed an error reduction of the electrical balance of all analyses below 5%.
4.2 Exceedance of limits

Ammonium and arsenic are the most critical parameters with respect to drinking water supply, whereas all other relevant parameters show elevated concentrations in single spots, only. Eight measurement points exceed the limits for arsenic by a multiple of the permitted 10 µg/l (Table 1). Ten measurement points have exceedingly high ammonium concentrations, but the exceedances do not reach twice the permitted concentration of 0.50 mg/l (Table 1). Three measurement points slightly miss the requirements with respect to uranium (Table 1). Antimony and nickel concentrations are by far too high in two and one springs, respectively. Springs 2–7 show both, the highest antimony and nickel concentration, the second highest concentrations are found in 2–9. Only one measurement points feature trace element concentrations significantly below the particular limit. Nitrite concentrations are too high in 1–14 and are undercutting the limit of 0.10 mg/l in 1–11 slightly (Table 1). The permitted pH range is observed in all springs and creeks, with the exception of 1–18 weakly exceeding the pH limit of 9.65.

Table 1. Reference of springs with elevated concentrations of ammonium, arsenic, uranium, nitrite, antimony, nickel or manganese compared to the next highest concentration fulfilling particular limits.

| Species | Measurement point | Concentration (µg/l) | Limit (µg/l) |
|---------|-------------------|----------------------|-------------|
| NH₄     | 8–3               | 890                  | 500         |
|         | 5–12              | 850                  |             |
|         | 1–3               | 670                  |             |
|         | 1–13              | 670                  |             |
|         | 1–22              | 670                  |             |
|         | 1–25              | 670                  |             |
|         | 8–5               | 670                  |             |
|         | 8–17              | 670                  |             |
|         | 1–15              | 660                  |             |
|         | 1–1               | 650                  |             |
|         | 2–4               | 480                  |             |
| As      | 2–7               | 88.4                 | 10          |
|         | 2–10              | 45.4                 |             |
|         | 5–3               | 41.9                 |             |
|         | 5–2               | 38.4                 |             |
|         | 5–1               | 32.2                 |             |
|         | 2–9               | 24                   |             |
|         | 3–11              | 14.2                 |             |
|         | 6–13              | 11.8                 |             |
|         | 6–12              | 8.1                  |             |
| U       | 3–11              | 17.3                 | 15          |
|         | 3–1               | 15.7                 |             |
|         | 5–8               | 15.3                 |             |
|         | 2–7               | 9.8                  |             |
| NO₂     | 1–18              | 180                  | 100         |
|         | 7–14              | 120                  |             |
|         | 1–11              | 95                   |             |
|         | 5–9               | 49                   |             |
| Sb      | 2–7               | 27.8                 | 5           |
|         | 2–9               | 10                   |             |
|         | 3–5               | 1.1                  |             |
| Ni      | 2–7               | 56.1                 | 20          |
| Mn      | 7–15              | 76.1                 | 50          |
|         | 6–4               | 22.5                 |             |

4.3 Groundwater composition

As the hydrochemical map also aims to illustrate influences of different rock types on the water composition, the different petrological units from Figure 1 are gathered in our classification. Each sample is assigned to one of these six rock types: calcareous phyllite, unconsolidated rock, marble, phyllite, gneiss and schist. Arithmetic mean values for each rock unit are calculated (Tables 2 and 3). In a first step, this classification based on field observations of the dominant rock type of the individual catchment area and the rock distribution on the geological map in Figure 1. In a second step, this preliminary classification is controlled by plotting all analyses of one group in a particular Stiff diagram (Stiff, 1951), shown in Figure 2, and checking the resulting ‘multi Stiff diagrams’ (Sass et al., 2016) for outliers. In a third step, a discriminant analysis improves the classification based on statistical arguments (Backhaus et al., 2018; Ludwig, 2013). A discriminant analysis is a statistical method to predict group membership from a set of metric predictors. Here, 27 metric predictors (e.g. 15 trace elements, 9 major elements, T, pH, and EC) were used to determine six different groups (gneiss, phyllite, schist, marble, unconsolidated rock, and calcareous phyllite). To qualify the results, all five discriminant functions are statistically significant with a Wilk’s lambda distribution, an inverse quality criterion, of 0.022 (Mardia et al., 1982).

