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Integrative assessment of urban groundwater quality in the city of Munich, Germany: Spatio-temporal patterns of hydrochemical and selected microbial indicators

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A R T I C L E I N F O

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A B S T R A C T

Urban areas are expanding worldwide. Consequent changes to the environment, such as surface sealing, underground structures, and alterations to vegetation, do not only affect the surface but also impact the subsurface. Groundwater, a crucial natural resource for humankind, an essential water resource to plants, and a huge aquatic ecosystem, is potentially threatened by these changes. In particular, the hydraulic conditions and the water quality in shallow urban aquifers are being altered significantly. This study focuses on the shallow aquifer of the city of Munich, Germany, examining it in terms of urban land use classes (dense and discontinuous sealed surfaces, parks, forests, and agricultural sites) and typical physical and chemical measures used in standardised groundwater monitoring. In addition, the groundwater quality assessment is complemented by selected microbiological indicators. The objective of the study was to evaluate if physical, chemical and microbiological variables are suited for a routine groundwater monitoring in an ecological manner and if they show the same distribution patterns in an urban environment. Groundwater below the five land use categories distinguished showed differences in variables such as chloride concentration, temperature, and total bacterial cell counts. However, the considerable natural variation in the depth of the groundwater table across the city partly masked the effect of urban land use on groundwater hydrochemistry. Bacterial activity in shallow urban groundwater, measured as cellular ATP concentrations, on average, was in the range of clean surface waters rather than near-natural groundwater. Concentrations of dissolved organic carbon (DOC) and nutrients, on the other hand, were overall low. In summary, Munich's shallow gravel aquifer mirrors an energy-limited, oligotrophic ecosystem. Strong correlations were observed between bacterial cell counts and DOC concentrations, with groundwater temperature being a significant influencing factor alongside the concentration of major ions. Some of the physical–chemical variables and microbiological measures exhibited variations between two sampling seasons, as well as between well water and pumped groundwater. In conclusion, the consideration of land use classes provided useful information on the impact of urbanisation on groundwater hydrochemistry and microbiology. Both sets of criteria sensitively indicated deviations of the urban to rural groundwater characteristics. Finally, seasonal effects and differences in the type of water sampled need to be considered for the setup of a routine integrative monitoring scheme.

1. Introduction

The overall percentage of the human population living in large cities is continuously growing, with a rise from 33 % to 66 % between 1950 and 2018 (United Nations, 2019). Continuous urbanisation yields expansion of sealed surfaces, extraction and redistribution of soil, changes in vegetation, the production and release of significant amounts of waste and significant changes in the hydrological cycle (Becher et al., 2022; Grimm et al., 2008). In cities, the anthropogenic pressures on groundwater bodies are manifold and most pronounced in shallow aquifers. Among typical impacts on groundwater quantity are altered flow regimes by pumping or the hydraulic effect of subsurface

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infrastructure. Also, groundwater recharge rates are altered due to changes in evapo(transpi)ration, infiltration, and runoff rates from sealed surfaces (Kløve et al., 2011; Weatherl et al., 2021). Groundwater quality beneath built-up areas is often modified as well. Many urban environments are hot spots of chemical pollution and there is considerable leakage from wastewater pipes (Foster, 2020; Popp et al., 2024). Salts are introduced into the environment from de-icing agents, and heavy metals from waste and traffic accumulate in urban areas (Becher et al., 2022). It is well-documented that the chemical composition of groundwater is affected in urban environments, with increased levels of nutrients, i.e., phosphate (PO_4^{3-}) (Huang et al., 2020) and nitrogen compounds (Kuroda & Fukushi, 2008). Although urban surfaces are sealed to a large degree, some groundwater recharge takes place (Sharp, 2010). Due to increased surface runoff and temporarily decreased evapotranspiration, groundwater recharge in urban areas can still be significant (Barron et al., 2013; Passarello et al., 2012; Sharp, 2010), introducing contaminants into the subsurface. Additional sources of groundwater recharge and pollutants include leaking sewer pipes and losses from supply networks (Lerner, 2002; Minnig et al., 2018; Tubau et al., 2017; Vázquez-Suñé et al., 2005). The average urban groundwater recharge of Munich, Germany is about 280 mm/a (Zosseder et al., 2015). Currently, the city of Munich is implementing a sponge city concept with various infiltration systems enabling a higher groundwater recharge all over the city. Such approaches can reduce flood risks, compensate groundwater recharge, replenish groundwater with dissolved oxygen (DO), and limit peak flows and volumes of surface runoff (Lucassou et al., 2024; Pitt et al., 1995). However, implementing sponge city concepts also present challenges. Urban runoff is typically highly contaminated with salts, heavy metals, and organic compounds like pesticides and biocides, which could infiltrate soil and reach groundwater (Pinasseau et al., 2020). Additionally, modifying existing cities and infrastructure to introduce new sewage systems and rainwater storage capacities can be difficult. In Munich, 46 % of the surfaces are sealed, and space to implement new structures is limited especially in highly sealed districts like Maxvorstadt (Al-Azzawi et al., 2022; Statistisches Amt München, 2017).

Another pressure to the urban subsurface is warming. Temperatures in shallow urban groundwater are typically much higher than in near-natural rural environments. This is mainly due to enhanced heat input from sealed surfaces and basements of buildings (Benz et al., 2016; Böttcher & Zosseder, 2022; Menberg et al., 2013a). In addition, local heat sources such as district heating networks, tunnels or underground car parks contribute to warming (Epting et al., 2017; Noethen et al., 2023). The superpositioning of various heat sources in cities is described as subsurface urban heat islands (SUHIs). Presence of SUHIs are reported for many cities worldwide (Böttcher & Zosseder, 2022; Headon et al., 2009; Hemmerle et al., 2019; Menberg et al., 2013a; Previati et al., 2022; Visser et al., 2020; Zhang et al., 2022). Changes in groundwater hydrochemical composition and temperature are expected to affect and alter microbial and faunal communities as well (Griebler et al., 2016; Gruzdev et al., 2023).

Groundwater is not only an important water resource essential for human well-being, but it represents the largest freshwater biome on Earth, hosting a diverse range of prokaryotic and eukaryotic organisms (Fillinger et al., 2023; Hose et al., 2023; Karwautz et al., 2022; Marmonier et al., 2023; Ruff et al., 2023). Shallow aquifers are open systems in continuous exchange with surface aquatic and terrestrial environments and may exhibit a considerable high biodiversity (Hubalek et al., 2016; Ward et al., 2017). The active and diverse microbial communities, in particular, play a crucial role in biogeochemical cycles and self-purification processes within the subsurface (Griebler & Avramov, 2015).

In addition to microbes, shallow aquifers harbour an array of invertebrates contributing important ecosystem functions through active bioturbation, unclogging pore space (Hose & Stumpp, 2019; Stumpp & Hose, 2017), and their feeding activity on biofilms, stimulating microbial activity (Griebler & Avramov, 2015; Mermillod-Blondin et al., 2023; Schmidt et al., 2017). While groundwater ecosystems on the one hand provide important services, they are specifically sensitive to disturbance on the other hand (Griebler et al., 2019). Although groundwater ecosystems depend on input of organic carbon and nutrients from the surface, a surplus of energy leads to severe changes in environmental conditions and ecosystem disturbance, i.e., groundwater warming, oxygen depletion and a shift to anoxic conditions.

Our current understanding of the interactions between changing environmental conditions and of microbial communities and their activities in groundwater ecosystems is limited. This is due to the challenging and commonly only punctual access to groundwater bodies when compared to surface waters. Modern groundwater ecology, which aims to systematically investigate and understand the relationships and interactions between biotic and abiotic components, has developed to its current form since the 1990 s (Danielopol & Griebler, 2008; Koch et al., 2024). In particular, urban environments with their diverse and mosaic-like land use patterns are still underrepresented in research, despite potentially serving as model systems for studying effects of diverse contamination and warming on ecosystem biodiversity and functions. In fact, cities often have a well-established and dense groundwater monitoring network, allowing a high spatial resolution.

One aim of modern groundwater ecological research is to develop integrative and sound assessment strategies comparable to protocols existing for surface waters (EU, 2014; Griebler et al., 2014; Hose et al., 2023; Marmonier et al., 2018; Saccò et al., 2024). Currently, groundwater monitoring routines primarily focus on quantity and quality, with the latter defined by its chemical and hygienic status. Ecological criteria, i.e., microbial communities and invertebrate fauna, are not routinely considered so far (Hahn et al., 2018). In Germany, physical and chemical thresholds are defined by the German Drinking Water Directive (BRD – Bundesministerium der Justiz, 2023) with monitoring and analysis protocols agreed upon decades ago. The list of priority and target chemicals is steadily growing. Additionally, for the assessment of hygienic water quality, *Escherichia coli* and coliform bacteria are applied as indicators to detect the influence from faecal pollution (Jiang et al., 2018; Wicki et al., 2015). However, beyond drinking water monitoring, the assessment of groundwater bodies as complex ecosystems and the definition of an ecological status are rarely included in management plans and strategies. In consequence, there are current efforts in identifying and testing ecological criteria that can be incorporated into groundwater monitoring routines (Fillinger et al., 2019; Retter et al., 2021). Microbial communities appear well-suited for this purpose, as they are ubiquitous and respond rather fast to environmental disturbances. Moreover, groundwater microbial communities differ significantly from their surface water counterparts in terms of activity, cell abundance, and community composition (Retter et al., 2023). Consequently, these measures provide indication of surface water intrusion and organic pollution. Based on these assumptions, the D-A-C (density – activity – carbon) index, delivering a water sample's microbial fingerprint, was developed. It is applied to detect deviations in the microbiological-ecological water quality in comparison to a predefined reference state and can help to define management strategies (Fillinger et al., 2019; Retter et al., 2021).

The overarching objective of this study is to evaluate urban groundwater quality by means of selected microbiological criteria in combination with routine physical and chemical variables. Groundwater quality is further assessed with respect to water levels, urban land use gradients and different seasons. We carried out two repeated field campaigns, sampling about 100 monitoring wells each, distributed all over the city of Munich, Germany. A multitude of physical, chemical, and microbial key variables were recorded with sampled well water and pumped groundwater, evaluating the suitability of different sampling routines. We hypothesised that physical, chemical, and microbial conditions of well water and groundwater significantly differ in various parameters. A particular focus of the study was on groundwater temperature as a potential key driver steering microbial dynamics. As highlighted in previous studies by Böttcher et al. (2022), we expected to find SUHIs below the city. The city of Munich, Germany, was chosen as study site to benefit from the dense network of monitoring wells available and rich background information on hydrology, hydrochemistry, and in-situ conditions (Böttcher et al, (2022), Zosseder et al. (2022), Kiecak et al. (2023)), Munich is considered a representative Central European city underlain by a productive, oxygen-rich shallow aquifer. It represents a well-studied showcase for assessing urban effects on shallow groundwater ecosystems.

2. Material and methods

2.1. Study area

The study was conducted in the city of Munich, Germany. Munich is a large (310 km^2) and densely populated (1.56 m inhabitants) urban area. The land use in Munich is highly diverse, with the primary forms being residential buildings and industrial areas (58.5 %). Streets and other traffic areas cover 16.9 % of the city. Parks, forests, and water bodies also constitute a significant portion of land surface (24.7 %) and consequently influence the city's climate and subsurface temperatures (BLS, 2023). In particular, 13.4 % of the area is covered by parks, with the English Garden being the largest one, located directly in the city centre close to the Isar River. This river is the largest water body in Munich, flowing through the city from south to north for 13.7 km. As the primary receiving stream for groundwater, the Isar River influences the direction of groundwater flow in its vicinity. Overall, groundwater flow direction in the shallow Quaternary aquifer of Munich is from south to north and northeast (Bauer et al., 2006; Zosseder et al., 2022) (Fig. 1).

