5.7 Geogenic Groundwater Quality

Most of the drinking water demand in Germany is covered by groundwater. It must be available in sufficient amounts and required quality. Maps 5.1 – 5.6 and 7.2 show important aspects of the groundwater occurrences in Germany.

Groundwater naturally contains numerous dissolved minerals. Increasingly, it also contains substances from human activities, e. g. fertilizers and substances from sewage, landfills, and industrial sites. Map 5.7 shows groundwater quality in terms of the geogenic background, i. e. the natural chemical content of the groundwater.

The chemical content (type and amount) of the groundwater is determined mainly by the minerals in the aquifer. Other factors are the cover layers through which surface water percolates into the groundwater, the depth of the groundwater table, and the residence time of the groundwater in the aquifer, which is determined by the permeability of the rock.

Hydrogeological regions (Maps 1.6 and 5.1) can be defined on the basis of the properties of the rocks the water passes through. These regions are characterised by relatively homogeneous hydrogeological and hydrochemical properties. Accordingly, the groundwater in a hydrogeological region can be expected to have a typical chemical composition. Owing to the differences in the geology in different parts of Germany, there are many hydrogeological regions and the natural quality of the groundwater varies accordingly.

Methodology

Map 5.1 "Hydrogeological Regions" was used as the base map for the map of groundwater quality. On Map 5.1, the representative chemical content of the groundwater is shown for five hydrogeological regions and 23 subregions.
There are considerable differences in the chemical content of the groundwater within the hydrogeological subregions, e. g. between the pre-Weichselian and Weichsel moraine regions of northern Germany and those of the Alpine foreland. For this reason, the subregions were subdivided in many cases further.

The groundwater observation wells of the individual Federal States provided the water quality data. Other data is from the Central Geological Institute of the GDR. Of the observation wells, 7575 were selected according to the following criteria:

- The analysis of the last sample taken was usually selected (if two samples were taken each year, the last one in the autumn was chosen).
- To avoid uneven weighting of the data, a mean value was taken in the case closely spaced wells, e. g. well fields.
- The samples were taken at depths of less than 100 m in order to exclude the highly mineralized water often found at depths greater than 100 m.
- All of the main ions (Na, K, Ca, Mg, HCO_3, Cl, SO_4, NO_3) were analysed.
- The ion balance error was less than ± 10 %.
- The pH lies between 4 and 10.
- K < 5 mg/l, or if > 5 mg/l then < 5 mol-%. Higher values are viewed as including an anthropogenic component.
- NO_3^- < 20 mg/l. Higher values are viewed as including an anthropogenic component. In areas with a low density of observation wells, samples with a somewhat higher nitrate content were accepted in order to avoid having too few values. In such cases, the amount > 20 mg/l (viewed as being anthropogenic) was subtracted from these values; elevated Ca and K concentrations were reduced by an equivalent amount. In the case of a low sample density, if the K concentration was elevated it was reduced in the same way and corresponding to the K value, the NO_3 and SO_4 concentrations were also reduced.
- Cl < 50 mg/l. If there were very few samples from an area, concentrations in samples with elevated chloride concentrations which were viewed as anthropogenic (normally > 20 mg/l) were reduced by subtraction of the anthropogenic component, and the Na and K concentrations were reduced by an equivalent amount. Often in the case of an elevated chloride concentration, there was also an elevated Ca concentration and corresponding low alkali concentrations. Such water results from ion exchange during the percolation of alkali water into rocks with a high alkaline earth component. In such cases, the equivalent calcium concentration was subtracted. Regions with a wide distribution of elevated chloride concentrations are shown in Figure 3.
- SO_4 < 250 mg/l. Regions with a wide distribution of elevated sulfate concentrations are shown in Figure 3.

