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Interpretation of hydrogeochemistry of the Upper Freshwater Molasse (*Obere Süßwassermolasse*) in the Munich area (Bavaria, Germany) using multivariate analysis and three-dimensional geological modelling

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Section S1. Supporting Figures and Tables

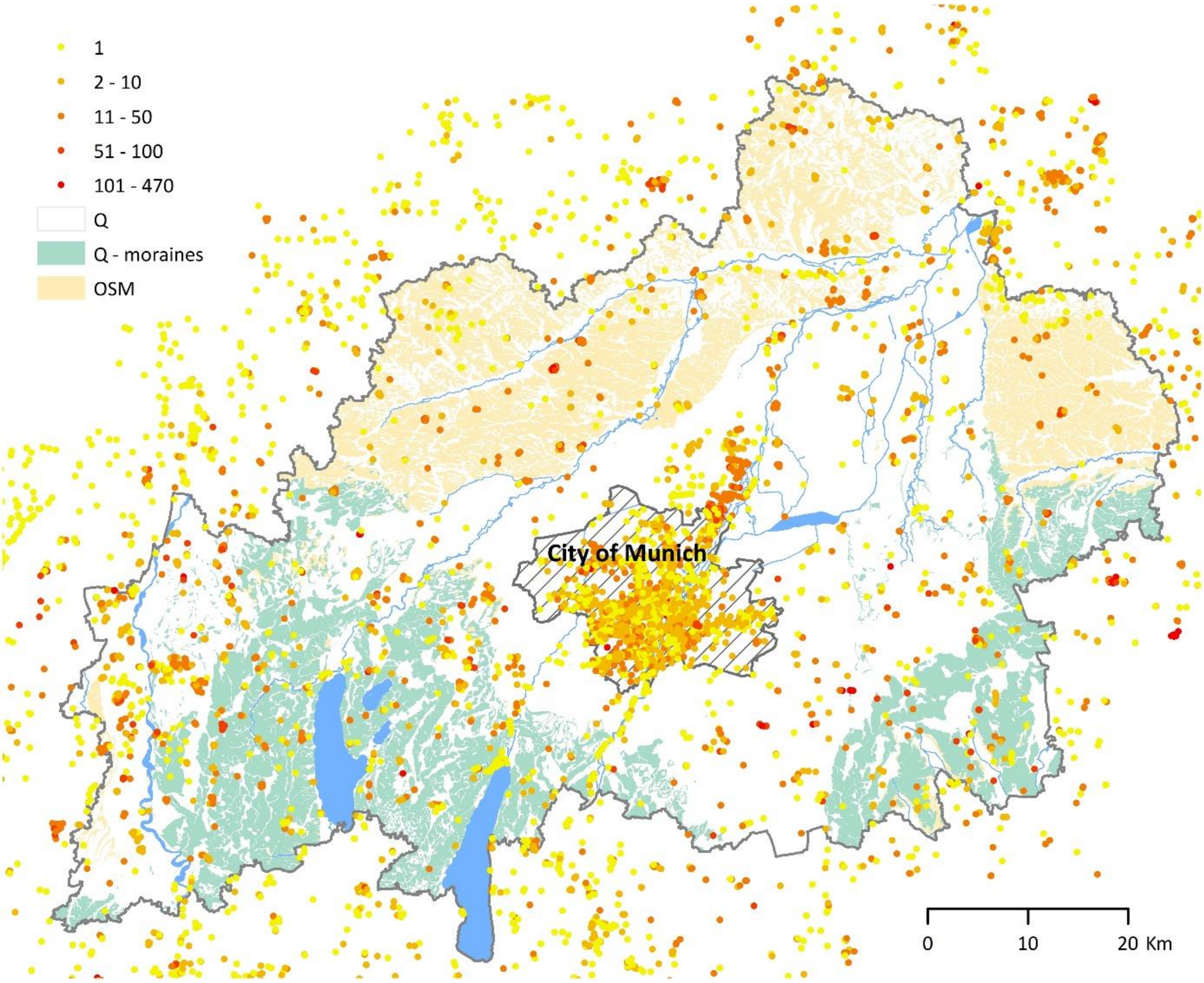

Figure A1 Location of all available data points. The colour scale indicates the number of single chemical analyses performed at a particular well or piezometer.