Focus of the study is set on shallow groundwater in the Quaternary aquifer, with water levels below land surface (b.l.s.) ranging from less than 2 m depth in the north of the city to more than 22 m in the south. The southward decrease in groundwater levels is attributed to the inclination of the 2,000 km^2 Munich Gravel Plain, which thins out to the north and dips northwards by 0.5 % (Böttcher & Zosseder, 2022; Jerz,

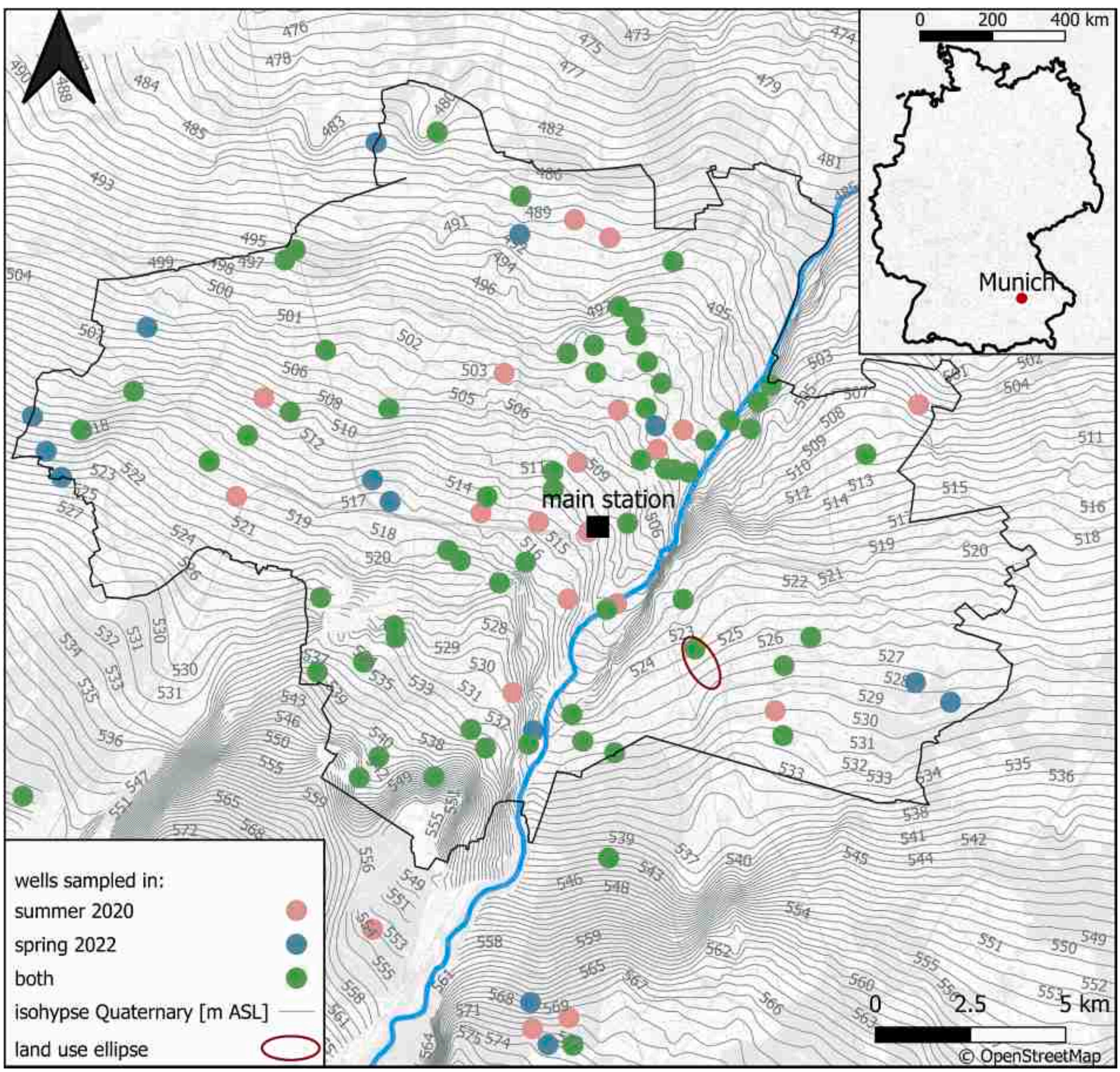

Fig. 1. Map of the city of Munich with sampled groundwater wells highlighted, shallow groundwater contours, and an exemplary ellipse of land-use class calculation; for further explanation, see the text.

1993; Zosseder et al., 2022). Consequently, the Munich Gravel Plain is situated at an altitude of 650 m above sea level in the south and 430 m above sea level in the north, with a slope varying from 12 ‰ in the southern part to 2 ‰ in the north (Dohr & Gruban, 1999). The lithographic units of the Munich Gravel Plain primarily consist of glaciofluviatile gravel terraces deposited during the Pleistocene (Bauer et al., 2006). The porous aquifer is highly productive, with an average hydraulic conductivity of about 3.7×10^{-3} m/s (Theel et al., 2020).

The Quaternary terraces overlay Neogene sediments that filled the Bavarian Molasse Basin (Bauer et al., 2006; Zosseder et al., 2022). These Tertiary fine-grained deposits of fluviatile and lacustrine origin attain thicknesses of several kilometres and also host a deeper aquifer where groundwater extraction occurs at depths of up to 150 m (Bauer et al., 2006; Zosseder et al., 2022). The first shallow Tertiary aquifers sometimes show hydraulic connection to the Quaternary aquifer (hydraulic exchange) (Rauert et al., 1993; Zosseder et al., 2022). Likewise, about four aquifer horizons exist within the Tertiary sediment and interact with each other and with the Quaternary aquifer, influencing the hydrochemistry of different aquifers (Kiecak et al., 2023).

In addition to the data generated in our study, two datasets of previous sampling campaigns in the city of Augsburg, Germany (groundwater from the Lech River wetlands) and the city of Freising, Germany (urban to rural groundwater) are used for reasons of comparison. Data from the city of Freising originate from a study conducted by Brielmann et al. (2009) in rural locations outside the city. Freising is located about 15 km north of Munich and belongs to the same Quaternary aquifer system. Rural groundwater data from Freising therefore serve as reference for comparison with samples from the urban environment of Munich. Groundwater samples from the Lech River wetlands (Augsburg), collected in 2016, also originated from a Quaternary porous gravel and sand aquifer. Further details are found in Fillinger et al. (2019).

2.2. Sampling and laboratory analysis

Groundwater and well water were collected in August and September 2020 (summer campaign: *su*) and April 2022 (spring campaign: *sp*). For these campaigns, we preselected 102 wells for the first campaign distributed throughout the entire city area of Munich (Table 1, Fig. 1). Due to inaccessibility of some wells during the second field campaign and the need to include rural groundwater sites with shallow water levels, data sets slightly differ between the two field campaigns. Also, unsuitable wells (clogged wells, wells with a low water column, wells with inappropriate diameter) were ignored for the second campaign. In total, 99 wells were sampled during the second campaign. In total, 201 samples of well water and 160 samples of pumped groundwater were collected during the two campaigns: less pumped groundwater samples were due to small well in which the submersile pump could not fit and wells characterized by very short water columns and low hydraulic conductivity, unsuitable for groundwater production.

During sampling, temperature profiles in the wells were initially recorded at each site in 1-m-depth intervals from the top of the groundwater level to the bottom of the wells. Temperature and electrical conductivity (EC) profiles were recorded using an electric contact gauge (Type 120 – LTC, Hydrotechnik, Obergrünzburg, Germany) in wells with a diameter of $\geq$ 2 in.. Additionally, a multiparameter probe (KLL-Q-2 with MPS-D8, SEBA, Kaufbeuren, Germany) was used to monitor pH, redox potential (Eh), and the concentration and saturation of DO. These results will be referred to as well water samples in the following.

The sampling routine was continued by taking samples from the well water column and subsequently pumping groundwater, both types of samples dedicated to hydrochemical and microbial analyses. Water samples from the well were obtained using a bailer, and extraction of groundwater was conducted using a Grundfos submersible MP1 pump (Eijkelkamp, The Netherlands). Pumped groundwater samples were taken after replacement of twice the well water volume and once

Table 1
Land use classes summarised from CORINE Land Cover database 2018 (Copernicus, 2020) and number of sampled wells within both field campaigns, assigned land use class for each site correlates to highest amount of land use within individual ellipse of each well; S.S. – sealed surfaces, n – number of sampled wells.

Land use class	Land use classes according to the CORINE Land Cover database 2018 (Copernicus, 2020)	n summer	n spring
Dense urban (S.S. > 80 %)	Continuous urban fabric (S.S. > 80 %)	22	17
Discontinuous urban (S.S. 10–80 %)	Discontinuous dense urban fabric (S.S. 50–80 %)	49	38
	Discontinuous medium density urban fabric (S.S. 30–50 %)		
	Discontinuous low density urban fabric (S.S. 10–30 %)		
	Isolated structures		
	Traffic structures (other roads and associated land)		
	Industrial, commercial, public, military, and private units		
Parks	Green urban areas	11	14
	Sports and leisure facilities		
	Sports and leisure facilities		
Agriculture	Arable land (annual crops)	6	15
	Permanent crops		
	Pastures		
	Complex and mixed cultivation patterns		
	Orchards at the fringe of urban classes		
Forest	Forest	14	15
	Herbaceous vegetation associations		

stability of key variables (temperature, EC, DO, Eh) was reached. Except for Section 3.3, the reported results refer to pumped groundwater samples (referred to as groundwater). Samples dedicated to hydrochemical and adenosine triphosphate (ATP) analysis were filled into clean and sterile glass bottles without treatment. Samples for total (prokaryotic) cell counts (TCC) were collected in sterile 15 ml Falcon tubes containing a fixative (glutardialdehyde 0.5 % f. conc.). Additionally, samples for the analysis of dissolved organic carbon (DOC) were filtered through prerinsed 0.45 µm polyvinylidene difluoride (PVDF) syringe filters on-site. Hydrochemical analysis of well and groundwater included the measurement of major anions and cations by ion chromatography (Dionex, Thermo Fisher Scientific Inc, Waltham, MA USA), as well as the quantification of DOC (Shimadzu, Japan). To assess the microbiological-ecological state of groundwater, TCC (in cells/L) and the concentration of cellular ATP (in pM) were determined. Prokaryotic cell counts were quantified using flow cytometry (FC500 CYTOMICS; Beckman Coulter, Brea, CA, USA). A detailed description of the corresponding protocol is found in Fillinger et al. (2019).

For ATP measurements, the BacTiter-Glo Microbial Viability Assay Kit (Promega, Madison, WI, USA) was applied. The protocol, based on Hammes et al. (2010) and detailed in Fillinger et al. (2019), was used with slight modifications. Sample preparation and measurements were conducted at room temperature as recommended by the manufacturer's instructions. To detect the luminescence emerging from the ATP-dependent oxidation of luciferin catalysed by luciferase, a GloMax 20/20 luminometer (Promega, Madison, WI, USA) was used. The ATP calibration curve was prepared by serial dilution of an external ATP standard (100 nMol, BioThema, Handen, Sweden) in ATP-free water (Invitrogen™ UltraPure™, Fisher Scientific, Waltham, MA, USA). Total and external ATP were measured on unfiltered and 0.1 µm filtered (Millex® 33 mm PVDF, 0.1 µm) samples, respectively. Cellular ATP concentrations were calculated by subtracting external ATP from total ATP (Hammes et al., 2010). All measurements were performed in triplicates.