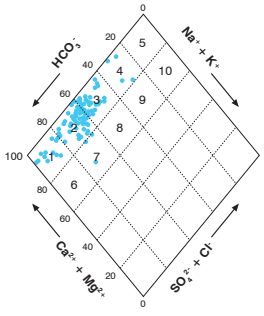

Fig. 1 **Classification of the chemical composition of the groundwater using a Piper diagram;** data points = water in the valley sediments of the Upper Rhine graben (each point represents one observation well)

Map Structures

In order to determine the representativity of the chemical content of the groundwater, the water data for each hydrogeological subregion was classified. The most important chemical parameters of groundwater are the TDS value (total dissolved solids), i. e. the residue on evaporation (which correlates with the electrical conductivity of the sample), and the ionic composition (i. e. the relative amounts of the main components: Na, K, Ca, Mg, Fe, Mn, HCO_3, Cl, SO_4, and NO_3).

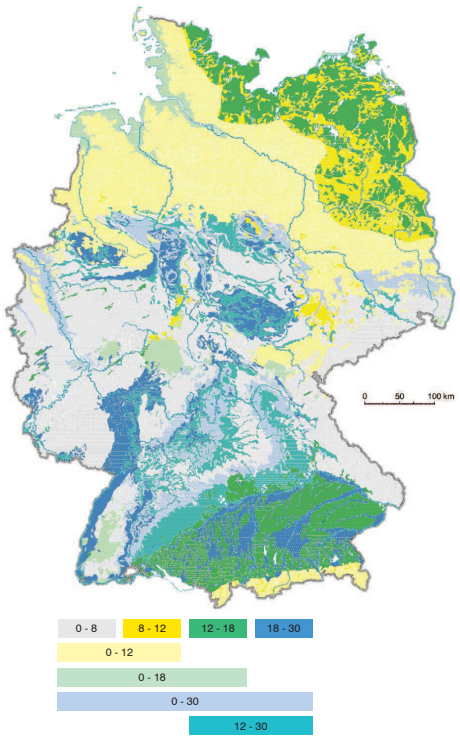

Fig. 2 **Distribution of water hardness in °dH**

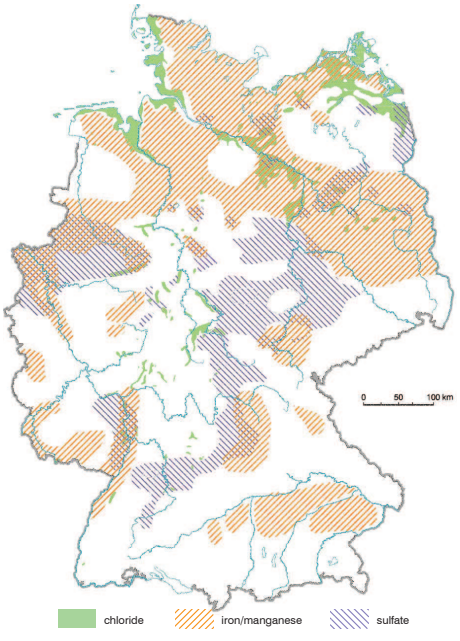

Fig. 3 **Distribution of elevated chloride, sulfate, and iron/manganese concentrations**

The TDS value of the groundwater is strongly influenced by the composition of the aquifer rock. This parameter is, therefore, the main one for classifying the hydrochemical composition. Five TDS classes were formed on the basis of the median values (the middle values) as follows:

- very low TDS (50–200 mg/l)
- low TDS (200–350 mg/l)
- medium TDS (350–500 mg/l)
- high TDS (500–700 mg/l, sometimes as high as 1000 mg/l)
- highly varying TDS (200–700 mg/l)

The scatter in the values (the range between the 25 and 50 percentiles) was normally <50 – 100 mg/l.

The chemical composition of the groundwater is the second classification parameter. For this purpose, the equivalent percents of the main cations and anions are plotted in a Piper diagram (Fig. 1).

Most groundwater is represented by fewer than ten of the 25 classes. The chemical composition of the water of a hydrogeological subregion is characterised by the field or fields in the Piper diagram in which most of the analytical values plot (normally more than 50 % of the values that are considered representative of the subregion). The fields (Fig. 1) are characterised as follows:

1. alkaline earth-carbonate water
2. alkaline earth-carbonate, low sulfate water
3. alkaline earth-carbonate-sulfate water
4. alkaline earth-sulfate, low carbonate water
5. alkaline earth-sulfate water

6.–10. alkaline earth, low alkali water, anions as in 1. - 5.