Calcareous phyllite group contains the phyllites and calcareous phyllites of the Glockner Nappe System. Marble group is composed mainly by springs within the Hochstegen Formation. Phyllite group are the quartz phyllites of the Innsbruck Quartzphyllite Nappe mainly. Gneiss group consists of samples from the Ahorn Core as well as the Tux Core. Schist group summarises different schists from the Seidlwinkel-Moderockeck Nappe and the Wolfendorn Nappe. At least, the unconsolidated rock group comprises springs located at several metre-thick quaternary deposits in the valley floor or on slopes and which could therefore not be assigned to the rock types mentioned above.

According to a Piper diagram (Piper, 1944) in Figure 3 nearly all waters are of Ca–(Mg)–HCO₃–(SO₄) type, which is typical for vadose groundwater. Ten analyses manifest a differing chemistry. It is worthy to note that the electrical balance of these analyses is acceptable. 2–6 and 2–8 are Mg–Ca–HCO₃–waters, 2–7 and 2–9 are Mg–Ca–HCO₃–SO₄–waters. These four springs are located close to an abandoned magnesite-scheelite mine (Haditsch & Mostler, 1982, 1983; Pirkl, 1986). Thus the Mg-dominance can be traced back directly to the magnesite. 4–9 and 8–3 are Ca–Mg–SO₄–HCO₃–waters, 1–24 is of Ca–SO₄–HCO₃-type. A reason for the SO₄-dominance is
Table 2. Arithmetic means of in-situ parameters and IC analytical results displayed in accordance to the dominant rock type of individual catchments.

| Rock type               | n   | T (°C) | K (µS/cm) | pH (-) | Q (l/s) | Na⁺ (mg/l) | K⁺ (mg/l) | Mg²⁺ (mg/l) | Ca²⁺ (mg/l) | Sr²⁺ (mg/l) | NH₄⁺ (mg/l) | HCO₃⁻ (mg/l) | NO₃⁻ (mg/l) | NO₂⁻ (mg/l) | SO₄²⁻ (mg/l) | F⁻ (mg/l) | Cl⁻ (mg/l) | F⁻ (mg/l) | Cl⁻ (mg/l) |
|-------------------------|-----|--------|-----------|--------|---------|------------|-----------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| Calcareous phyllite     | 48  | 10.1   | 314       | 8.12   | 0.9     | 1.26       | 0.73      | 13.54       | 48.3        | 0.54        | 0.16        | 184.1       | 1.21        | 0.01        | 23.64       | 0.06        | 2.49        |
| Unconsolidated rock     | 27  | 11.2   | 303       | 7.91   | 0.8     | 1.22       | 0.62      | 11.23       | 59.9        | 1.19        | 0.12        | 188.9       | 2.30        | 0.01        | 39.41       | 0.14        | 2.03        |
| Marble                  | 25  | 8.4    | 249       | 7.92   | 2.5     | 0.54       | 0.53      | 5.49        | 46.9        | 0.16        | 0.09        | 161.3       | 1.67        | 0.01        | 7.19        | 0.03        | 0.72        |
| Phyllite                | 19  | 8.8    | 157       | 7.93   | 1.1     | 1.00       | 0.42      | 9.96        | 18.9        | 0.08        | 0.14        | 85.7        | 0.59        | 0.01        | 17.58       | 0.06        | 0.82        |
| Gneiss                  | 17  | 6.6    | 63        | 7.60   | 2.4     | 0.42       | 0.50      | 1.16        | 11.9        | 0.06        | 0.09        | 38.2        | 1.10        | <0.01       | 2.90        | 0.03        | 0.25        |
| Schist                  | 17  | 9.5    | 242       | 7.78   | 0.6     | 0.44       | 0.83      | 7.80        | 48.9        | 0.19        | 0.05        | 173.2       | 3.03        | <0.01       | 6.51        | 0.03        | 0.65        |
| Total                   | 153 | 9.4    | 246       | 7.93   | 1.3     | 0.92       | 0.62      | 0.36        | 42.5        | 0.45        | 0.12        | 151.6       | 1.59        | 0.01        | 18.77       | 0.06        | 1.46        |

Table 3. Arithmetic means of ICP-MS analytical results (µg/l) displayed in accordance to the dominant rock type of individual catchments.