2.3. Data evaluation

2.3.1. Statistics and categories

Besides the abiotic (physical–chemical) and biotic (microbiological) variables measured, selected environmental drivers were included in the statistical analysis as categories, each with three to five classes. The predefined categories included the depth of the groundwater table (water level), land use, and distance to the city centre (CCD). Depth to the groundwater table was recorded during the field campaigns and categorised into the classes: 0–5 m, 5–10 m, 10–15 m, and > 15 m. Different land use classes were computed via Python using the digital atlas of Germany from the CORINE Land Cover database 2018 (v2020_20u1, (Copernicus, 2020)). To improve statistical testing, the 27 original land use categories were combined to five categories, namely (1) dense urban, (2) discontinuous urban, (3) parks, (4) agricultural area, and (5) forests (Table 1). The dense urban class contained areas with a surface sealing of more than 80 %. Surface sealing between 10 and 80 % is represented by the class discontinuous urban (Table 1). Recognising that a single point value defined by the coordinates of each well is not representative for the impact on groundwater with respect to flow direction and residence time in the subsurface, we estimated individual catchments of impact for each groundwater well considering the upgradient region of the wells with respect to local groundwater flow (Böttcher & Zosseder, 2022). These catchments are ellipse-shaped, with the well at the downgradient end (Fig. 1). The size and shape of each ellipse were calculated individually using Eq. (1). The width l thereby is the groundwater flow velocity in m/day which is calculated using values determined by Böttcher & Zosseder (2022) and Zosseder et al. (2022) (Eq. (2). Also, height h is calculated using groundwater flow velocities (Eq. (3).

$$A = \pi \bullet l \bullet h \tag{1}$$

$$l = 365 \bullet \vartheta \tag{2}$$

$$h = l/4 \tag{3}$$

Each ellipse was individually rotated according to groundwater flow directions according to Böttcher & Zosseder (2022) and Zosseder et al. (2022) (Eq. (4).

$$\alpha = 360 - (\varphi - 180) \tag{4}$$

Ellipses were drawn in the way that the well was placed at the top of the ellipse (S.1.1) and the middle of the ellipses were calculated using the point positions of each well (*x0, y0*) with Eqs. (5)–(7). The dominating land use class covering the most part of each ellipse was then assigned to the related well.

$$x = x0 + d \bullet \cos(theta\_rad) \tag{5}$$

$$y = y0 + d \bullet \sin(theta\_rad) \tag{6}$$

$$theta\_rad = \frac{\pi}{2} - radians(theta) \tag{7}$$

Distance to the city centre was calculated using GIS methods (distance to next neighbour). The city centre was defined as the Munich main train station (Fig. 1), and the distance of each well to this point was assigned to distance classes of 0–0.2 km, 0.2–0.4 km, 0.4–0.6 km, and > 0.6 km.

Normal distribution of the data was tested using the Shapiro-Wilk test. As no normal distribution was observed for any dataset, non-parametric tests were employed for all subsequent statistical analyses. Land use classes, depth to the groundwater table, and CCD underwent testing through the Kruskal-Wallis H test, an extension of the Mann-Whitney U test and the non-parametric equivalent of ANOVA. The non-parametric Mann-Whitney U test was used to examine differences between sampling campaigns. Differences between well water and pumped groundwater were tested using the non-parametric Wilcoxon rank-sum test for paired samples. Correlation analyses were conducted using the ranked Spearman test for all variable combinations. All statistical tests were conducted using SPSS (IBM Corp. Version 28.0). The presented maps were generated with QGIS (QGIS Development Team, version 3.12), and plots were created with Python (Python Software Foundation, version 3.11.7, https://www.python.org/), in addition to SPSS.

2.3.2. D-A-C index

As introduced by Fillinger et al. (2019), the D-A-C approach is a statistic outlier test assessing the deviation of a sample, defined by 3 variables, i.e., cell density (TCC = D), microbial activity (intracellular ATP = A), and DOC (= C), from the mean of the entire data set or from a reference group. The D-A-C index is calculated using the Mahalanobis distance which combines all selected variables in a multivariate outlier analysis. This multivariate analysis is more robust and sensitive in detecting outliers compared to univariate analysis (Retter et al., 2021). In this multivariate space, normally distributed data will form an ellipsoid cloud defined by the mean values of the microbiological variables and the covariance matrix determining the shape and slope of the ellipse (Retter et al., 2021). To achieve normal distribution, data were log-transformed prior to the analysis.

We may distinguish a guided and unguided application of the D-A-C index. In an unguided approach no reference group is defined, and the analysis is based on the entire dataset. With the guided approach, one or more reference groups are defined, and outliers are classified as significantly different from these references. For our study, in a first step, reference groups consisted of all urban pumped groundwater samples displaying a good chemical status according to the German Drinking Water Directive (BRD, 2023) and natural hydrogeological background values delineated for Munich. A second reference group combined groundwater samples collected in forested areas which we assumed to be representative for most natural conditions in the vicinity of Munich. In the end, we combined both reference groups since the outliers detected in the unguided approach showed that both reference groups clustered together.

All calculations were performed with R Statistical Software (v4.3.0, R Core Team, 2021).

3. Results and discussion

3.1. Temporal patterns

3.1.1. Physical and chemical variables

Groundwater temperature and DO values from both field campaigns in summer 2020 and spring 2022 are illustrated in Fig. 2. Median groundwater temperatures from pumping over the entire study area in 2020 were 13.2 °C (9.7–20.4 °C), which is 1.7 K higher than during the spring campaign in 2022, where a median temperature of 11.5 °C (7.1–17.2 °C) was calculated ($p = 0.000$, Table S.1, Table 2). The most pronounced temperature change between the two campaigns was observed for a sampling site in the city centre with a shift of 2.8 K. Highest temperatures with 20.2 °C and 20.4 °C were recorded in the same area, indicating a well-developed SUHI with groundwater temperatures above the recommended maximum of the German Drinking Water Directive (BRD, 2023) (Table 2). Groundwater temperatures in the Munich city centre ranged from 13.0 to 20.4 °C with a median temperature of 16.3 °C in the summer of 2020, while in spring 2022 a median temperature of 14.1 °C was measured, with values ranging from 10.2 to 16.0 °C (Table S.2). At the same time, groundwater temperatures in forested sites outside the city were much lower with differences to city centre of 5.8 K during the summer and 4.1 K during the spring campaign. Similar spatial temperature differences as well as seasonal dynamics were also detected in previous studies for Munich, Germany (Böttcher & Zosseder, 2022) or Vienna, Austria (Steiner et al., 2024). In Europe,

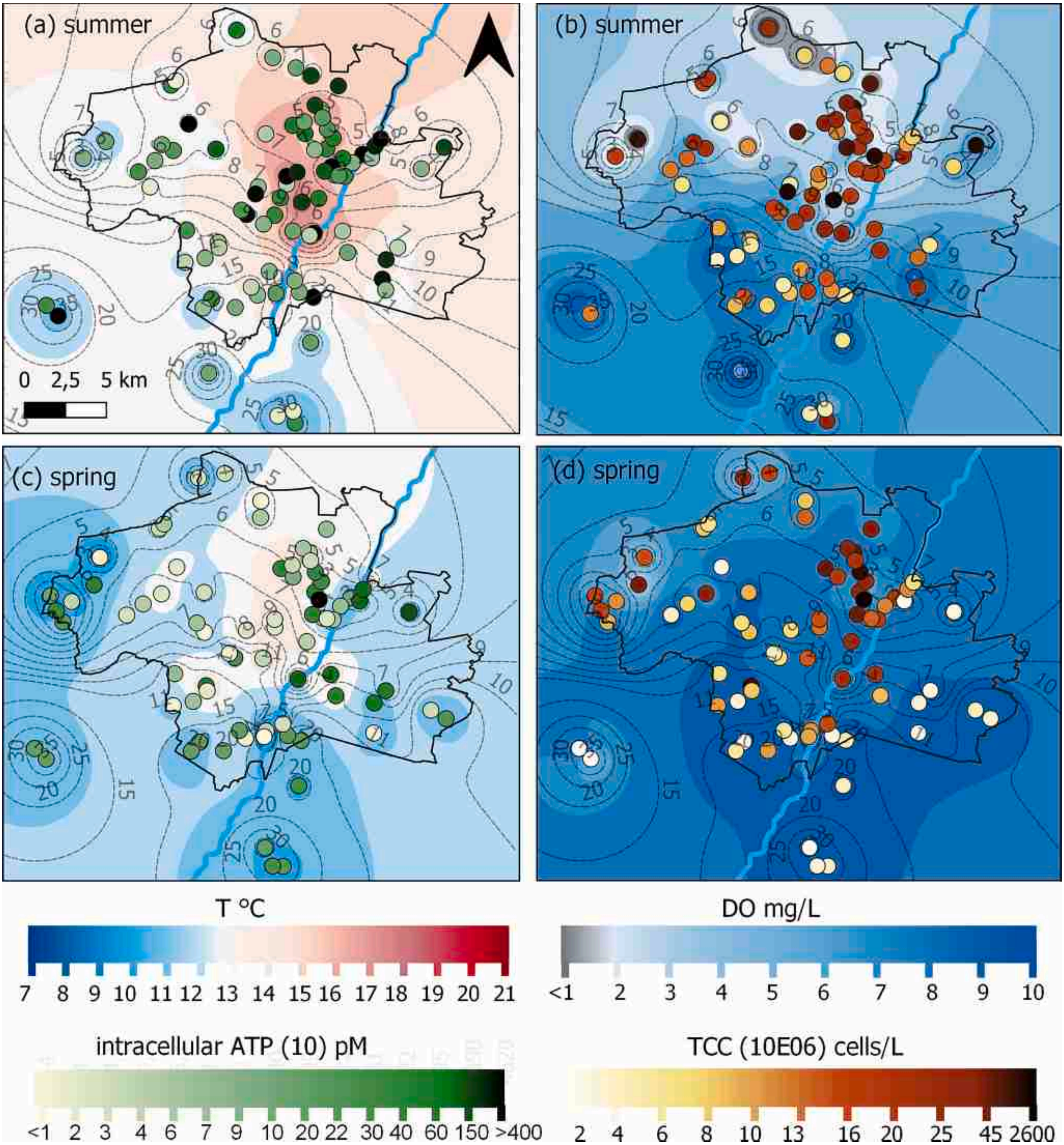

Fig. 2. Maps of temperature and intracellular ATP concentration (a, c) and oxygen concentration and bacterial cell counts (b, d) measured in Munich during summer 2020 und spring 2022.

SUHIs tend to be most developed during summer and autumn, and differences observed in winter and spring are not as pronounced (Zhang et al., 2022). This is consistent with the observations from our campaigns in Munich.

As Zhang et al. (2022) pointed out, seasonal variation in urban groundwater temperature can be attributed to multiple factors. Firstly, sealed surfaces have a lower buffer capacity than grassland or bare soils, leading to a faster heating of built-up areas during summer. The SUHI effect during summer is also exacerbated due to lower albedo and decreased evaporation cooling effect (Schweighofer et al., 2021; Zhang et al., 2022). Moreover, winter temperature fluctuations are influenced by cold fronts, assuming a faster temperature drop due to rain and snow. Factors affecting temperature on a smaller scale include microclimate, regional rainfall, urbanisation degree, infiltration from surface waters, and infrastructures (Zhang et al., 2022).