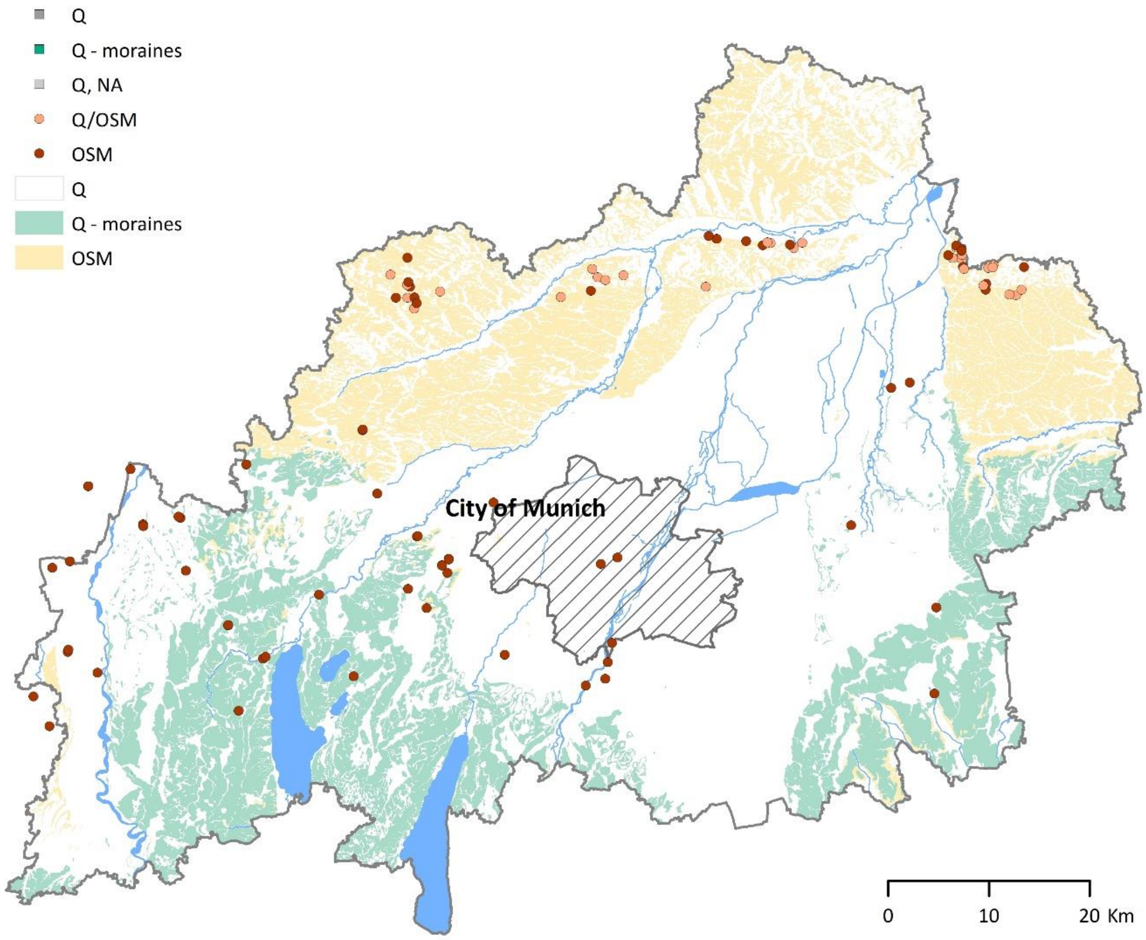

Figure A2 Location of data points associated with samples taken during three sampling campaigns in 2017–2019.

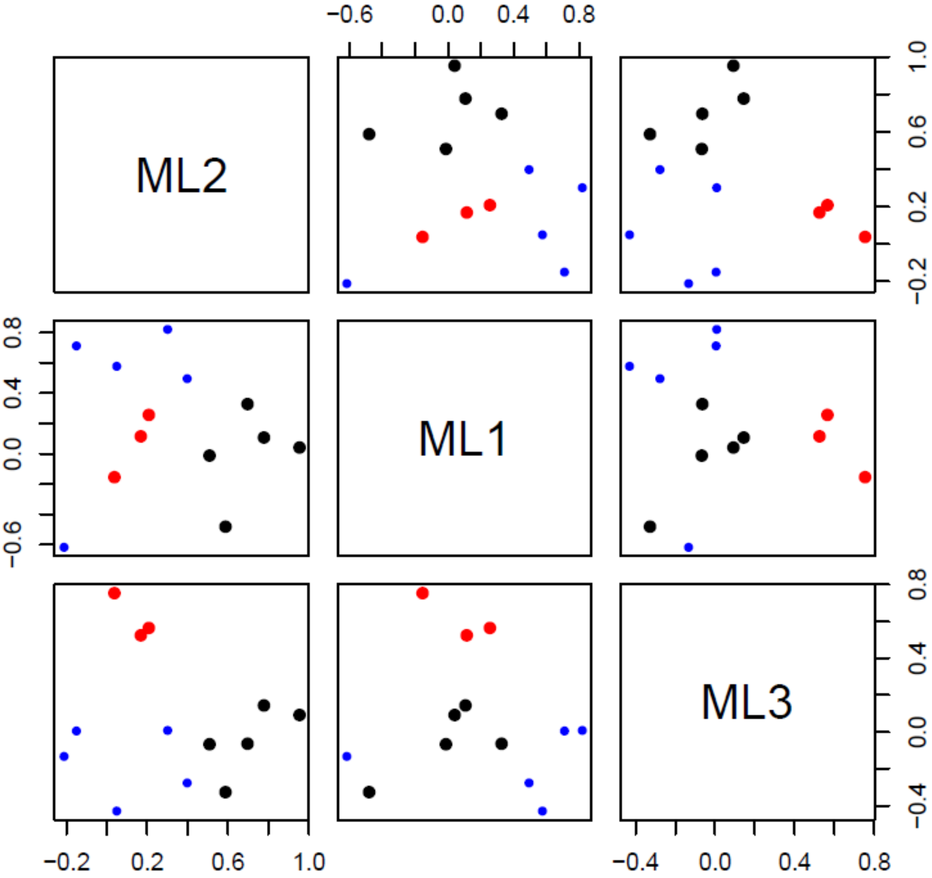

Figure A3 Factor loadings obtained in EFA

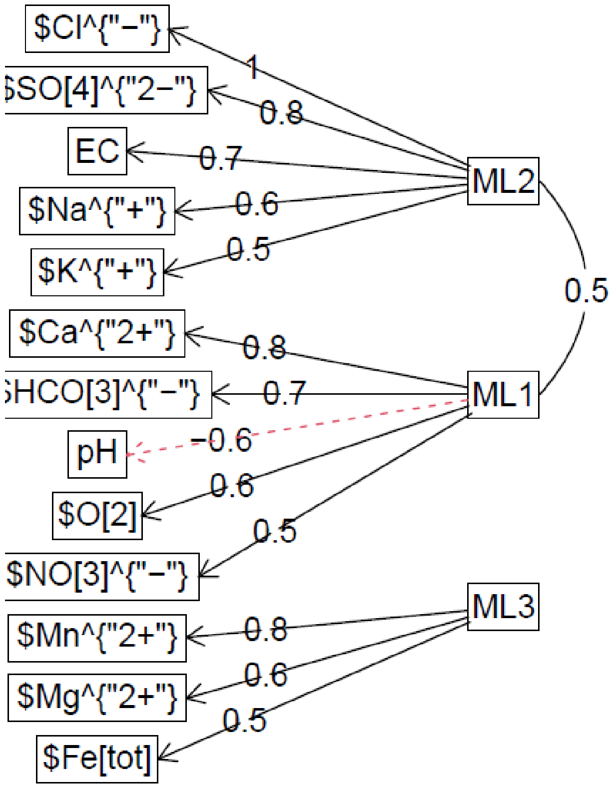

Figure A4 Factor loadings for the exploratory factor analysis (EFA) with the maximum likelihood method and oblique (oblimin) rotation