| Rock type               | n   | Al   | Ti  | V   | Cr  | Mn  | Fe  | Co  | Ni  | Cu  | Zn  | As  | Se  | Mo  | Ag  | Cd  | Sn  | Sb  | Ba  | Tl  | Pb  | U  |
|-------------------------|-----|------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Calcareous phyllite     | 48  | 2.5  | 0.1 | <0.1| 0.2 | 0.7 | 3.1 | 0.1 | 1.5 | 1.7 | 1.0 | 2.1 | 0.3 | 0.1 | <0.1| <0.1| 0.7 | 13.0| <0.1| 0.1 | 0.8 |
| Unconsolidated rock     | 27  | 4.4  | 0.1 | 0.1 | 0.1 | 0.1 | 3.4 | <0.1| 0.4 | 1.9 | 2.3 | 4.6 | 0.5 | 0.7 | <0.1| <0.1| 0.2 | 36.3| <0.1| 0.1 | 1.8 |
| Marble                  | 25  | 3.1  | 0.1 | <0.1| 0.1 | 0.1 | 3.0 | <0.1| 0.4 | 1.6 | 1.9 | 2.0 | 0.3 | 0.4 | <0.1| <0.1| <0.2| 13.3| <0.1| 0.1 | 1.9 |
| Phyllite                | 19  | 3.8  | <0.1| <0.1| 0.1 | 4.8 | 7.7 | <0.1| 0.6 | 3.6 | 3.1 | 4.4 | 0.2 | <0.1| <0.1| <0.1| <0.2| 8.9 | <0.1| 0.1 | 0.6 |
| Gneiss                  | 17  | 18.3 | 0.2 | <0.1| 0.1 | 1.5 | 10.9| <0.1| 0.2 | 2.2 | 13.9| 2.5 | 0.4 | 0.2 | <0.1| <0.1| <0.2| 3.1 | <0.1| 0.1 | 3.3 |
| Schist                  | 17  | 2.6  | 0.1 | 0.1 | 0.1 | 0.2 | 3.5 | <0.1| 0.3 | 3.0 | 2.5 | 0.7 | 0.4 | 0.1 | <0.1| <0.1| <0.2| 173.7| <0.1| <0.1| 1.2 |
| Total                   | 153 | 4.9  | 0.1 | <0.1| 0.1 | 1.1 | 4.6 | 0.1 | 0.7 | 2.2 | 3.2 | 2.7 | 0.3 | 0.3 | <0.1| <0.1| <0.2| 33.6| <0.1| 0.1 | 1.4 |
unclear as these springs are located in different locations, altitudes and petrological units, as shown in the hydrochemical map. 1–21 is a Ca–Na–HCO₃-water, 1–10 a Ca–Mg–Cl–HCO₃-water and 8–5 a Ca–Mg–HCO₃–Cl-water (Figure 3). At last, in 1–10 and 1–21 the low amount of dissolved solids allowed sodium and chloride to exhibit a share in equivalent concentrations above 20%.

5. Discussion

5.1 Limits

In terms of drinking water supply, arsenic and ammonium are the most critical parameters. The hydrochemical map indicates that critical ammonium concentrations appear almost exclusively in the north-western part of the Tuxertal. This inadmissible ammonium concentrations are anthropogenic as this part of the valley is comprehensively used as grassland. In contrast, arsenic originates from different geogenic sources and, like the hydrochemical map displays, occurs sometimes with other high metal concentrations. First, elevated arsenic concentrations occur in single springs originating from the Innsbruck Quartzphyllite Nappe, namely in 1–24 and 2–10, probably associated with arsenopyrite bearing layers within the Silurian phyllites (Haditsch & Mostler, 1983). Second, a local paragenesis contains antimonite (Sb₂S₃), arsenopyrite (FeAsS) and ullmannite (NiSbS) next to the abandoned magnesite mine (Haditsch & Mostler, 1983; Raith & Grum, 1992) causing elevated antimony, arsenic and nickel concentrations in 2–7 and 2–9. Third, inadmissible arsenic and uranium concentrations are associated with gneisses of the Ahorn Core Complex in the south-eastern part of the Tuxertal and can be found in 3–1, 3–3, 3–11 and 5–8. This observation accords well with geogenic arsenic and uranium concentrations detected in the east-bound neighbouring valley Zemmgrund (Schäffer et al., 2020b). Fourth, noticeable high arsenic and uranium concentration occur in the thermal springs of Hintertux (analyses 5–1, 5–2, and 5–3) and appear diluted in 6–12 and 6–13, two karst springs nearby. Such elevated arsenic and uranium concentration are untypical for springs associated to unconsolidated rocks or marbles. As the hydrochemical map shows, they are not observed in other parts of the catchment area (Table 4). This finding supports the hypothesis of Heldmann et al. (2020b) that the thermal water consists of several components, the
gneisses southeast above Hintertux being one of them and causing high arsenic and uranium concentrations.