Similar to groundwater temperatures, DO concentrations differed significantly between the two campaigns ($p = 0.000$, Table S.1), however, in an opposite manner. The median DO concentration in summer

Table 2
Background values and measured median values of key physical and chemical variables in the Munich area; all ion concentrations are given in mg/L.

Variable	Threshold values for Germany[1]	Background values of Munich[2]	Measured values of Freising[3]	Background values of gravel and moraine deposits of alpine foreland[4]	Median values & ranges **2020**	**2022**
T (°C)	± 6 K, max. 20 °C[5]	12 °C (average)			13.2 (9.7–20.4)	11.5 (7.1–17.2)
EC (µS/cm)	2790	972	> 670/900	641	684 (376–1040)	688 (393–923)
DO (mg/L)			< 2.8/2.3	7.4	5.8 (0–10)	7.88 (0.77–9.67)
pH	6.5–9.5	7.62		7.3	7.6 (6.9 – 9.2)	7.4 (7.1–7.9)
Cl^-	250	65.8		16.3	37.0 (1.6–114)	38.3 (2.08–157)
F^-	1.5	0.22		0.08		
NO_2^-	0.5			0.001		
NO_3^-	50		> 9.0/24.8	16.8	15.6 (1.3–30.7)	16.6 (3.37–31.7)
HCO_3^-		465		359		
SO_4^{2-}	250	77.2		20	15.9 (5.22–169)	17.4 (7.33–130)
PO_4^{3-}			> 0.2/0.1	0.02	0.25 (0.16–1.34)	0.02 (0.001–1.06)
K^+		4.63		1.4	2.44 (0.17–9.77)	1.88 (0.28–5.84)
Na^+	200	24		5.9	28.1 (1.39–98.3)	19.3 (1.87–48.1)
NH_4^+	0.5	0.04	> 0.01/0.006	0.001	0.16 (0.05–0.22)	0.05 (0.02–0.12)
Ca^{2+}				101	76.2 (23.7–140)	73.1 (34.7–105)
Mg^{2+}		33.7		22.2	20.2 (5.52–48.4)	16.8 (10.1–36.0)
TOC/DOC			0.8	−/> 2	0.89 (0.49–6.92)	1.06 (0.8–2.31)

1: BRD – Bundesministerium der Justiz (2023), 2: Landeshauptstadt München (2024), 3: Brielmann et al. (2009), 4: Kunkel et al. (2004), 5: VDI (Verein Deutscher Ingenieure) (2010).

was 5.8 mg/L (0.0–11.6 mg/L), whereas DO concentrations during the spring campaign ranged from 0.8 to 9.7 mg/L with a median concentration of 7.88 mg/L (Table 2). Higher DO concentrations in spring can be explained by lower groundwater temperatures, characterised by a higher solubility of oxygen and simultaneous lower consumption rates of organisms. Groundwater recharge is quantitatively most pronounced during early spring replenishing oxygen into the aquifer. In summer, microbiological activity was higher, and oxygen consumption was increased compared to the wintertime (see also subsequent section 3.1.2).

DOC did not show significant differences between the two field campaigns ($p = 0.350$, Table S.1). In general, DOC concentrations were low and point to an energy-limited, oligotrophic aquifer status. This contrasts with our earlier assumption that the urban aquifer may experience elevated inputs of organic contaminants, e.g., through urban groundwater recharge and wastewater contribution from leaking sewage pipes. Similar to our study, Griebler et al. (2016) reported DOC values around of 1 mg/L for groundwater collected in Munich.

Significant differences between the two field campaigns were observed with individual ions. Groundwater samples collected in summer contained higher sodium (Na^+) and magnesium (Mg^{2+}) levels, with median concentrations of $Na^+ = 28.1$ mg/L and $Mg^{2+} = 20.2$ mg/L when compared to spring ($Na^+ = 19.3$ mg/L, $Mg^{2+} = 16.8$ mg/L, Table S.2). Possible explanations for this observation include the origin of the water from different recharge events and temperature-related differences in mineral dissolution of seepage water. Similar patterns, though not statistically significant, were observed for ammonium (NH_4^+) (0.16 vs. 0.05 mg/L), and PO_4^{3-} (0.25 vs. 0.02 mg/L). Higher levels of macronutrients, such as PO_4^{3-} and NH_4^+, in summer may be related to their application to land surface during spring and summer. Overall, PO_4^{3-} and NH_4^+ concentrations were very low. This is expected in an oxic aquifer, where a surplus of NH_4^+ is oxidised to nitrate (NO_3^-) by nitrifying bacteria (Utom et al., 2020) and PO_4^{3-} tends to adsorb and complex with metal species and humic substances (Bengtsson, 1989; Brielmann et al., 2009; Hofmann & Griebler, 2018). Groundwater from several wells exceeded NO_3^- concentrations of 15 mg/L, which may be linked to the infiltration of river water, the application of fertilisers in parks and arable land surrounding the city, or domestic wastewater leaking from sewage pipes (Hansen et al., 2017). Worth mentioning is that the threshold value of 50 mg/L, set by the German Drinking Water Directive, was by far not reached.

For a comprehensive assessment and interpretation of the physical and chemical state observed in urban groundwater of the shallow Quaternary aquifer in Munich, Table 2 provides threshold values from the German Drinking Water Directive, as well as natural background values for Munich and Freising, and values for other gravel deposits in the alpine foreland. In fact, none of the chemical parameters recorded in urban groundwater of Munich exceeded its drinking water threshold values. Indeed, groundwater from some individual wells exhibited elevated concentrations of Na^+ and chloride (Cl^-), indicating effects of winter salt application (Becher et al., 2022). Similarly, slightly increased concentrations of nutrients (NO_3^-, NH_4^+, PO_4^{3-}) compared to reference sites from Freising and other gravel aquifers of the alpine forelands were observed, potentially stemming from fertilisers applied to arable land and inner-city parks and wastewater. Similarly, DO concentrations were in good agreement with reference values for gravel aquifers of the alpine forelands (Kunkel et al., 2004, Table 2). The only exception is groundwater temperature, which showed values from Munich exceeding legal thresholds. Within the city limits of Munich, groundwater pattern from the city revealed a stronger signal of urbanisation than groundwater collected in the rural areas of the city outer margins. This is especially true for groundwater temperature, the concentration of Cl^- and sulphate (SO_4^{2-}), all higher on average in wells of the city centre.

3.1.2. Microbiological variables

Results of TCC and intracellular ATP values for both campaigns are depicted in Fig. 2. Statistical analysis revealed significant differences between the two campaigns for both variables ($p = 0.000$, Table S.1), indicating higher median cell numbers of 1.7×10^7 vs. 1.1×10^7 cells/L and median intracellular ATP concentrations (206 pM vs. 69.4 pM, Table 3) during the summer season. While higher cell numbers and microbial activities might be explained by higher groundwater temperatures in summer, it is important to mention that cell-specific activities were slightly higher during the spring campaign (0.016 vs. 0.021 fmol ATP/cell). This indicates that groundwater recharge in spring may stimulate microbial growth in shallow groundwater, first increasing the cell-specific activity, followed with some delay by cell production as has been observed in other studies (Hofmann & Griebler, 2018). Independent from the season, cell numbers and microbial activities in the urban groundwater of Munich needs to be compared to reference values from non-urban and near-natural sites. Similar to physical and chemical variables, which are widely used in groundwater quality assessment and monitoring, microbiological indicators. i.e., TCC and cellular ATP, can be applied to assess anthropogenic impacts and groundwater contamination (Fillinger et al., 2019; Noethen et al., 2024; Retter et al., 2021). In this regard, reference values from oligotrophic aquifers and various less impacted sites have been considered (Table 3). Surprisingly, total cell numbers in the urban shallow groundwater of Munich aligned well with values observed at different reference sites in Germany and a hypothetical oligotrophic aquifer (Table 3, Griebler et al. (2014)). Only very few groundwater samples contained more than 1×10^8 cells/L. Here, surface water influence, impact from agricultural land use and/or organic contamination from various potential sources, as well as a shift to anoxic conditions, are common causes (Griebler et al., 2014). Sites with groundwater containing elevated cell numbers mainly clustered in the northern part of the city and the city centre (Fig. 2). As visible in Fig. 2, the same wells showed high TCC concentrations in both campaigns. Those sites that were sampled only once during the summer campaign (Figs. 1 and 3) were all located within the land use classes 'dense urban' and 'discontinuous urban' characterised by the most elevated groundwater temperatures (Fig. S.1). Individual wells delivered groundwater with a high turbidity, and consequently high cell numbers and high microbial activities. In conclusion, it is hard to say if these high TCC and ATP concentrations were due to high temperatures in summer season, location in the city centre or because of clogging. While only a limited number of groundwater samples contained high TCC, microbial activity, i.e., cellular ATP concentrations, were high in most samples with only a few wells displaying values comparable to oligotrophic and near-natural aquifer conditions (up to 30 pM cellular ATP) (Griebler et al., 2014). Cellular ATP concentrations in Munich groundwater were found in the range typical for undisturbed surface waters. Summing up, our microbiological-ecological indicators point at a microbial community in urban shallow groundwater that deviates in its biomass and activity pattern from reference sites (Fig. 3). However, it is mainly the microbial activity which is elevated while cell numbers are insignificant. That microbial biomass and activity are sensitive indicators of ecosystem disturbances is supported by other studies, i.e., on anthropogenically impacted aquifers (De Lambert et al., 2021), groundwater bodies with direct connections to the surface (Bougon et al., 2012), or groundwater quality in the vicinity of an urban open-loop ground source heat pump system (Barnett et al., 2023). Samples with similarly low values of cellular ATP, like those from the Lech River wetlands, originated from sites of different land use and groundwater levels, strongly indicating that besides the factors recorded, additional abiotic or biotic drivers may influence the microbiological pattern.

3.2. Spatial patterns

3.2.1. Physical and chemical variables along different land use gradients

Looking at groundwater temperatures first, there is a noticeable agreement with the temperature distribution across the city reported by Böttcher & Zosseder (2022), with the highest temperatures present in the city centre in both sampling campaigns. Higher groundwater temperatures indeed correlate with extent of sealed surfaces and built-up areas in Munich. Comparable results were also reported for other cities like Karlsruhe, Germany (Koch et al., 2021; Menberg et al., 2013b), Nuremberg, Germany (13.2 °C, 10.2–16 °C) (Schweighofer et al., 2021), Nanjing, China (Zhang et al., 2022), Cologne, Germany (Hemmerle et al., 2022), Paris, France (Hemmerle et al., 2019), Vienna, Austria (Steiner et al., 2024), or Amsterdam, The Netherlands (Visser et al., 2020). However, cities do not necessarily have the highest groundwater temperatures in the city centre. Frequently, there are several SUHIs related to specific land use, including industrial areas, landfills, and shallow geothermal energy use facilities.

Besides groundwater temperature, Cl^- concentrations and levels of DO showed correlations with land use classes (Fig. 4) and distance to the city centre (Table S.4). Moreover, differences in aquifer temperatures, Cl^- and DO concentrations were statistically significant for land use classes (p_{su} and $p_{sp} = 0.000$ for temperature, $p_{su} = 0.000$ and $p_{sp} = 0.003$ for DO, Table S.3) for both campaigns. In detail, pairwise comparison revealed a relation of the land use class 'dense urban' to elevated groundwater temperatures (Table S.4). Lowest temperatures (summer: 9.7–12.7 °C, spring: 9.4–10.8 °C) were recorded at forested sites, which are located outside of the densely populated city area (Table S.2). A similar temperature distribution with land use classes was observed by Tissen et al. (2019) or Schweighofer et al. (2021) in Nuremberg and by Steiner et al. (2024) in Vienna. In case of Munich, low groundwater temperatures can not only be associated to moderate land use. Many of the sampling points located in the forested area of Munich are characterised by deep groundwater levels. On the other hand, even when only looking to shallow sampling sites with water levels between 0 and 15 m b.l.s., groundwater below forested sites showed significantly lower temperatures than below other land use classes. In addition, groundwater collected from wells in parks displayed lower median temperatures compared to sealed areas (10.0 °C, 7.1–14.86 °C, Table S.2). This is especially true for the spring campaign and may underline the cooling influence by recharge of rain and snow in non-sealed areas. Worth mentioning, many park sites in Munich are located close to the Isar River, receiving infiltrating cold river water in winter/spring (Böttcher & Zosseder, 2022).