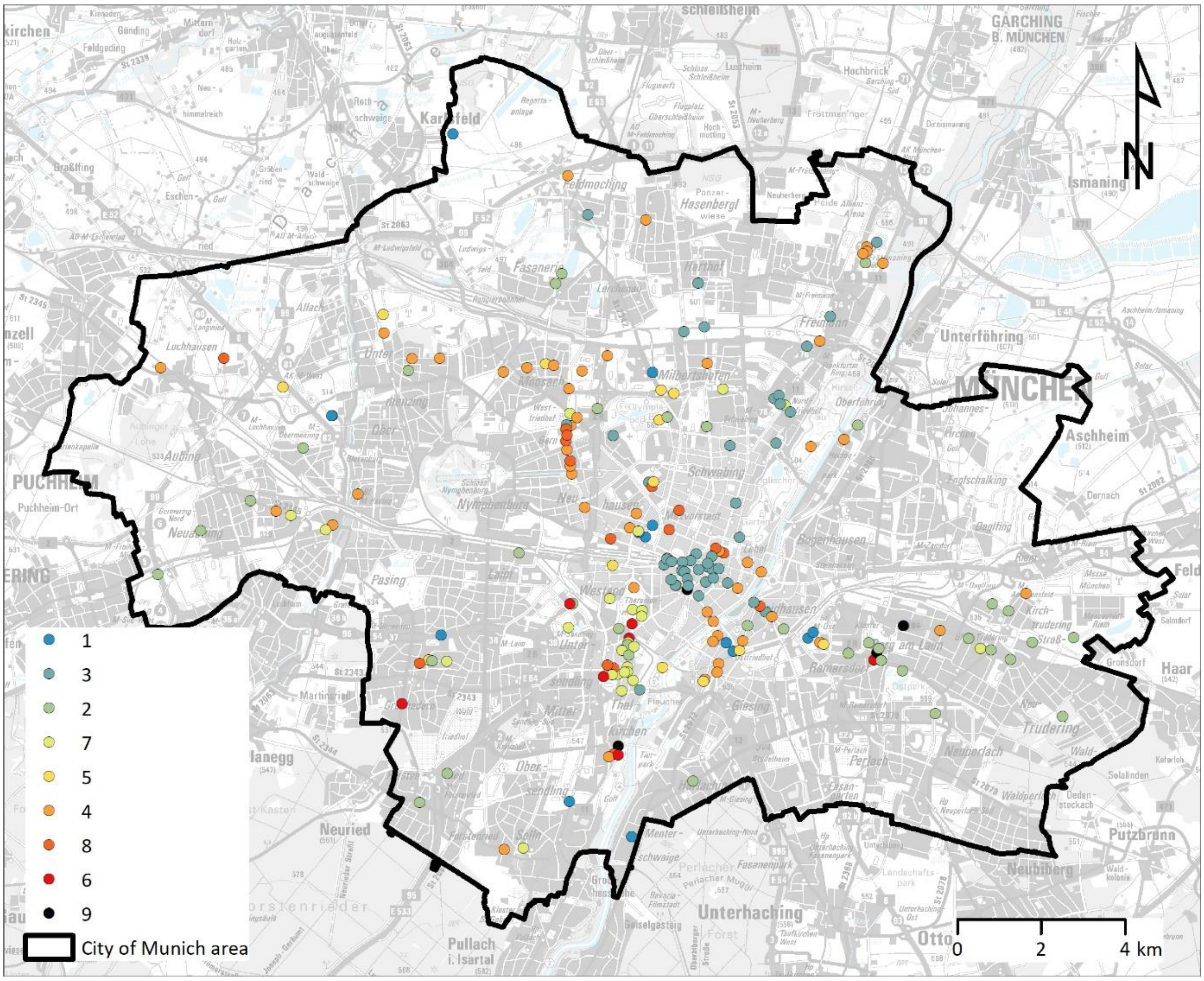

Figure A5 The location of wells assigned to clusters in the City of Munich area. Numbers 1-8 indicate clusters, number 9 indicates outliers, excluded from HCA