The reason for a single elevated manganese concentration in 7–15 remains undiscovered. All other metal concentrations are suitable for drinking water (Figure 4). Therefore, groundwater quality appears unproblematic for local water supply in the future, as springs matching the requirements are found all over the valley. However, available groundwater quantity will be challenging in the near future, as the majority of the investigated springs show a discharge below 5 l/s, indicated by rhombi or small circles in the hydrochemical map. These low-discharging springs are at risk to dry out occasionally due to climate change. A single measurement as presented here is insufficient, neither to recognize the discharge behaviour, nor to identify intermittent springs. Enhanced long term hydrologic monitoring is required, urgently.

5.2 Statistical evaluation

The discriminant analysis improves the classification significantly (Table 4). Statistical testing often indicated assignments of springs to other rock types, when rock types of catchment areas and spring location did not match. Hence, 20 samples were

Table 4. Classification results of the discriminant analysis before (left two columns) and after (right two columns) modifying membership to rock types due to statistical reasons.

| Rock type          | n  | Fit of group membership (%) | n  | Fit of group membership (%) |
|--------------------|----|-----------------------------|----|-----------------------------|
| Calcareous phyllite| 47 | 74.5                        | 48 | 83.3                        |
| Unconsolidated rock| 30 | 66.7                        | 27 | 77.8                        |
| Marble             | 29 | 65.5                        | 25 | 84.0                        |
| Phyllite           | 18 | 83.3                        | 19 | 94.2                        |
| Gneiss             | 17 | 94.1                        | 17 | 100.0                       |
| Schist             | 12 | 66.7                        | 17 | 82.4                        |
attributed to rock types which are not the outcropping host rock at the particular spring. However, statistical suggestions had to be checked carefully and some were refused, because they were arbitrary from a geological or hydrogeological perspective (Figure 1). For example, a relocation of 3–10 from gneiss to marble was indicated. Some reclassifications suggested by the discriminant analysis need a verification by an additional field survey to be accepted: 3–7 and 3–13 from schist to marble, 5–10 from marble to gneiss, 4–1 and 4–8 from unconsolidated rock to schist, 8–17 from unconsolidated rock to calcareous phyllite, as well as 2–14 and 8–15 from calcareous phyllite to phyllite and unconsolidated rock, respectively.

Figure 4. Boxplots of trace element concentration in groundwater, sorted by petrological units of the springs. Distant upper outliers are plotted with their values and element on the top for each petrological unit. The whiskers are defined as the interquartile range multiplied by 1.5, therefore applies for the lower whisker $Q_1 - 1.5 (Q_3 - Q_1)$, and for the upper whisker $Q_3 - 1.5 (Q_3 - Q_1)$. Outliers are smaller than the lower whisker or larger than the upper whisker.
Furthermore, some classifications in the triangle Kleiner Kaserer, Hornspitze and Hintertux are uncertain (Figure 1). Due to the complex geological situation, this area needs to be mapped more thoroughly. Additionally, some springs are evidently influenced not only by one single rock type. For example, it is well recognizable in the hydrochemical map that 5–8 and 5–19 have hydrochemical characteristics of both marble and gneiss.

With respect to the electrical conductivity, and thus total dissolved solids, waters originating from gneisses have significantly lower values followed by waters from phyllites, as the boxplots demonstrate in Figure 4. Waters from schists, marbles, unconsolidated rocks and calcareous phyllites feature a similar electrical conductivity range. Indeed, schists and marbles waters have a similar median of 239 and 249 μS/cm, respectively, whereas waters from calcareous phyllites and
unconsolidated rocks have higher medians of 303 and 307 μS/cm, respectively (Figure 5a). Bicarbonate and calcium mainly cause the relatively increased electrical conductivity followed by sulphate and magnesium with a secondary influence (Figure 5b). The higher concentrations of these ions, the greater is electrical

Figure 5. Boxplots of (a) groundwater electrical conductivity at 25 °C and (b) major elements, sorted by petrological units of the springs; UR = unconsolidated rock, CP = calcareous phyllite. The whiskers are defined as the interquartile range multiplied by 1.5, therefore applies for the lower whisker $Q_1 - 1.5 (Q_3 - Q_1)$, and for the upper whisker $Q_3 - 1.5 (Q_3 - Q_1)$. Outliers are smaller than the lower whisker or larger than the upper whisker.
conductivity. Comparatively low sulphate concentrations in marble waters are the only exception.