Eight types of groundwater can be distinguished using the Piper diagram. Each of these types occurs in different concentrations, leading to 22 geogenic groundwater subtypes in Germany (Map Legend).

An example of such a classification is the water in the valley sediments of the Upper Rhine graben, which is classified as carbonate, low sulfate water and carbonate-sulfate water (Fig. 1).

The *water hardness* (i. e. content of Ca and Mg, Fig. 2) is classified according to Kluth-Olszewski: (0 - 8° dH, very soft and soft; 8 - 12° dH, medium hard; 12 - 18° dH, rather hard; 18 - 30° dH, hard; >30° dH, very hard).

Areas with locally elevated chloride, sulfate, iron and manganese concentrations are shown in Figure 3.

Elevated *chloride* values can be due to salt water intrusion along the coast, ascent of saline water from deeper depths or from salt rocks, as well as anthropogenic input.

Elevated *sulfate* values can be due to the weathering of pyritic rocks, but is usually due to anthropogenic activities. Areas with sulfate values frequently > 240 mg/l (the limit for drinking water in Germany) are shown on the map.

Elevated *iron and manganese* values often occur in groundwater with little or no oxygen and low pH values. Areas with Fe values > 0.1 mg/l and Mn values > 0.05 mg/l are shown on the map.

Regional Groundwater Quality

The brief descriptions of groundwater composition in the hydrogeological regions given here are generalised and the composition within a region can vary somewhat or considerably. The statistical parameters are given in Table 1. The geogenic composition, especially for aquifers in consolidated rocks, depends largely on the minerals in the aquifer rocks. The hydrogeological regions, however, are not petrographically homogeneous. Moreover, the composition can be locally influenced by other factors, such as inflow of water from other hydrogeological units or overlying soil layers, e. g. calcareous loess.

Of the *consolidated rocks*, the *strongly indurated and crystalline* rocks normally contain water with a low concentration of dissolved minerals, i. e. soft, usually carbonate-sulfate water whose chemical composition is relatively uniform.
The chemical composition of the water in *slightly indurated* rocks that have been subjected to little diagenesis is less uniform. Medium concentrations and water hardness occur with large variations in clastic sediments (e. g. sandstone and claystone). Water in chemical sediments (e. g. limestone, marlstone, gypsum) is characterised by high concentrations and water hardness. Except for the gypsum-bearing rocks, the water in these rocks is carbonatic and, at the most, weakly sulfatic.

Unconsolidated rock, in contrast to consolidated rock, usually contains many kinds of rock components. Thus, the water composition varies considerably. The higher groundwater flow rates in unconsolidated rock, and thus shorter residence times and less dissolution, also lead to more heterogeneity in the water in these rocks.
The groundwater in gravel, sand, and till on the North German Plain is carbonatic, highly mineralized hard water in the Weichsel deposits northeast of a line from Flensburg-Hamburg-Schwerin-Wittstock-Brandenburg-Jüterbog-Guben. In the pre-Weichselian deposits southwest of this line, the water is softer, has a low mineralization, and has a higher sulfate concentration.

In the following description, the waters are characterised mainly in a qualitative manner. L defines solute content in mg/l, H hardness in °dH. More detailed descriptions with statistical figures can be obtained from Table 1.

Coastal region

Coastal dunes
TDS 200–300 mg/l. Ca-carbonate-low sulfate water, hardness: very soft to medium hard.

Coastal marsh
TDS 250–600 mg/l. Mostly Ca-carbonate, sometimes low sulfate water or low alkali concentrations. Widespread elevated chloride (200–<1000 mg/l) due to salt water intrusion (Fig. 3). Hardness: very soft to medium hard.