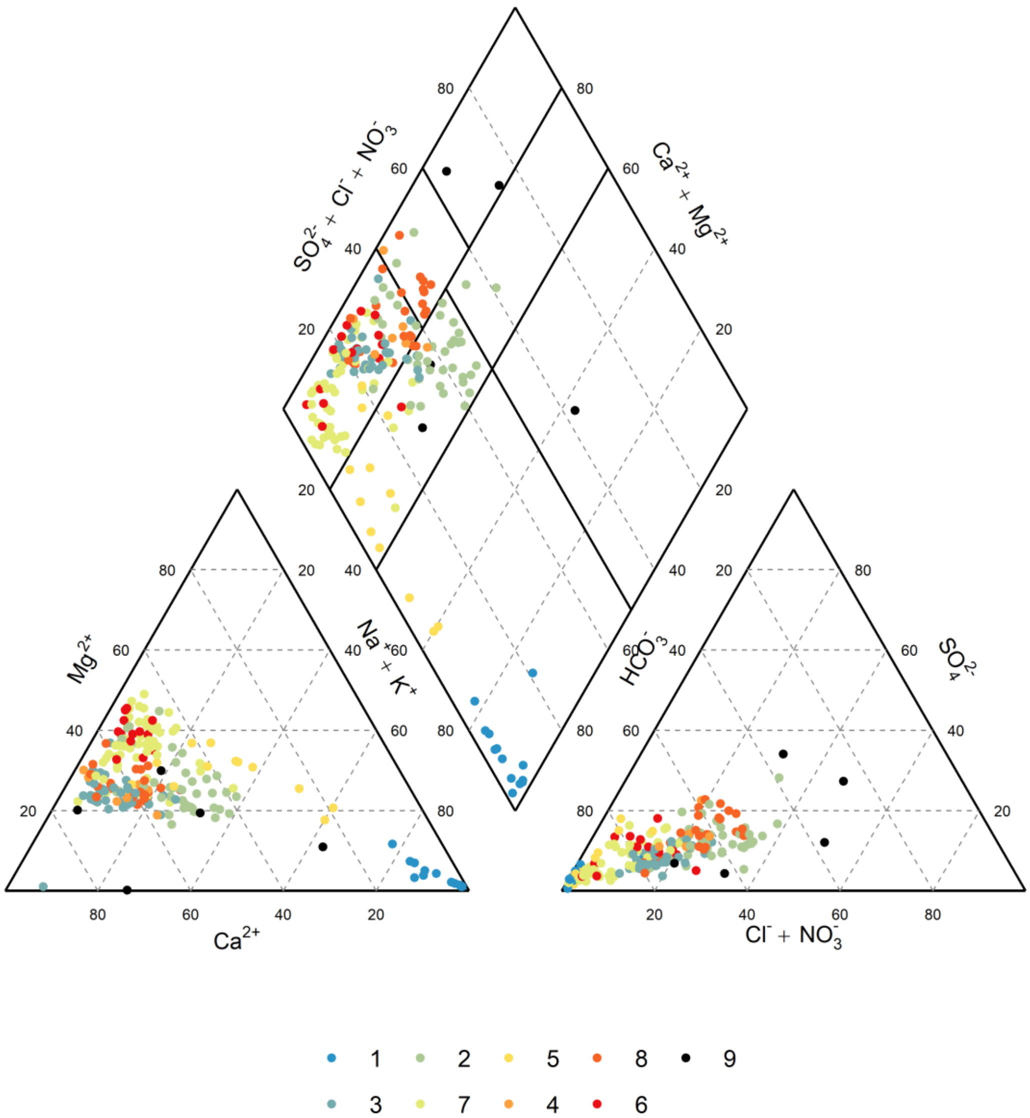

Figure A6 Piper plot presenting clusters in the city area. Numbers 1-8 indicate clusters, number 9 indicates outliers, excluded from HCA