Spearman’s rank correlation matrices (Engel et al., 2019) reveal positive or negative correlations of many different parameters. A Spearman’s rank correlation is a non-parametric measure of statistical dependence of two variables. Actual data values are replaced by their ranks and the closer the correlation is to ±1, the stronger the monotonic relationship. In the Spearman’s rank correlation in Figure 6, the best correlations for all 153 analyses exist between calcium, magnesium, bicarbonate and electrical conductivity. This result is expected, because calcium, magnesium and bicarbonate are the main ions which have the strongest influence on the electrical conductivity. Among the heavy metals, significant statistical correlations emerge among arsenic and antimony, copper and zinc, vanadium and antimony, uranium and potassium as well as uranium and nitrate. The first four correlations are explainable by the paragenesis discussed above. A correlation between uranium and nitrate can be a result of uranium mobilization caused by nitrate as oxidizing agent (Berk & Fu, 2017; Bonotto et al., 2019). Spearman’s rank correlation matrices become more meaningful, if single rock types are evaluated. Many additional correlations are visible for the gneiss group, for example the relationship among arsenic and uranium concentrations discussed above (Figure 7). On the one hand, this is due to the fact that the gneiss group consists of two different units only, the gneisses of the Ahorn Core Complex and the Tux Core Complex (Figure 1). On the other hand, the

Figure 6. Spearman’s rank correlation matrix of hydrochemical parameters for all 153 analyses of different rock types.
gneisses are relatively homogeneous. There is also a statistical effect due to the significantly smaller number of samples \((n = 17)\), of course.

6. Conclusion

Field observations, hydrochemical and statistical evaluations are well suited to assign spring waters to rock units and to derive typical hydrochemical parameters controlled by water–rock interaction. In some parts of the study area, groundwater composition varies on a small scale due to the complex geology on the north-western edge of the Tauern Window. Most of the local hydrochemical specialities and anomalies are explainable by the presented results.

Large-scale reference-date sampling as shown in this study is feasible in alpine terrains and may lead to meaningful results, compiled and illustrated in a hydrochemical map. It is a helpful tool to identify monitoring needs and to anticipate worrisome trends induced by global climate change. In alpine regions, those trends are developing much faster due to glacial melt, so it is required to establish such maps sooner than in moderate regions. Water shortness will also impact the water quality which has to be compared with a status quo given herein.

Limits for heavy metal concentrations and other relevant parameters are exceeded only locally, so far. A recent challenge for drinking water supply is the low discharge (<5 l/s) of springs which are needed to produce drinking water. In these springs, long-term
monitoring is necessary to evaluate the discharge behaviour. Based on such results, springs can be selected which fulfil legal requirements and are robust against temporary water shortness induced by climate change. However, spatial long-term spring water discharge and groundwater quality hydrographs are the most important data to obtain a chance to manage climate change.

Software
Lithological layers, nappe borders and rivers were compiled with ArcGIS, version 10.6. The hydrochemical and geological legend, as well as all symbols, numbers and names were added with CorelDRAW 2017, version 19.1.

Open Scholarship
This article has earned the Center for Open Science badge for Open Data. The data are openly accessible at https://doi.org/10.11583/tudatalib-400.

Acknowledgements
Jan Christopher Hesse, Meike Hintze, Dirk Scheuvens, Rainer Seehaus and participants of the field exercise ‘Hauptgeländeübung II 2018’ (Main Field Exercise II) helped to collect samples and did in-situ measurements. Comments and suggestions of Marco Donnini, Domenico Antonio De Luca, Arthur Merschat and Chris Orton improved the manuscript as well as the hydrochemical map considerably. We acknowledge support by the Deutsche Forschungsgemeinschaft (DFG – German Research Foundation) and the Open Access Publishing Fund of Technical University of Darmstadt.

Disclosure statement
No potential conflict of interest was reported by the author(s).

Data availability statement
The groundwater analyses of the Tuxertal (Tux Valley) during the reference-date sampling described here are freely available as xlsx and csv-file at TUDatalib, https://doi.org/10.11583/tudatalib-400.

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