

## A PROCEDURE TO DEFINE NATURAL GROUNDWATER CONDITIONS OF GROUNDWATER BODIES IN GERMANY

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### ABSTRACT

Commissioned by Germany's *Working Group of the Federal States on Water Problems (LAWA)* the authors developed a procedure to define natural groundwater conditions from groundwater monitoring data. The distribution pattern of a specific groundwater parameter observed by a number of groundwater monitoring stations within a petrographical comparable groundwater typology is reproduced by two statistical distribution functions, representing the "natural" and "influenced" component. The range of natural groundwater concentrations is characterized by confidence intervals of the distribution function of the natural component. The applicability of the approach was established for four hydrochemical different groundwater typologies occurring throughout Germany. Based on groundwater monitoring data from 7920 groundwater monitoring stations, 15 different hydrochemical parameters were evaluated for each groundwater typology. For all investigated parameters the range of natural groundwater concentrations have been identified. According to the requirements of the *EC Water Framework Directive* (article 17) (WFD) this study is a basis for the German position to propose criteria for assessing a reference state for a "good groundwater chemical status".

**Keywords :** EC Water Framework Directive (article 17), WFD, good groundwater chemical status, groundwater typologies, groundwater protection, groundwater quality

### INTRODUCTION

The solution content of groundwater is determined by a variety of factors, such as the properties of the vadoze zone and the groundwater bearing rocks as well as the hydrological and hydrodynamic conditions. Additional to these "natural" factors groundwater quality is influenced by anthropogenic influences, e.g. landcover changes, diffuse intakes from agriculture and the atmosphere, point source intakes (see fig.1). Whereas the occurrence some groundwater parameters (e.g. pesticides) are direct indicators of human impact, most inorganic contents may originate both from natural and anthropogenic sources. This makes it difficult to decide whether an observed groundwater condition is reflecting the "good groundwater chemical status" according to the requirements of the WFD or not, which would imply that measures to decontaminate the groundwater have to be drawn.

Because of the omnipresence of human impacts strictly „natural“ groundwater occurs at best at regionally limited locations. Especially groundwater from aquifers taking part in the active water cycle (surface-near aquifers), in most cases those aquifers which were used for water supply, are influenced since decades and centuries by anthropogenic activities, e.g. soil cover induced changes of percolation water quality or fertilizer inputs. In Germany this situation is true for more than 99% of the entire area. Consequently, the present solution content of groundwater samples from surface-near aquifers do hardly represent strictly "natural" groundwater concentrations. Deriving natural groundwater concentrations from samples from unaffected deeper aquifers, however, would be of no relevance for practical water resources management, as it reflects "untypical" groundwater conditions.

Against this background a more pragmatical understanding of the term "*natural groundwater condition*", which considers the human impacts on groundwater to a certain degree as inevitable, needs to be developed. This is done by Schenk (2001), who considers natural groundwater concentrations to be present, if "*the concentrations of the most important cations and anions originate from not significant anthropogenic influenced soils and the rocks of a watershed, including groundwater from areas under agricultural use or from areas where landcover changes occurred over the last centuries*".

### METHODS

The definition of natural groundwater quality by Schenk was the starting point for this research project, which has been commissioned by the *Working Group of the Federal States of Germany on Water Problems (LAWA)*. The aim of this project was to provide data for the definition of "good groundwater chemical status" from existing data from groundwater monitoring networks provided by the Federal States. As a reference four groups of aquifers, each with comparable petrographical and hydrodynamic properties (groundwater typologies) were investigated. The selected groups, Triassic limestones, Triassic sandstones, Loose-rock sediments of the Saale glaciations and Jurassic limestones, occur throughout Germany and have a high relevance for water supply. For these typologies in total 10 different data sets from 8 Federal States (50000 groundwater samples from 19500 monitoring stations) were made available by the involved State authorities.

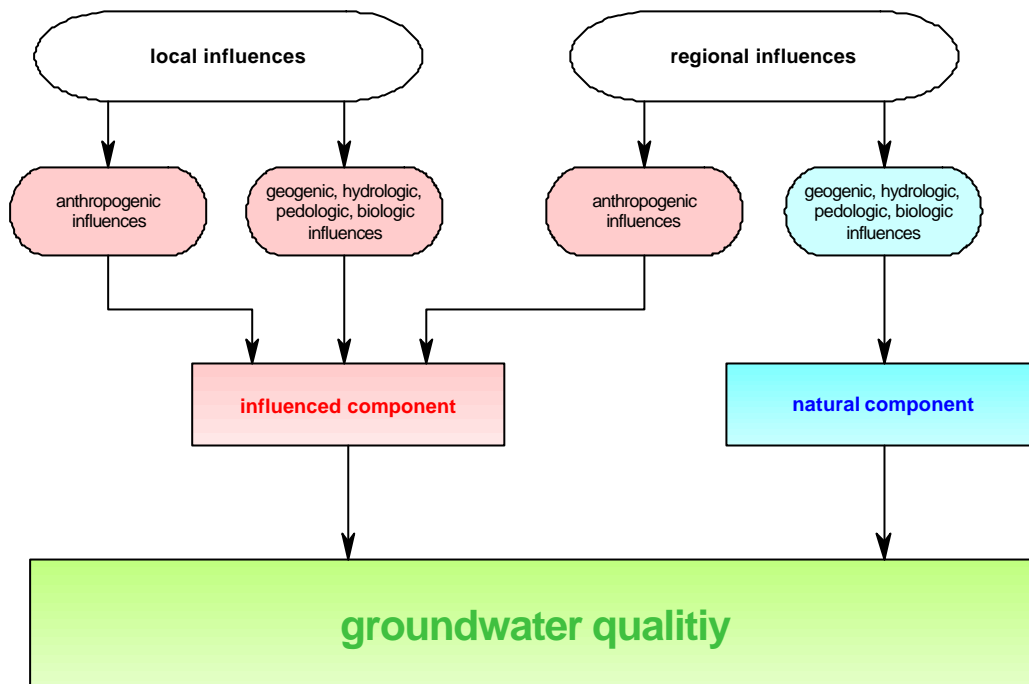


Figure 1: Factors influencing groundwater quality (LfU, 1996, modified)