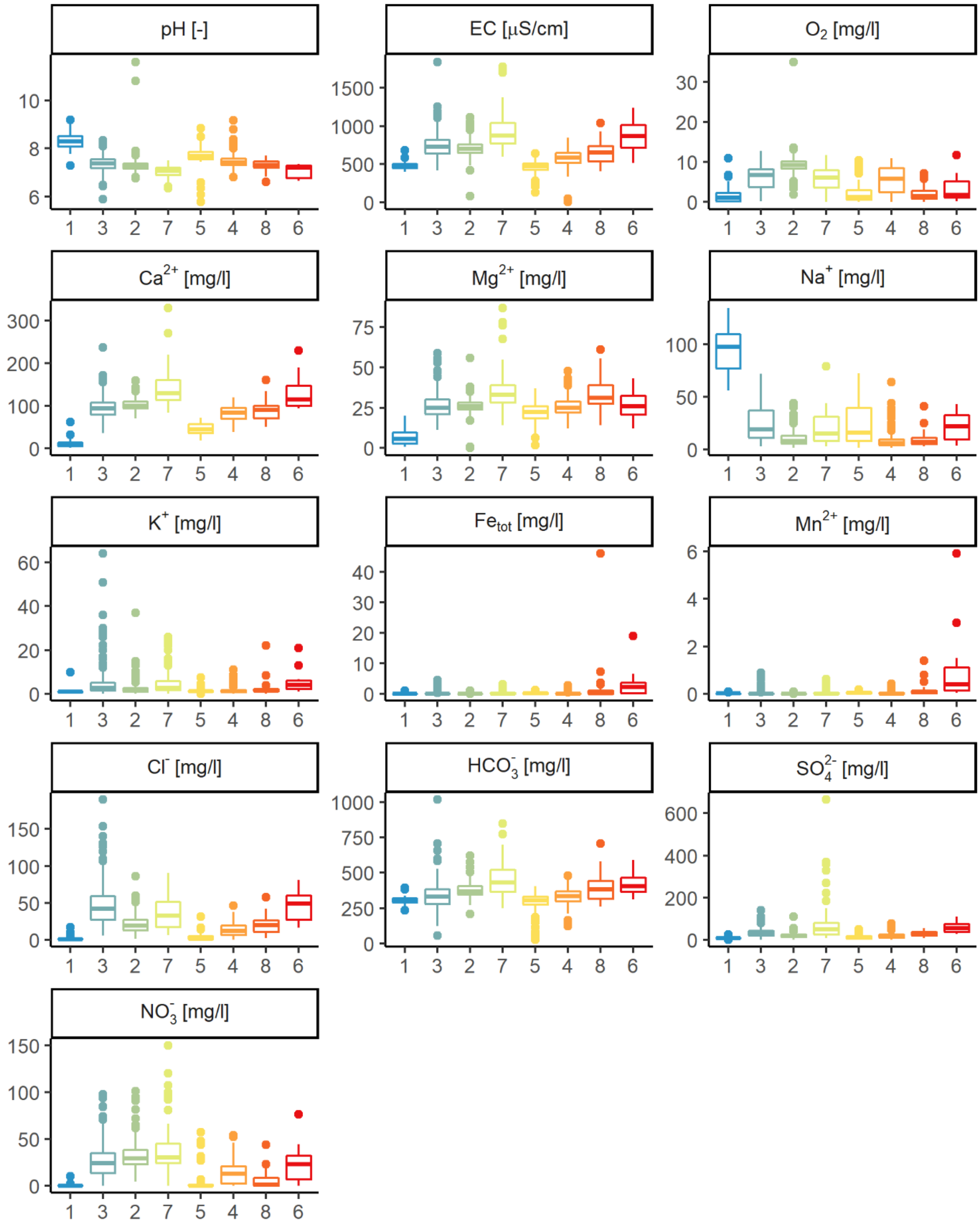

Figure A7 Box plots for clusters associated with the whole study area

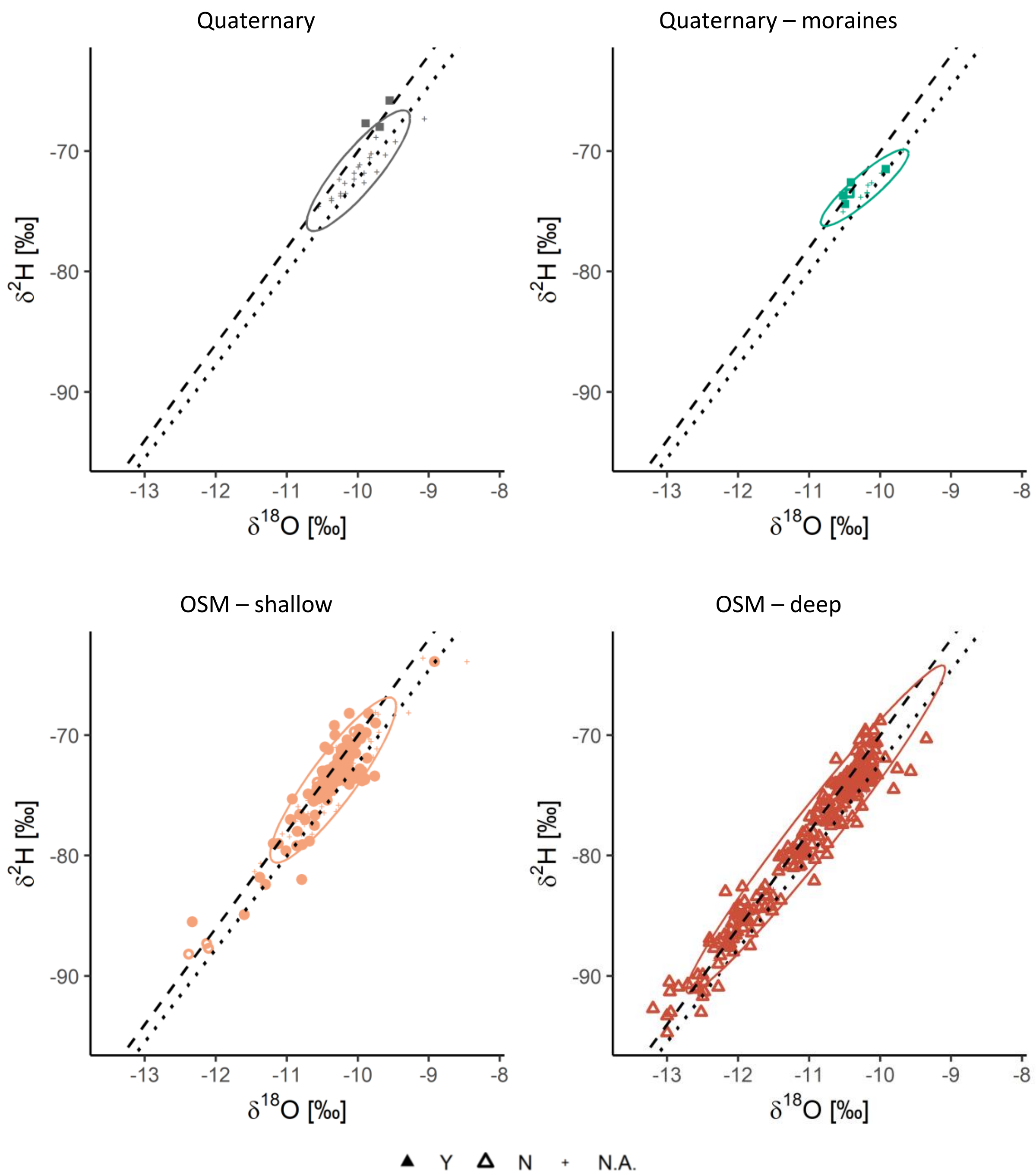

Figure A8 δ^2H versus δ^{18}O for each hydrogeological unit. Tritium content is presented as follows: filled symbols (Y) – tritium is present in the water sample, empty symbol (N) – no tritium present, + (N.A.) – no tritium-data available. The colours indicate the hydrogeological unit (see Fig 8a in the paper)

Table A1 Relationship between clusters and groundwater horizons from the 3D lithofacies model of the City of Munich

		C1	C3	C2	C7	C5	C4	C8	C6	total
Q	**Q**			9	1		5			15
Q/T1	**Q/OSM**		2	4	1	1	3			11
T1	**OSM-shallow**	3	40	25	22	7	41	16	7	161
T1/T2		1	1			3	3			8
T2	**OSM-deep**	2				2	2			6
T3		1								1
T4		4								4
TX		2								2
total		13	43	38	24	13	54	16	7	208

Section S2. Descriptive statistics

1. Methods

Descriptive statistics were calculated for four predefined hydrogeological units. The statistics were minimum, maximum, median, quantiles (10%, 25%, 75%, 90%).

Additionally, censored box plots were prepared. Values of some water constituents (e.g. NO_3^-, SO_4^{2-}, minor elements) were below the detection limit, i.e. censored. Moreover, as already mentioned, the detection limits in the available historical data varied over time. Therefore, simple methods such as replacing censored data with the detection limit or ½ of the detection limit couldn't be applied. For that reason, descriptive statistics were calculated using the NADA package in the statistic programme R (R Core Team, 2021) with "regression on order statistics" (ROS) (Helsel, 2012). ROS is a semi-parametric method used to estimate summary statistics and plot model distributions with censored data; it assumes that data can be fit to a known distribution by a least-squares regression on a probability plot (ITRC, 2013). For each observation a number and a logical value of a censoring indicator was assigned (TRUE for censored, FALSE for uncensored). In the resulting censored boxplots, the line indicating the limit of detection is drawn at the highest detection limit in the data set. Percentiles above this line are unaffected by censoring, while percentiles below this line are estimated, for example by ROS.