Overall, DO concentrations in urban groundwater of Munich were high and only a few samples indicated oxygen depletion (< 1 mg/L, Fig. 2 (c) and (d)). These sampling sites were located in a forested area with shallow groundwater, in the northern outskirts, and one in the English Garden. Apart from these exceptions, median aquifer DO concentrations of forested sites showed highest and almost saturated DO

Table 3
Results from the urban shallow aquifer in Munich are compared to reference values of TCC and cellular ATP from an oligotrophic aquifer in Freising, for hypothetic German oligotrophic groundwater, and for various German surface waters.

	Freising[1]	Reference of a hypothetic oligotrophic aquifer[1]	Reference dataset of Germany[2]	Surface water average[2]	Munich median 2020	2022
ATP (pM)		25.2 (0.3–50.0)	6.2 (0.6–44.7)	729 (69.9–4267)	206 (9.69 – 4625)	69.4 (4.43 – 14302)
TCC (cells/L)	4.2×10^7 (8.7×10^6 – 7.6×10^7)	0.6×10^8 (< 0.9×10^6 – 1.2×10^8)	88×10^6 (1–450 $\times 10^6$)	3500×10^6 (350–23,0 $\times 10^9$)	1.7×10^7 (4.92×10^6 – 2.21×10^9)	1.1×10^7 (1.95×10^6 – 2.62×10^9)

1: Griebler et al. (2014), 2: Griebler et al. (2018).

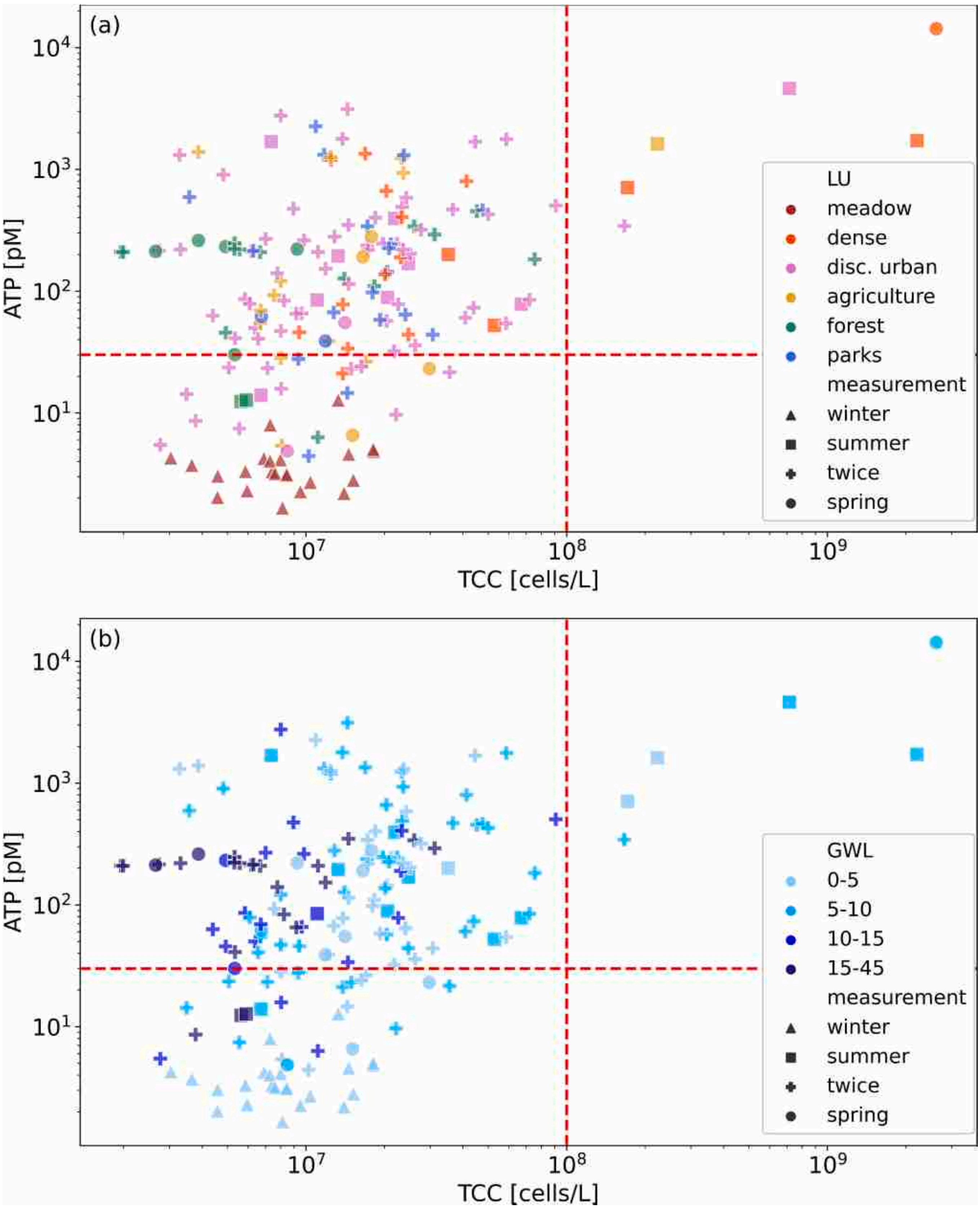

Fig. 3. Scatter plot of ATP concentrations in pM and TCC values in cells/L for the spring and summer campaign as well as reference values from 2016 in Augsburg/floodplains of the Lech River; colours depict (a) land use classes and (b) groundwater depth classes, triangles depict the campaign from Augsburg, crosses depict sampling sites of Munich sampled in both campaigns, circles depict sampling sites which were sampled only during spring campaign, squares depict sampling sites which were only sampled during summer campaign, red lines depict threshold values of ATP (30 pM) and TCC (10^8 cells/L) which indicate elevated microbiological fingerprint due to urban or organic pollution.

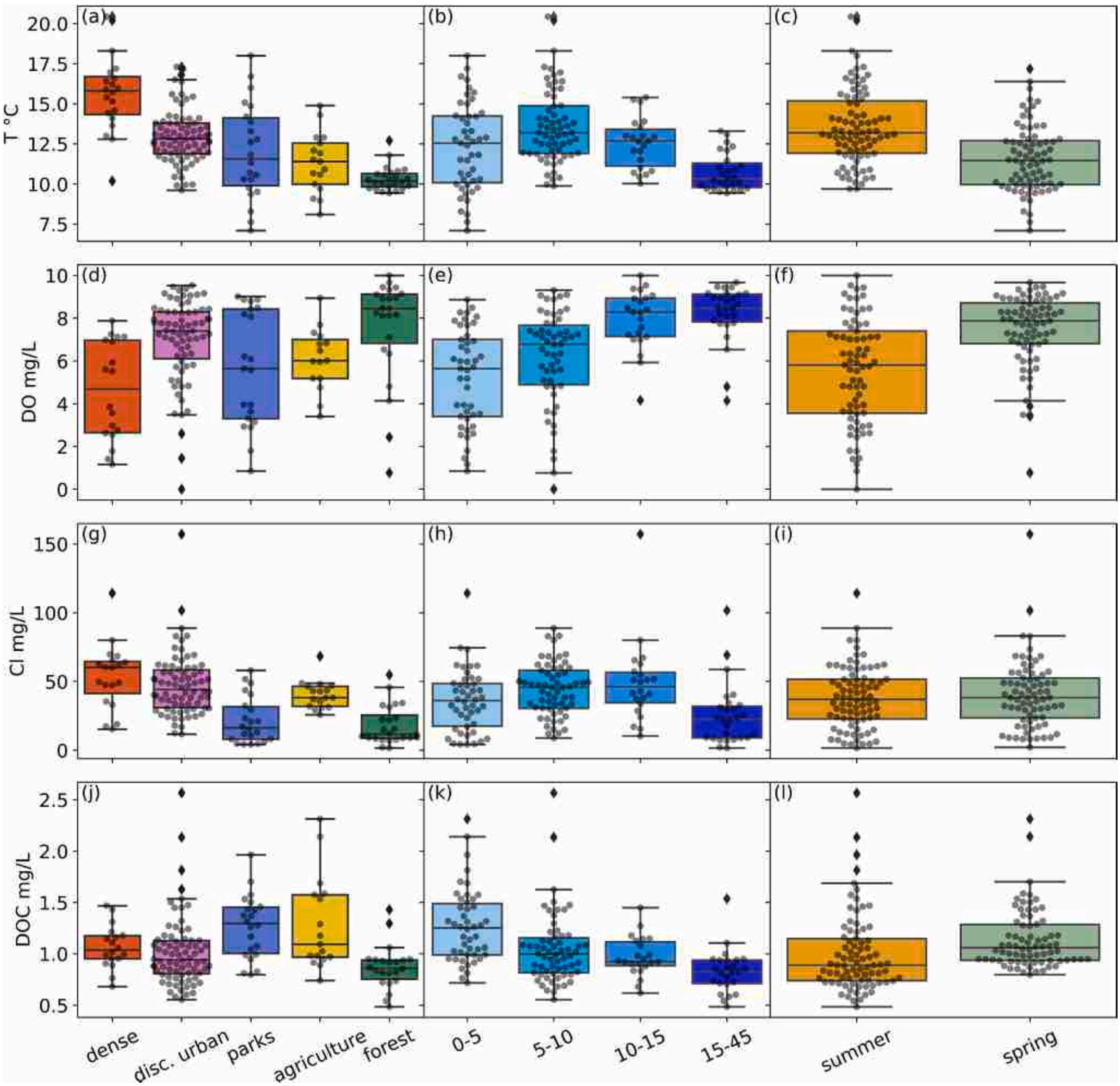

Fig. 4. Boxplots of selected physico-chemical parameters in relation to different land use categories ((a), (d), (g), (j)), groundwater level ((b), (e), (h), (k)), and sampling season ((c), (f), (i), (l)).

concentrations with 8.46 mg/L (summer) and 8.37 mg/L (spring). Pairwise tests revealed dense urban and park sites harbouring groundwater with significantly lower DO concentrations than forest sites and discontinuous urban land use for the summer campaign (Table S.6). Overall, DO concentration of park sites varied greatly with medians of 3.15 mg/L during summer and 8.31 mg/L during spring measurements. Although one may have expected higher DO levels in shallow groundwater near the river due to surface water infiltration, pairwise tests regarding distance showed the opposite.

Cl^- concentrations in the urban shallow groundwater showed a dependency on the different land use classes (Fig. 4 (e) and (f)). Median concentrations were highest in the land use classes dense urban (60.3 mg/L in summer) and discontinuous urban (49.0 mg/L in spring). Lowest median concentrations were detected for park sites with 8.39 mg/L in the summer campaign and 26.6 mg/l in the spring campaign, as well as for forested sites (13.5 mg/L and 9.79 mg/L). Thereby, differences were statistically significant ($p_{sp} < 0.001$, $p_{su} < 0.001$, Tables S.3 and S.7) and underline the strong influence of the degree of urbanisation. What is seen for Cl^- is also mirrored in Na^+ concentrations.