5.7 Geogenic Groundwater Quality – Continuation

Regions of unconsolidated rocks

River valleys
- Pre-Weichselian deposits in northern Germany: TDS 200–400 mg/l. Alkaline earth (Ca) water, sometimes with low alkali concentrations, with a large variation in the anion species present. Hardness: very soft to medium hard.
- Weichsel deposits in northern Germany: TDS 300–500 mg/l. Alkaline earth (Ca) water, sometimes with low alkali concentrations; mainly carbonate water, sulfate reaches a maximum of 50 c (ec) %. Hardness: medium hard to hard.
- Lower Rhine embayment: TDS 200–500 mg/l. Alkaline earth (Ca) water, sometimes with low alkali concentrations, with a large variation in the anion species present. Hardness: varies greatly.
- Upper Rhine graben: TDS 450–700 mg/l. Ca-carbonate-low sulfate and Ca-carbonate-sulfate water. Hardness: hard.
- Alpine foreland: TDS 500–600 mg/l. Ca-carbonate water. Hardness: hard.

High terraces, sandur
- Pre-Weichselian deposits in northern Germany: TDS 150–350 mg/l. Alkaline earth (Ca) water, sometimes with low alkali concentrations, with a large variation in the anion species present (mostly carbonate-sulfate, but also carbonate and sulfate water). Hardness: soft to medium hard.
- Weichsel deposits in northern Germany: TDS 300–500 mg/l. Mostly Ca-carbonate, sometimes low sulfate water; widespread elevated chloride (200–<1000 mg/l) in the coastal area due to salt water intrusion (Fig. 3). Considerably more carbonate-rich, more strongly mineralized, and harder than the water in the pre-Weichselian deposits. Hardness: medium hard to hard.
- Rhine–Main–Neckar region: TDS 350–550 mg/l. Ca-carbonate-sulfate water. Hardness: medium hard to hard.

Tertiary basin sediments
- Rhineland: TDS 150–350 mg/L. Ca-carbonate-sulfate water. Hardness: very soft to soft.
- Northern and Central Germany: TDS 300–500 mg/l. Mostly Ca-sulfate water, sometimes sulfate–carbonate water; the sulfate-rich water often has low alkali concentrations. Hardness: medium hard.
- Rhine–Main region: TDS 500–800 mg/l. Ca-Mg-carbonate-low sulfate water. Hardness: hard.
- Bavaria: TDS 400–550 mg/l. Ca-Mg-carbonate water. Hardness: medium hard.

Moraines
- Pre-Weichselian deposits in northern Germany: TDS 200–450 mg/l. Ca-carbonate to carbonate-sulfate water, distinctly softer than the Weichsel deposits, due to dissolution of carbonate in the near-surface deposits over a long period of time. In the deeper aquifers, the groundwater is similar to the groundwater in the Weichsel deposits.
- Weichsel deposits in northern Germany: TDS 400–550 mg/l. Ca-carbonate and carbonate-low sulfate water; widespread elevated chloride (200–<1000 mg/l) in the coastal area due to salt water intrusion (Fig. 3). Hardness: medium hard to hard.
- Alpine foreland: TDS 450–550 mg/l. Similar to the groundwater in the Weichselian deposits in northern Germany, but purely Ca-carbonate water, due to the mostly calcareous rocks of the northern Alps that were the source of the till. Hardness: medium hard to hard.

German uplands – slightly indurated rocks

Sandstones and conglomerates
TDS 150–500 mg/l; hardness: usually soft, but sometimes medium hard to hard. The partly elevated TDS values are due to dissolved gypsum or anhydrite in the upper Bunter or to salt from the Zechstein. Mostly alkaline earth (Ca-Mg)-carbonate-low sulfate water. Groundwater in the Rotliegend in the Saar–Northern Palatinate region is distinctly less mineralized (50–250 mg/l) than that in the Bunter.

Limestones
TDS 450–650 mg/l. Ca- and Ca-Mg-carbonate and carbonate-low sulfate water. Hardness: medium hard to hard.

Volcanic rocks
TDS 100–200 mg/l. Ca-Mg-carbonate and carbonate-low sulfate water. Hardness: very soft to medium hard.