2. Results

The statistics were summarised in tables separately for each hydrogeological unit (Tab.A2). The censored boxplots allowed one to compare the values of parameters in each unit (Fig.A9). A Piper diagram graphically represents the hydrogeochemical facies of groundwater in the study area (Fig.A10). Stiff diagrams show the medians as well as quantiles (10 %, 90 %) of the main constituents of groundwater samples in particular hydrogeological units (Fig.A11).

Table A2 Table of descriptive statistics of selected parameters (23 out of 64) calculated for Quaternary groundwater samples

Parameter	Unit	No of samples	No < LOD	LOD	Minimum	10% - Quantile	25% - Quantile	Median	75% - Quantile	90% - Quantile	Maximum
Temperature	°C	590	0		4.7	8.5	9.2	10.1	11.4	13.3	24.1
pH		604	0		6.03	7.00	7.13	7.29	7.40	7.50	9.10
EC (25 °C)	µS/cm	457	0		83.7	560	617	703	781	943	1840
DO	mg/l	588	4	0.3	<LOD	2.7	5.5	8.3	9.7	10.5	15.5
DO-saturation	%	449	5		<LOD	20.6	49.5	75.2	88.0	96.9	137.1
F^-	mg/l	379	96	1	<LOD	<LOD	0.059	0.088	0.1	0.2	12
Cl^-	mg/l	612	3	5	<LOD	7.2	12	19	29	51	200
Br^-	mg/l	34	27	1	<LOD	<LOD	<LOD	<LOD	0.1	1	1
NO_3^-	mg/l	612	10	1	<LOD	8	15	23.2	33	50.1	192
NO_2^-	mg/l	441	388	0.16	<LOD	<LOD	<LOD	<LOD	<LOD	0.02	0.5
SO_4^{2-}	mg/l	606	2	0.1	<LOD	9.2	13	18	27	43	665
S^{2-}	mg/l	35	34	0.5	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	0,5
PO_4^{3-}	mg/l	82	60	0.02	<LOD	<LOD	<LOD	<LOD	0.044	0.1	0.88
orth.-PO_4^{3-}	mg/l	387	253	0.2	<LOD	<LOD	<LOD	0.008	0.03	0.08	0.84
HCO_3^-	mg/l	612	0		64.1	306.3	336.3	368.9	408.8	452.7	1150.2
NH_4^+	mg/l	549	353	0.26	<LOD	<LOD	<LOD	0.006	0.023	0.053	15
K^+	mg/l	606	30	1	<LOD	0.7	1	1.8	3.3	6	64
Na^+	mg/l	612	0		0.3	3.3	5	8.7	15	29.05	113
Ca^{2+}	mg/l	612	0		21	82	91	100	112	130	330
Mg^{2+}	mg/l	612	0		7.3	19	22.1	25	28	32	87
Fe_{tot}	mg/l	557	300	0.05	<LOD	<LOD	<LOD	0.00279	0.035	0.16	22
Mn^{2+}	mg/l	534	369	0.05	<LOD	<LOD	<LOD	<LOD	0.006	0.0523	1.6
Si	mg/l	123	0		0.43	2.3	2.8	3.2	3.8	5.4	18