DOC concentration, in contrast to other key variables discussed above, showed a lower relationship to urbanisation, i.e., the CCD or land use classes, with some exceptions (land use: $p_{su} = 0.013$, $p_{sp} = 0.004$; Table S.3; CCD: $p_{su} = 0.097$, $p_{sp} = 0.010$, Table S.4). Pairwise tests revealed that groundwater below arable land and park sites show increased DOC concentrations whereby groundwater from forested sites had significantly lower concentrations (Table S.8). Overall, the comparable high spatial but low temporal variations in DOC are in good agreement with other studies (Pabich et al., 2001).

Summarising, groundwater from dense urban and discontinuous urban locations were different in their physical and chemical composition, i.e., with highest concentrations in Cl^-, Na^+, SO_4^{2-}, PO_4^{3-}, and total nitrogen (Table S.2). These compounds are typical for urban pollution from heterogeneous sources like sewage, fertiliser and salt application, or road runoff (Becher et al., 2022). For example, SO_4^{2-} in urban environments, contained in bricks, gypsum, wallboards, and cement, is often elevated in shallow groundwater due to release from construction waste and artificial fillings into seepage water (Jang & Townsend, 2001). In agreement with this, SO_4^{2-} was especially high in groundwater of the city centre and much lower in forested sites ($p_{su} = 0.000$, $p_{sp} = 0.003$, Tables S.3 and S.9). Concentrations of more than 100 mg/L were observed only occasionally, most of these were located under dense urban surfaces. Low SO_4^{2-} concentrations (< 10 mg/L), reported to occur in the uncontaminated gravel aquifer outside of Munich (Griebler et al., 2016), were only rarely observed in our study, i.e., at forested sites. Agricultural sites showed highest median concentrations of NO_3^- with 27.2 mg/L (summer) and 19.1 mg/L (spring) in both campaigns. Nevertheless, concentrations were in a similar range for dense urban (17.3 mg/L and 19.2 mg/L, respectively) and forested sites (18.1 mg/L and 18.7 mg/L, respectively). Especially park sites differed significantly from any other land use class in pairwise tests, which was more pronounced for the summer campaign with significantly lower NO_3^- concentrations. Also, PO_4^{3-} concentrations exceeding geogenic background values (< 0.05 mg/L) were frequently observed being significantly different with land use classes. Elevated PO_4^{3-} values, in general, indicate influence from agricultural activities or wastewater input, or a shift to anoxic conditions in the aquifer. Consequently, elevated PO_4^{3-} values in groundwater were preferably observed in dense urban locations (Table S.2).

3.2.2. Groundwater level effects on physical and chemical variables

Especially for Munich, the distance from land surface to the groundwater table plays an important role. As visible in Fig. 2, groundwater levels decrease from north to south, with the deepest wells being located in the southern parts of Munich. The groundwater table depth in the northern parts of the city ranged from 2–10 m b.l.s., while in the southern margin of the city, it ranged from 15–35 m b.l.s. As already emphasised by Böttcher & Zosseder (2022), the deeper the groundwater level, the smaller is the surface-related effect of warming, resulting in colder groundwater before the ambient geothermal gradient with increasing temperatures with depth dominates (Benz et al., 2024). During the summer campaign, the highest median temperature of 14.45 °C was measured in the groundwater level section of 0–5 m and consistently decreased to 11.0 °C for the depth interval of 15–50 m b.l.s. For the spring campaign in 2022, this pattern differed slightly, with the highest median temperature of 12.8 °C for the depth category 5–10 m b.l.s. and 10.5 °C in the depth of 15–50 m. Temperature differences especially between the groundwater level classes 5–10 m and 15–50 m were statistically significant ($p_{su} < 0.001$, $p_{sp} < 0.001$, Fig. S.2, Table S.10), visualised in Fig. 4.

There was a noticeable increasing trend in DO concentrations with decreasing water tables from north to south ($p_{su} < 0.001$, $p_{sp} < 0.001$, Table S.10, Fig. 3), which can be attributed to the decrease in groundwater temperature and less intensive land use (Pabich et al., 2001). For both campaigns, the highest concentrations were measured in the deepest groundwater level class at 15–50 m (7.06 mg/L in summer and 8.57 mg/L in spring), while the lowest concentrations were detected at 0–5 m depth (3.39 mg/L and 6.56 mg/L). This phenomenon might be explained by a lower surface impact in deeper wells which is accompanied by less organic carbon and nutrient input and lower temperatures (Pabich et al., 2001).

As observed for temperature and DO, DOC concentrations declined with increasing depth of groundwater levels (Fig. 4). Since organic carbon undergoes depletion being transported through soil and sediments, a decrease in DOC with depth in the unsaturated zone is expected (Lennon & Pfaff, 2005; Pabich et al., 2001; Shen et al., 2015) ($p_{su} = 0.002$, $p_{sp} = 0.000$, Table S.10). Overall, DOC concentrations in groundwater were low as can be expected for an oxic aquifer (Hofmann & Griebler, 2018; Regan et al., 2017).

In addition to the microbiologically most relevant variables such as temperature and DO, also Cl^-, potassium (K^+), and SO_4^{2-} exhibited distribution patterns related to the depth of the groundwater level (Fig. 3, $p_{su} = 0.013$, $p_{sp} = 0.003$, Table S.10) and exhibited their highest values in the most shallow groundwater level class.

3.2.3. Microbiological variables along land use gradients

The influence of land use patterns on the microbiological-ecological status of the Quaternary groundwater was not as pronounced as observed for certain abiotic variables (Fig. 3). This is not surprising since the gradients in DOC and essential nutrients (e.g., PO_4^{3-}) were moderate. Significant differences in TCC values of the urban shallow groundwater were only related to land use classes during the spring campaign in 2022 ($p_{su} = 0.168$, $p_{sp} = 0.018$, Table S.3). Here, pairwise testing indicated a significant difference between the forested and dense urban areas (Table S.5). Significant differences were also found in TCC ($p_{su} = 0.032$, $p_{sp} = 0.013$; Table S.4) and ATP ($p_{su} = 0.017$, $p_{sp} = 0.155$) with distance to the city centre. In particular, the distance classes 0–2 km and 6–10 km differed from each other. In detail, median cell counts of groundwater in dense urban areas were notably higher, while counts decreased with distance from the city centre (Fig. 3, Fig. S.2 (a)). Possible factors stimulating microbial biomass production and activity, such as wastewater influence and elevated temperatures, have already been mentioned above.

3.2.4. Microbiological variables with different groundwater levels

Particularly for the spring campaign, a significant north-to-south decrease in TCC with declining groundwater levels was evident (Fig. 2, $p_{su} = 0.003$, $p_{sp} = 0.000$, Table S.10). Lower groundwater levels generally go along with lower temperature dynamics, less import of energy, translating into lower microbial activities which again supports observation of increasing DO levels with depth. However, a relationship between groundwater levels and ATP concentrations was only observed for the spring campaign (Fig. S.2). Nevertheless, for both microbiological variables, highest values were detected in shallow groundwater at depths between 5 to 10 m.

The detected effects of groundwater levels on the measured variables must be taken into account when assessing groundwater quality, conducting groundwater monitoring, and developing groundwater management strategies. Caution must be taken when directly comparing groundwater from more shallow aquifers with those originating from deeper zones. We further recommend a dense monitoring network in areas with shallow groundwater levels and a sparser network in areas where the groundwater levels are deeper, as shallow sampling groundwater is at a higher risk of disturbance and contamination.

3.2.5. D-A-C analysis

Results of the D-A-C analysis identifying outlier samples following three different approaches are depicted in Fig. 5. The first approach used the samples from forested sites as 'internal' reference, while the second approach considered sampling sites from the Lech River floodplain in Augsburg as references. In the third approach, sites in Munich that did not show groundwater temperatures above 12 °C were used for comparison. For the first and third approach only very few sampling points were indicated as outliers by the Mahalanobis distance approach (Fig. S.4). This indicates that groundwater warming by a few degrees Kelvin did not alter the groundwater microbiology and DOC levels significantly. Moreover, while comparison between groundwater below forest and inner-city residential areas in Munich revealed differences, these were not statistically significant. Finally, using as reference the Lech River floodplain data set of rural groundwater, which stems from a protected area and is used for drinking water production, most urban

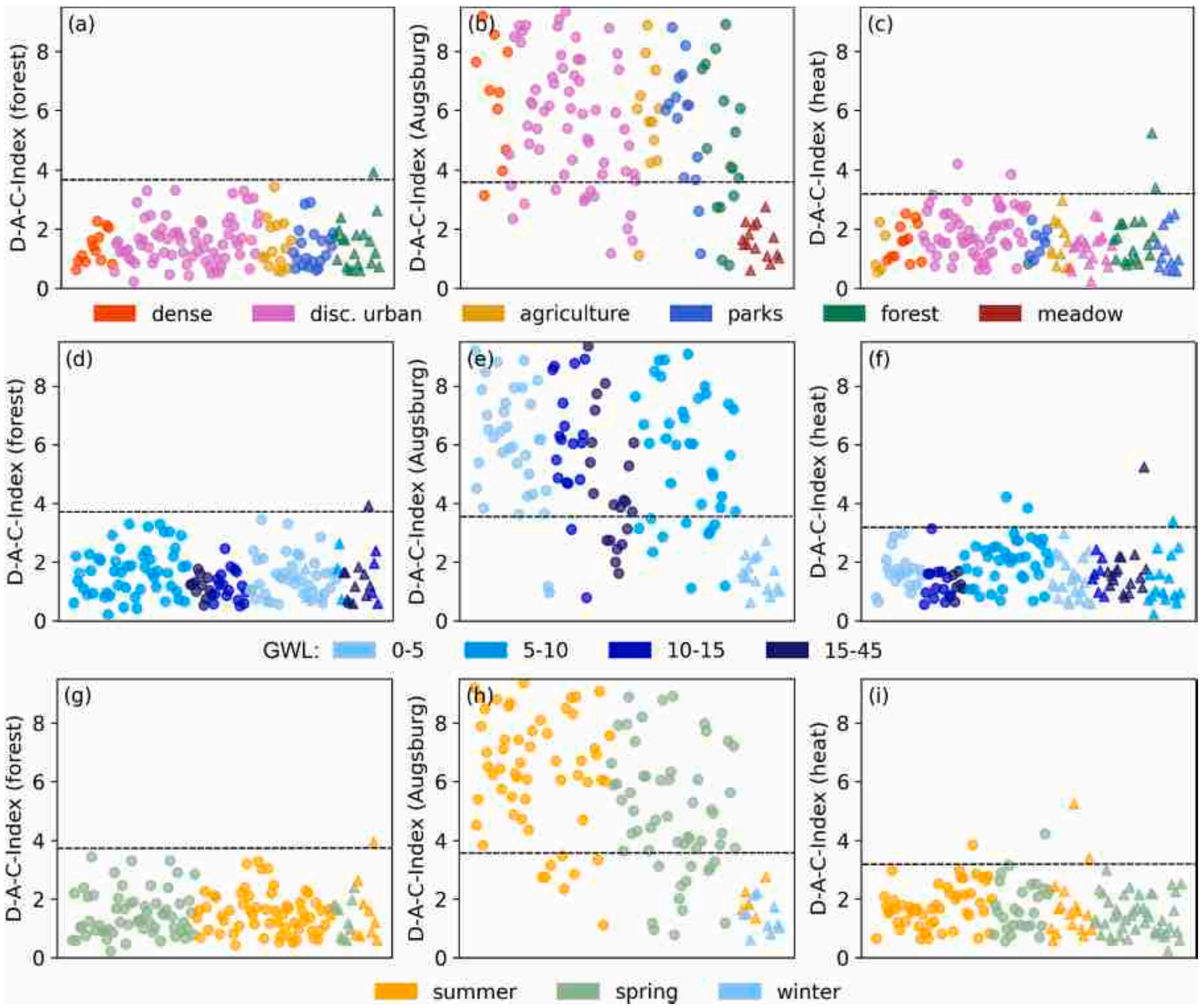

Fig. 5. Scatter plots of Mahalanobis distances from guided D-A-C approach, references for the calculation were forested sites ((a), (d), (g)), groundwater samples from Augsburg (floodplains of the Lech River) in 2016 ((b), (e), (h)), and warm groundwater samples with temperatures above 12 °C ((c), (f), (i)); triangles depict reference samples from Augsburg in winter 2016, circles depict groundwater samples from Munich; GWL – groundwater level; dotted line – threshold above which samples were indicated as outliers by the analysis.