Marlstones
TDS 400–650 mg/l. Ca-Mg-carbonate-low sulfate water. Hardness: hard.

Gypsum and gypsum-bearing rocks
TDS 400–600 mg/l. Ca-Mg-carbonate-sulfate water. Extremely hard sulfate gypsum water has limited distribution. Most of the water is in clayey, silty rock. Hardness: medium hard to hard.

Siltstones and claystones
- North-central uplands: TDS 250–500 mg/l. Ca-Mg-carbonate-low sulfate water. Hardness: varies from very soft to hard.
- Thuringian basin: TDS 650–800 mg/l. The Ca-Mg- and Mg-Ca-carbonate-low sulfate water has a considerably higher mineralization, and Mg concentration than the water in the north-central uplands. This is due to dissolved salt from the Upper Bunter and Keuper (chloride) and Zechstein in and around the Thuringian basin (sulfate). Hardness: hard.
- Southern Germany: TDS varies considerably, 250–700 mg/l. The Ca-Mg-carbonate and carbonate-low sulfate water in the Swabian and Franconian regions and southern Thuringia is similar to that in northern Germany but has a higher carbonate concentration. Hardness: varies considerably from very soft to very hard.

Valley fill
TDS 400–650 mg/l. Ca- and Ca-Mg-carbonate-low sulfate and carbonate-sulfate water. Hardness: medium hard to hard.

Table 1 **Values (mg/l) for the 25th, 50th, and 75th percentiles (P25, P50, and P75) of the ions dissolved in the groundwater in the hydrogeological subregions, i. e., the concentrations below which 25 %, 50 %, and 75 % of the values lie.**
(# insufficient data)

hydrogeological subregion		solute contents			hardness
		P 25	P 50	P 75	[°d H]
coastal dunes		228	261	307	0 - 12
coastal marsh		239	444	584	0 - 18
river valleys	pre-Weichselian North Germany	235	322	416	0 - 12
	Weichselian North Germany	316	420	511	8 - 18
	Lower Rhine embayment	230	382	495	0 - 30
	Oberrheingraben	445	593	692	18 - 30
	Alpine Foreland	489	546	597	18 - 30
high terraces, sandur	pre-Weichselian North Germany	151	244	331	0 - 12
	Weichselian North Germany	306	376	463	8 - 18
	Rhine-Main-Neckar region	365	447	574	12-18, partly >30
tertiary basin sediments	Rhineland	151	231	369	0 - 8
	North and Central Germany	324	394	511	8 - 18
	Rhine-Main region	509	573	832	18 - >30
	Bavaria	394	446	540	8-18, partly 30
moraines	pre-Weichselian North Germany	207	328	475	0 - 12
	Weichselian North Germany	395	470	546	12 - 18
	Alpine Foreland	430	466	557	12 - 30
sandstones, conglomerates		164	365	519	0-8, partly 30
mesozoic limestones		444	532	647	12 - 30
vulcanic rocks		118	149	191	0 - 18
marlstones		424	552	645	18 - 30
gypsum and gypsum-bearing rocks		405	506	629	12 - 30
siltstones and claystones	North-German uplands	250	424	518	0 - 30
	Thuringian Basin	645	725	814	18 - 30
	South Germany, South Thuringia	256	471	687	0 >30
valley fill in mesozoic rocks		425	548	649	12 - 30
paleozoic dolomites and limestones		409	423	523	12 - 18
graywacken and quartzites	Rhein. Schiefergebirge, Harz	66	84	122	0 - 8
	Thuringia, Saxony	227	334	434	0 - 12
highly jointed crystalline rocks		79	235	374	0 - 8
slightly jointed crystalline rocks		51	128	221	0 - 8
slates	Rhein. Schiefergebirge, Harz	70	107	169	0 - 8
	Thuringia, Saxony	194	289	418	0 - 12
tuff		345	496	714	0 - 8
valley fill in paleozoic rocks		193	233	340	8 - 12
Alps: consolidated rocks		225	228	248	8 - 18
Alps: coarse gravel				363#	

German uplands – strongly indurated and crystalline rocks

Dolomites and limestones
TDS 400–500 mg/l. Ca-Mg-carbonate, sometimes low sulfate water. Hardness: medium hard to hard.