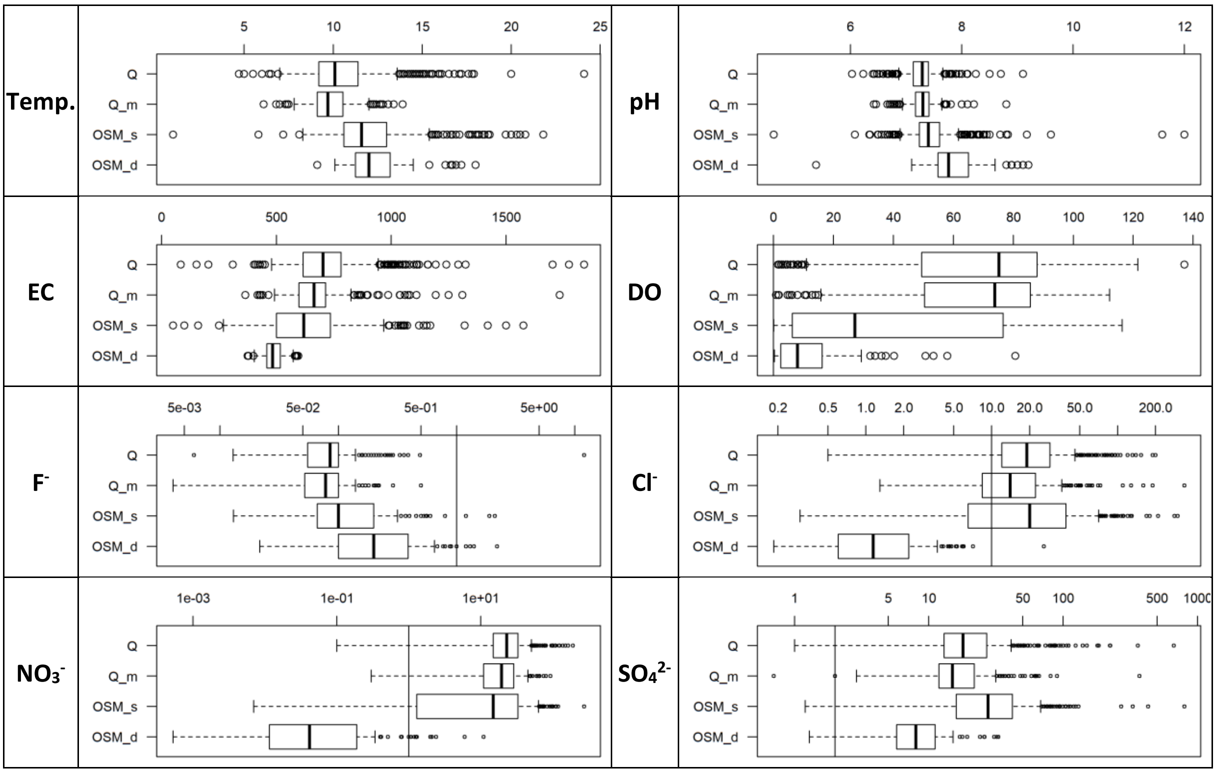

Fig. A9 Selected box plots

Anthropogenic impacts (mostly diffuse contamination sources i.e. use of fertilizers or road-salt in winter) are visible through elevated contents of nitrate, chloride, potassium, and sodium (Wagner et al., 2003, 2011). For example, German limit-values for drinking water of nitrate (> 50 mg/L) were exceeded in 62 analysed samples for Quaternary waters, in 10 waters samples in moraines, and in 54 samples of shallow OSM aquifers. Previous studies conducted in the immediate vicinity of the study area have shown that elevated concentrations of nitrate are caused by releasing high amounts of manure and, to a lesser extent, synthetic fertilizers due to intensified agriculture (Wild et al., 2020, 2018).

Quaternary groundwater in the study area is typically represented by a Ca-HCO$_3$ water type with total mineralisation varying from 138 to 1890 mg/L (477-580-766 mg/L). The pH-values (7.0-7.3-7.5) classify these water samples as neutral or low alkaline. DO median (8.3 mg/L) was the highest among all the four units. The iron and manganese concentrations are mostly low. Among the trace elements, the following are present: with the median above 100 µg/L; B, Ba – above 10 µg/L, Cs, Hg, Li, U, Zn – above 1 µg/L. The presence of uranium above 1 µg/L in more than 50 % of samples is noteworthy, not only in Quaternary deposits, but also in moraines and shallow OSM. As concluded by Banning et al. (2013), uranium primarily originates from lignitic inclusions in OSM sediment, was transported to and accumulated in lowland moor peats, and nowadays gets mobilised e.g. by agricultural fertiliser (nitrate) application.

The hydrogeochemical signatures of groundwater samples from the Quaternary moraine deposits are similar to the waters occurring in alluvial Quaternary deposits and belong to alkali mostly carbonated water facies. Total mineralisation varies between 276 and 2268 mg/L (460-571-704 mg/L) and EC between 365 and 1733 µS/cm (540-663-825 µS/cm).

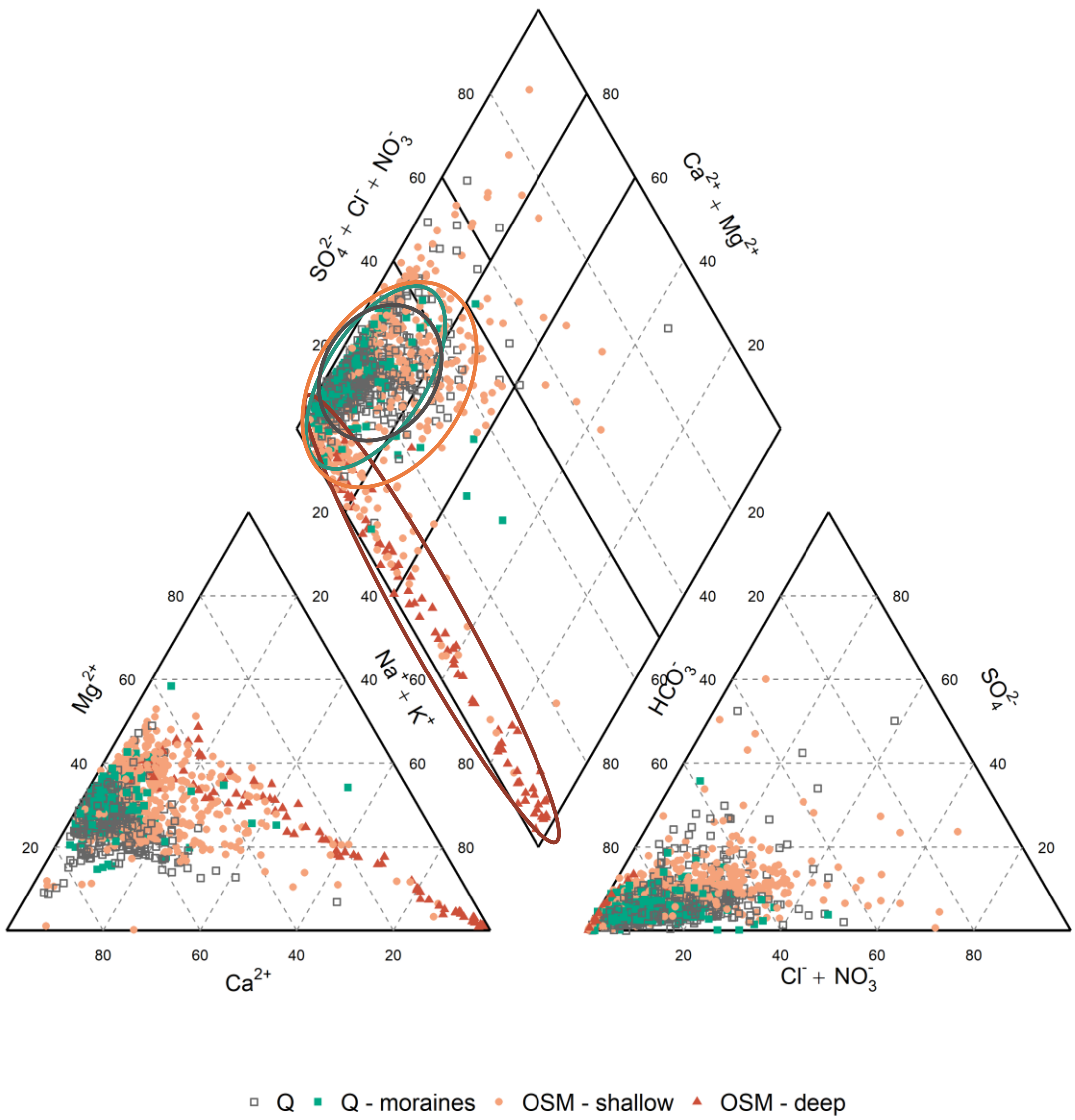

Fig. A10 Piper diagram of groundwater samples (the ellipses for each group are drawn approximately)