groundwater samples from Munich were classified as outliers. In fact, while the urban groundwater is in comparatively good shape, the D-A-C index sensitively provides evidence for the overall urbanisation effect. This underlines that in some parts of Munich's groundwater diverges in microbiological-ecological pattern from a natural state. Most of the outliers, in terms of sampling sites, are located in the city centre and northern part of the city (Fig. S.4). This result also aligns well with the assumption that impairment of groundwater quality is more pronounced where the groundwater levels are shallow. With respect to groundwater warming, it can be concluded that samples with very high TCC and cellular ATP concentrations, classified outliers, did not show any clear relationship to groundwater temperature. Groundwater temperature, in the range observed for the urban shallow aquifer in Munich, seems not to be a major driver of water quality deviations.

Although the D-A-C results did not show significant patterns in relation to land use or other tested categories (Fig. 5, Table S.4, Fig. S.3)., the approach revealed the generally urban overprint of the shallow aquifer. Looking at TCC and ATP values, some land use patterns as well as coherences with groundwater level emerge. Nevertheless, sampling sites with a comparable microbiological fingerprint as the oligotrophic aquifer from Augsburg are mainly located in the southern parts of Munich and characterised by higher DO concentrations and lower pH values (Figs. S.3–7, Table S.12).

Since the microbiological criteria selected have shown to sensitively indicate surface water influence and organic contamination, they are considered good proxies for detecting overall groundwater quality deterioration. Moreover, the analytical methods for these parameters are cost-efficient, well-established, and easy to implement. Including such integrative microbial criteria is thus highly recommended, with the D-A or D-A-C index approach ready to be included in regular groundwater monitoring routines (Fillinger et al., 2019; Retter et al., 2021).

Under the influence of climate change, Munich is expected to face increasing water scarcity, a growing number of hot days, and significantly more heavy rain events during the winter (StMUG, 2009). Al-Azzawi et al. (2022) hypothesised that Munich will need a sponge city concept to tackle the conflicts arising from these future challenges. Today, Munich already implemented first sponge city structures with several rainwater reservoirs, collection channels, and infiltration structures (Al-Azzawi et al., 2022). When considering targeted rainwater infiltration as a strategy to counteract climate change effects and increasing water demands, microbial criteria are useful assessing water quality issues at infiltration sites. Previous studies have shown that microbial activity and abundance may increase in shallow groundwater under stormwater infiltration basins (Foulquier et al., 2011; Lebon et al., 2023). The same is true for DOC concentrations (Lebon et al., 2023), salts (Burgis et al., 2020), and nutrients such as PO_4^{3-} (Lebon et al., 2023; Mermillod-Blondin et al., 2015) posing a risk for shallow aquifers.

3.3. Sampling method comparison

In qualitative groundwater monitoring, both from a chemical and ecological standpoint, sampling remains a critical issue. One approach involves obtaining water samples directly from the well using a bailer without purging, offering a quick and straightforward method. Routinely, a more thorough yet time-consuming method entails sampling fresh aquifer water through pumping and pre-purging multiple amounts of the well volume. In our field campaigns, samples from both well water and pumped groundwater (referred to simply as groundwater) were collected and compared.

In fact, some physical and chemical variables displayed significant differences between the two water types (Table S.13). The results for selected variables indicating anthropogenic and urbanisation impacts are illustrated in Fig. 6. Temperature differences between well water and pumped groundwater were significant for the summer campaign but not the spring campaign ($p_{su} < 0.001$, $p_{sp} = 0.11$). DO and Cl^- concentrations exhibited significant differences with both campaigns (Table S.13). Oxygen levels were generally higher in pumped groundwater, while Cl^- concentrations were higher in well water. DOC concentrations were significantly higher in well water during summer ($p_{su} < 0.001$, $p_{sp} = 0.528$), albeit with high variability in values. Additionally, other chemical variables such as SO_4^{2-}, NO_3^-, PO_4^{3-}, and K^+ showed differences between well and pumped groundwater samples. In contrast, Korbel et al. (2017) found no significant differences in DO, EC, temperature, nutrients, and pH between well water and pre-purged groundwater in

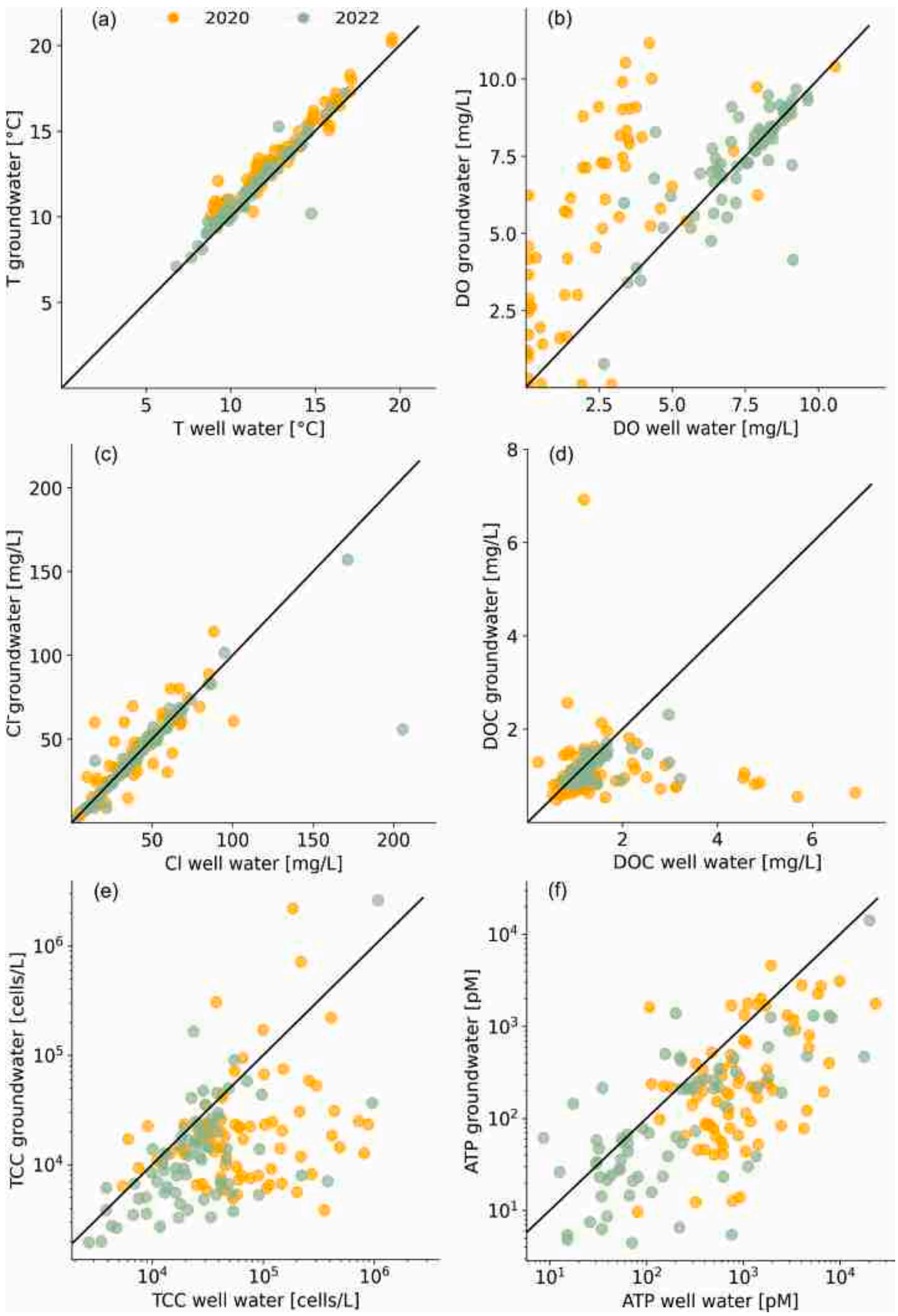

Fig. 6. Scatter plots of selected variables displaying values determined from well water and pumped groundwater distinguished by the year of sampling.

their comparative study. Opposite to this, Sorensen et al. (2013) observed lower pH values in well water samples from a Cretaceous chalk aquifer, along with an enrichment of DO, EC, calcium (Ca^{2+}), nutrients, and heavy metals, though not statistically significant. Consistent with our findings, Sorensen et al. (2013) also reported significant differences in DOC concentrations between the two water types.

Microbiological variables, including TCC and intracellular ATP concentrations, were notably higher in well water samples from Munich in our study (Fig. 6, Table S.13). This observation aligns with previous research (Korbel et al., 2017; Roudnew et al., 2014; Sorensen et al., 2013). In another groundwater study comparing pumped water from a pristine aquifer with water collected from inside an observation well, bacterial densities were significantly higher in the well water (Griebler et al., 2002). In a similar fashion, Roudnew et al. (2014) reported a decreased amount of virus-like particles in purged water compared to borehole water, and Sorensen et al. (2013) also observed significantly lower bacterial cell counts in pre-purged water. Furthermore, Korbel et al. (2017) also observed significant differences in bacterial community composition between well water and groundwater. Different to TCC, cell-specific ATP concentrations did not differ significantly between the two water types in our study. On average, cell-specific ATP in Munich's pumped groundwater was greater in well water of the spring campaign, but greater in pumped groundwater of the summer campaign.

As noted by other researchers (e.g. Korbel et al., 2017; Sorensen et al., 2013), wells or boreholes represent an artificial groundwater environment exhibiting a transition of environmental conditions (e.g., from anoxic to hypoxic to oxic) with frequently enhanced biogeochemical cycling. The transition from the open water column in the well to the atmosphere translates into conditions not as constrained as in the aquifer. Particularly for sampling of biological variables, pre-purging was consistently shown to be essential. Also, our results indicate that bailer samples do not reflect the true aquifer conditions and therefore may not be representative. Since biological measures offer a more holistic view of long-term groundwater conditions, the need for pumping and purging well water to obtain a representative depiction of actual aquifer conditions is evident (Korbel et al., 2017; Sorensen et al., 2013). The main disadvantage is the high time and cost requirements associated with pumping routines during groundwater sampling. Further studies, including long-term research, can help improve knowledge and identify indicative and representative sampling sites, where regularly pumped groundwater samples should be collected for monitoring shallow aquifer quality. Long-term monitoring will allow for early detection of contaminants, a better understanding of trends and patterns—such as those observed in the presented study—and enable the evaluation of management strategies (Svetina et al., 2024).