Graywackes and quartzites
- Rhenish Slate Mountains and Harz Mountains.: TDS 50–150 mg/l. Ca-Mg-carbonate-sulfate and sulfate water. Hardness: very soft to soft.
- Thuringia and Saxony: TDS 200–400 mg/l. The Ca-Mg-carbonate, sometimes low sulfate water has a low mineralization and hardness that is, however, considerably higher than in the water of the Rheinisches Schiefergebirge (Rhenish Slate Mountains.) and Harz Mountains. This is due to dissolved salt from the Zechstein along fault zones. Hardness: soft to medium hard.

Highly jointed crystalline rocks
TDS 100–400 mg/l. Ca-Mg-carbonate-sulfate and sulfate water. Hardness: very soft to soft.

Slightly jointed crystalline rocks
TDS 50–200 mg/l. Ionic concentrations vary greatly: Ca-Mg-carbonate and sulfate water, as well as low alkali concentrations. Hardness: very soft to soft.

Slates
- Rhenish Slate Mountains and Harz Mountains.: TDS 50–200 mg/l. Ca- and Ca-Mg-carbonate-sulfate and sulfate water. Hardness: very soft to soft.
- Thuringia and Saxony: TDS 200–400 mg/l. Ca-Mg-carbonate-sulfate and sulfate water. Like in the graywacke and quartzite hydrogeological region in Thuringia and Saxony, elevated mineralization and hardness are due to dissolved Zechstein salt. Hardness: very soft to medium hard.

Tuff
TDS 350–700 mg/l. Ca-Mg-carbonate-sulfate and Ca-Mg-sulfate water. Hardness: soft to very hard.

Valley fill
TDS 200–500 mg/l. Ca-carbonate-sulfate and Ca-sulfate water, sometimes with low Mg concentrations. The more sulfate-rich water often has low alkali (Na) concentrations. Hardness: very soft to soft.

Alpine region

Limestones, calcareous marlstones, sandstones and calcareous sandstones, marlstones
TDS 200–300 mg/l. Ca-Mg-carbonate water. Hardness: medium hard.

Coarse gravel
TDS 300–400 mg/l. Ca-Mg-carbonate water, like in the consolidated rocks. Hardness: somewhat harder and more highly mineralized.

Practical Information

Further information about water quality in Germany can be obtained from the "Geochemischer Atlas Bundesrepublik Deutschland, Verteilung von Schwermetallen in Wässern und Bachsedimenten" (Geochemical Atlas of Germany: Distribution of Heavy Metals in Surface Water and Stream Sediments) published by the Federal Institute for Geosciences and Natural Resources (BGR), Hannover (a new edition is in preparation to include the new Federal States of eastern Germany); "Beschaffenheit der Fließgewässer in der Bundesrepublik Deutschland, Beschaffenheit der Fließgewässer in der DDR, Grundwasserbeschaffenheit in der DDR" (Quality of Stream Water in the Federal Republic of Germany, Quality of Stream Water in the GDR" in "Daten zur Umwelt 1990/91" (Data on the Environment 1990/91) published by the Federal Environmental Agency (UBA), Berlin, 1992; and reports issued by the individual Federal States on groundwater. For Lower Saxony, information on "Digitaler Atlas Hintergrundwerte natürliche chemische Gehalte von Bachsedimenten, Böden, Gesteinen und Grundwasser" (digital atlas background values of natural chemical concentrations in streams sediments, soils rocks and groundwater) can be obtained from the CD issued by the Lower Saxony Geological Survey (NLfB), Hannover. For Baden-Württemberg, groundwater composition is available on the CD "Geowissenschaftliche Übersichtskarten" (Geoscientific Maps of Baden-Württemberg, 1 : 350 000) issued by the Landesamt für Geologie, Rohstoffe und Bergbau (Baden-Württemberg Geological Survey), Freiburg, 1998.