The main constituents of shallow OSM waters are calcium, magnesium and hydrogen carbonate. Some water samples represent the hydrogencarbonated-sulfatic water type. Total mineralization is 391-521-710mg/L. 80 % of pH-values range between 7.1 and 7.8 (7.4), which classifies the waters of the shallow as low alkaline. Relatively high concentrations of silica are observed, which may be related to the occurrence of feldspar in the OSM sediments (Wagner et al., 2003). Iron and manganese concentrations were higher in both OSM units in comparison with Quaternary horizons.

Groundwater samples from the level of deeper OSM show a broader typification, from Ca-HCO_3 to Na,K-HCO_3 waters. The pH-values are higher than samples from the "shallower" three units on average. DO is low (0.8 mg/L), similar to nitrate (<LOD), indicating reductive conditions. Also, chloride (1.1 mg/L), sulphate (8 mg/L), calcium (37 mg/L), and magnesium (20 mg/L) were lower than in other units. Sodium concentrations are the highest in this unit, the same as ortho phosphate and fluoride. According to lower content of major ions, total mineralisation and EC are lower. However, some trace elements (B, Ba, Li, Mo, Sr, Ti) show higher concentrations in these deeper-level samples than in

shallower-OSM samples or in the Quaternary. The opposite case is observed for Hg (<LOD), though. Also, uranium concentrations were the lowest among the four hydrogeological units (1.3 µg/L).

It is worth mentioning that some (47 out of 108) of the deep OSM samples show specialized hydrogeochemical signatures, characterized by little total mineralization (<500 mg/L), low EC, higher pH, and lower hardness. Besides other trace elements, also selenium and strontium reveal relatively high concentrations, which can be explained by the occurrence of weathered feldspars in the OSM sediments (Kainzmeier et al., 2007). In previous studies also from OSM, but located east from the study area (region 13-Landshut and 18-Südostbayern), the waters of low EC, low DO, high pH and specific chemistry were described as ion exchange waters (Chavez-Kus et al., 2016; Kainzmeier et al., 2007). The authors related these waters to uprising Malm waters and recalled that higher concentrations of tracer elements (B, Cz, Li, Rb, Th, Ta) present in some OSM wells are typical for Malm waters.

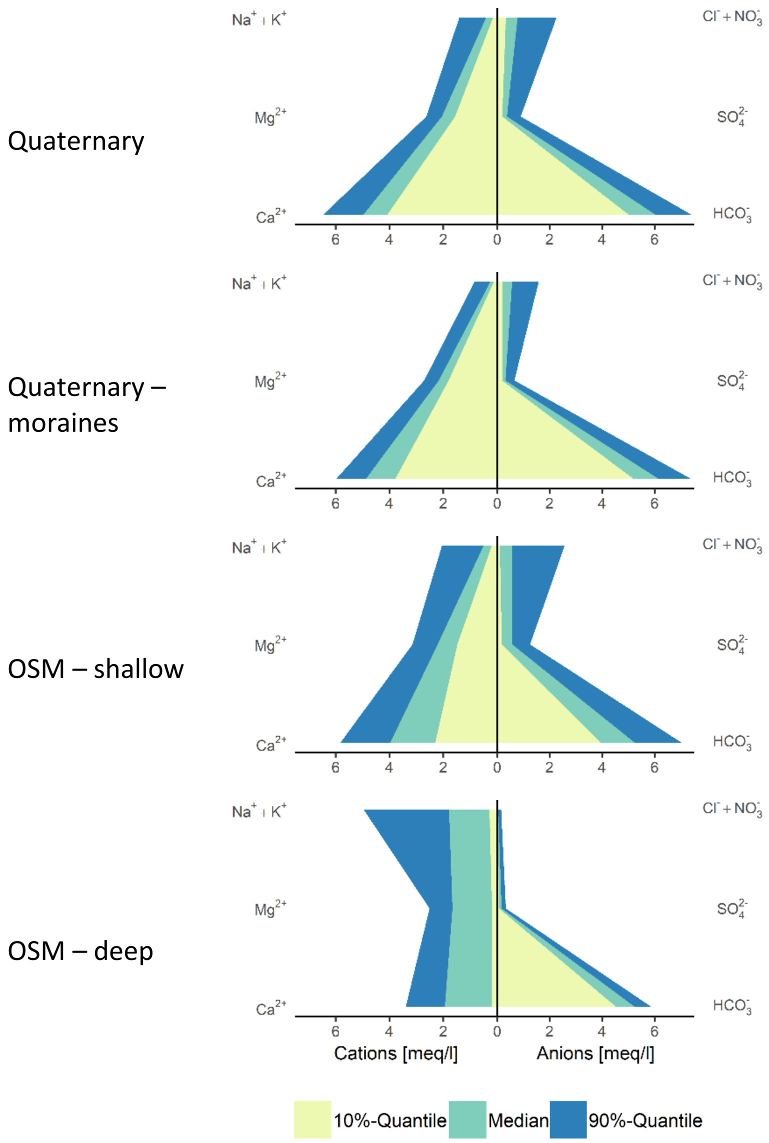

Fig.A11 Stiff diagrams

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