3.4. *Coherences affecting microbiological variables*

For a better understanding of interactions and relationships of abiotic and microbiological variables within the ecosystem, several correlation analyses were performed for both field campaigns individually. The correlograms are depicted in Figs. S8 and S9. Temperature in groundwater correlated moderately to strongly positively with Cl^- and Na^+ in both campaigns, emphasising the connection between groundwater warming and urbanisation. Moreover, temperature was positively correlated with DOC ($R^2_{su} = 0.3$), and TCC ($R^2_{su} = 0.4$, $R^2_{sp} = 0.3$) indicating a close link of microbial biomass, availability of organic material to bacteria with increased temperatures during summertime. Nevertheless, it is premature to draw conclusions on these correlations without further information about the DOC quality.

For both campaigns, significant and moderately negative correlations were found for DO and temperature; first due to the well-accepted physically declining solubility of oxygen in warming water, and second via the acceleration of microbial activity (Lawrence Clever et al., 2014; Riedel, 2019). Correlations indicating a link between temperature and microbiological processes were found for both field campaigns independent from the season. Additionally, moderately to strongly negative correlations of DO with TCC were observed ($R^2_{su} = -0.5$, $R^2_{sp} = -0.5$). Higher prokaryotic cell numbers in hypoxic and anoxic groundwater have already been documented in earlier studies (Retter et al., 2023). Weak correlations were found for the D-A-C indices. Regarding temperature, there was a weak positive correlation with the D-A-C index in summer ($R^2 = 0.3$).

Correlation of bacterial cell numbers with DOC was strongly positive for the spring campaign ($R^2_{su} = 0.3$, $R^2_{sp} = 0.7$). Since correlations with DOC were stronger than with temperature, this may point to the fact that the Munich gravel aquifer is especially energy limited, and bacterial cell numbers are influenced most by the availability of energy (DOC) rather than by groundwater temperature. However, average DOC concentrations did not differ greatly between the two campaigns and are not especially high overall.

To identify which physical and chemical variables reflect the heterogeneity between the sampling sites, principal component analyses (PCAs) for both campaigns were conducted and correlations of ATP and TCC with the four PCA axes were evaluated (Fig. 7 (a) and (b)). Results of the PCAs were quite similar for both campaigns with variation of temperature and the main ions explained by the first axis (32.9 % and 33.2 % of variations) and nitrogen species with the second axis (23.8 % and 23.7 %). The variability of pH values between wells was explained best by the third and DOC with the fourth axis (Fig. S.10). DO switched between the second axis for the first campaign to the fourth for the spring campaign, again indicating more heterogeneous concentrations during the summer campaign with higher temperatures. With groundwater temperature and EC being main factors in differentiating the sampling spots from each other, urbanisation effects (e.g., SUHI, deicing agents) are displayed quite well. This fact is also obvious when comparing the results to PCA for sites from rural areas in the vicinity of Munich (Kiecak et al., 2023). The authors showed that variations of EC and ions were displayed by the second axis of the PCA, indicating only mineralisation effects since no urbanisation gradient was present within the sampling sites. Overall, land use classes are separated by PCA analysis quite well (Fig. 7). This shows that even in this geological homogeneous gravel aquifer and at this small scale, sampling sites and land uses can be indicated by differing physical and chemical variables.

Linear regression of bacterial cell numbers with the first and second axis indicate weak linear relationships for both campaigns (Fig. 7 (a), (b)). Again, bacterial cell numbers are positively connected with temperature, which is more pronounced during the summer campaign. Other studies conducted in shallow Quaternary aquifers but without anthropogenic overprint did not find a positive correlation between bacterial cell numbers and temperature (Brielmann et al., 2009; Schmidt et al., 2024). Temperature increases may not have been strong enough at the time or temperature effects were cancelled out by other factors such as energetic limitation (Schmidt et al., 2024). For the third and fourth axis (Fig. S.11), significant linear regressions could be found with TCC, DO, and DOC, showing the same strong correlations already seen before.

4. Conclusions

Currently, Munich primarily obtains its drinking water from the alpine forelands through gravity systems (Al-Azzawi et al., 2022). Furthermore, mainly groundwater from the Tertiary aquifer, rather than the shallow Quaternary aquifer is used these days. However, additional water sources may become necessary or beneficial in the future, due to climate change and the city's continued growth. Shallow aquifer resources could help meet these future demands when other supplies may face challenges (Al-Azzawi et al., 2022). This raises the question of whether shallow urban groundwater can be used safely. To address this, the chemical, physical, and biological quality of urban groundwater must be carefully monitored and understood.

An intact, ecologically pristine groundwater ecosystem is characterised by several key factors, including a hydrogeological setting

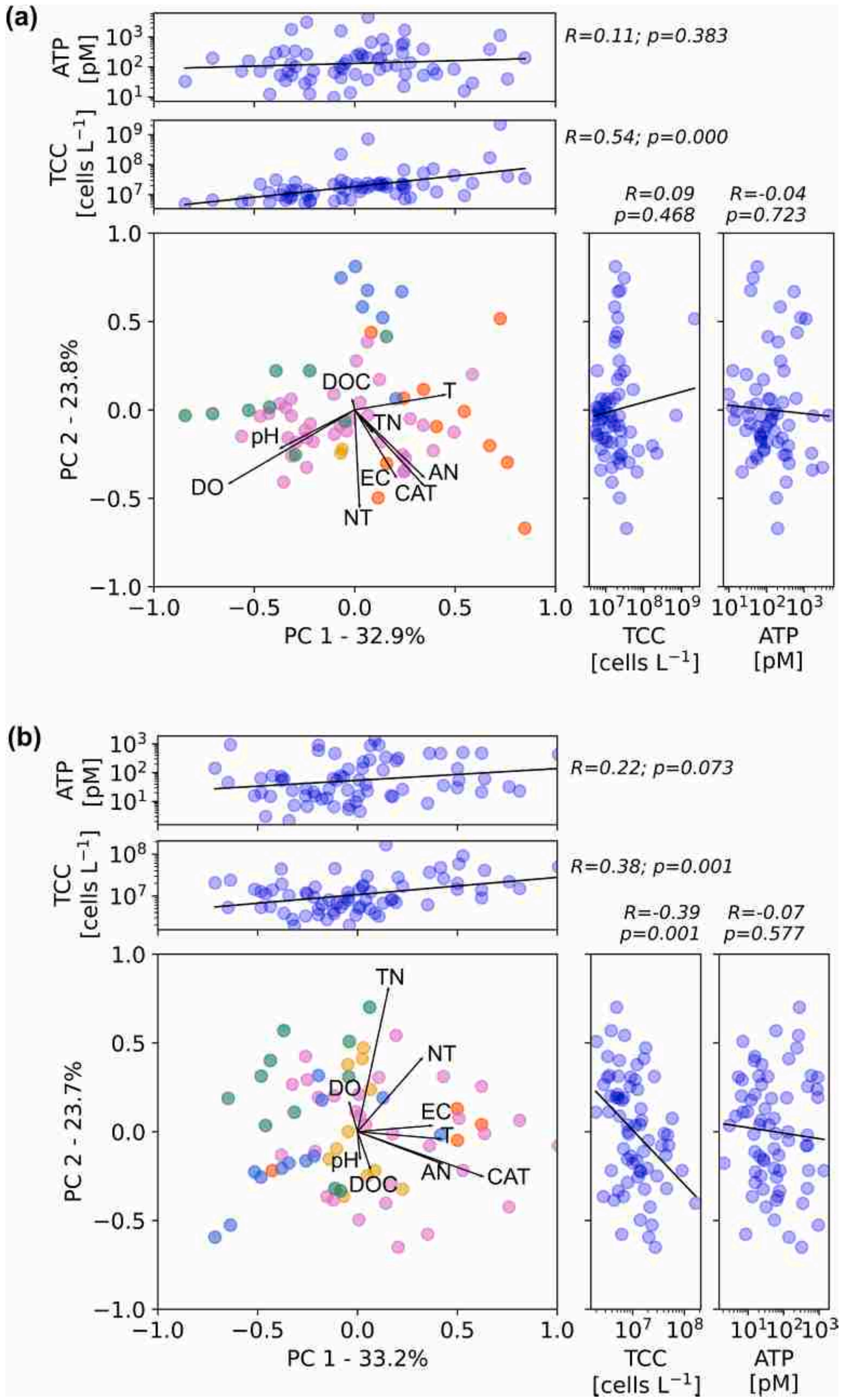

Fig. 7. Principal component analysis (PCA) with axis one and two for (a) summer campaign and (b) spring campaign, including scatter plots and linear regression analysis of total bacterial cell count (TCC) and intracellular bacterial ATP (bacterial activity) with both PCA axes; in the central part, colours signify land uses: red – dense urban, pink – discontinuous urban, blue – parks, yellow – agriculture, green – forest.

typical for the location, low concentrations of particulate and DOC, minimal levels of nitrogen compounds (such as NH_4^+) and reactive PO_4^{3-}, oxygen-rich conditions (> 1 mg/L), low microbial biomass and total abundances, and limited microbial activity (Griebler et al., 2014). An analysis of the shallow Quaternary groundwater in Munich revealed deviations from the natural state in some features but at the same time the urban groundwater in Munich does not exceed critical thresholds. Chemical variables like Cl^- exhibited increased concentrations, particularly in dense urban areas. Chemical thresholds outlined in German drinking water regulations have not been exceeded. Groundwater temperature showed an urban gradient, with significantly higher temperatures in the city centre compared to rural and forested areas. Microbial activities, measured by intracellular ATP concentrations, were consistently elevated throughout the city's groundwater, while TCC were in the range of different reference samples. Worth mentioning is that urban areas are complex in terms of impacts on groundwater. Moreover, natural heterogeneity contributes to complexity with varying groundwater depths and the local influence from surface water, to give two examples, both of which influence groundwater microbiology. In Munich, the combination of TCC, microbial activity, and DOC hints at a deviation from a natural reference state and the D-A-C index points to an overall urbanisation impact. Results showed that microbiological variables are suitable for detecting the effects of urbanisation. However, the D-A-C index was not able to differentiate between land use classes within the city. Other variables, such as Cl^-, EC, temperature, and, in some cases, DO and TCC, differed between land use categories. Overall, the tested combination of variables—including temperature, Cl^- or EC, ATP, and TCC—was able to detect the urban impact on the natural aquifer state. Regarding sampling methods, pre-purging and pumping before sampling are strongly recommended, as several variables, especially microbiological ones, differed significantly between well water and pumped groundwater. Consequently, well water may not accurately reflect surrounding aquifer conditions in a representative manner. Additionally, seasonal effects and variations in groundwater levels were observed and should be considered in groundwater monitoring. Pumped groundwater samples should therefore be collected under different hydrological conditions, and the monitoring network should be adjusted to capture more heterogeneous groundwater conditions, particularly in areas with shallow groundwater levels. However, taking the urbanisation into account, the groundwater quality in Munich, based on the authors' experience of monitored hydrochemical variables and fulfilled microbiological-ecological criteria, has a good status. Therefore, the shallow aquifer might be well suited for further implementation of infiltrations structures. Nevertheless, groundwater must be monitored especially at such structures with focus on microbiological and organic parameters.

CRediT authorship contribution statement

Julia Becher: Writing – original draft, Visualization, Investigation, Formal analysis, Data curation, Conceptualization. **Christian Griebler:** Writing – review & editing, Validation, Methodology, Data curation, Conceptualization. **Kai Zosseder:** Writing – review & editing, Methodology, Data curation. **Peter Bayer:** Writing – review & editing, Supervision, Resources, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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