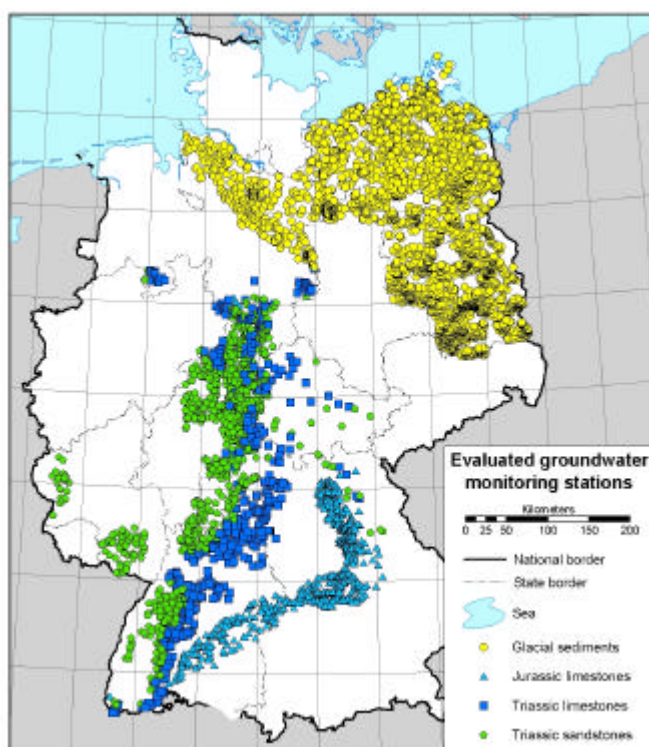


Figure 2: Evaluated groundwater monitoring data

Before assessing natural groundwater concentrations the individual heterogeneous data sets needed to be joined together in one data base with unified structure and referenced to the groundwater typologies. In addition, a number of consistency checks, e.g. the elimination of analyses with incorrect ion balances, salt effected stations and elimination of time series by median averaging had to be performed. At the end, a total of 7920 monitoring stations in the investigated groundwater typologies with one representative groundwater analysis each were used for the analysis.

The 15 evaluated groundwater parameters include environmental and redox parameters (O<sub>2</sub>, pH), summary parameters (electric conductivity, DOC), main substances of content (Na, K, Ca, Mg, Cl, HCO<sub>3</sub>, SO<sub>4</sub>) and adjoining substances of content (Fe, Mn, NH<sub>4</sub>, NO<sub>3</sub>). Table 1 lists the total number of observations available for each parameter in the individual groundwater typologies. The number of evaluated observations for each parameter in each typology was in the range between 500 and about 4900, allowing a statically relevant analysis.

**Table 1: Number of observations for each groundwater typology and each parameter.**

	Sediments of the Saale glaciation	Jurassic Limestones	Triassic Limestones	Triassic Sandstones
El. Conductivity	3012	921	541	533
O <sub>2</sub>	824	902	622	1378
PH	4769	923	650	1469
DOC	4309	211	399	433
Ca	4699	809	649	1460
Mg	4683	810	648	1461
Na	2105	810	648	1459
K	2086	388	537	1409
NH <sub>4</sub>	4549	809	512	510
Fe	4615	806	626	1309
Mn	4260	808	570	1187
HCO <sub>3</sub>	4741	807	649	1447
Cl	4846	810	649	1464
SO <sub>4</sub>	4654	810	649	1461
NO <sub>3</sub>	4521	810	650	1468

It can be expected that the solute content of a typical groundwater is affected both by natural and anthropogenic factors. Anthropogenic inputs of a certain substance of content into groundwater, will lead to an increase of groundwater concentration of this substance. Because of the variability both of natural and anthropogenic influences it is not possible to separate these two influencing factors by just looking at one single groundwater sample. Therefore it is necessary to analyse a large number of groundwater samples statistically, with the condition that these samples were taken from aquifers, which can be regarded as being almost hydrochemically homogenous. This is the case for the groundwater typologies investigated here.

Starting point of the analysis is the frequency distribution of the observed concentrations of a groundwater parameter, illustrated as black dots in figure 3. It is assumed that this concentration profile can be expressed by the superimposition of two components, representing the natural and influenced contributions. In that case the observed concentration distribution ( $f_{obs}$ ) may be described by the sum of two statistical distribution functions, representing the natural ( $f_{nat}$ ) and the influenced ( $f_{infl}$ ) component:

$$f_{obs}(c) = f_{nat}(c) + f_{infl}(c) \quad (1)$$

The mathematical forms of the two distribution functions are not known from a priori. But it can be expected that concentration patterns, which are predominantly resulting from redox reactions in the soil or the groundwater bearing rocks may be represented by lognormal distributions, whether concentration patterns originating from direct inputs from the soil are more or less proportional to the inputs into the soil and may be represented by normal distributions. Therefore, the natural component should follow a lognormal distribution, whereas the anthropogenic component should usually follow a normal distribution.

The explicit shape of both distribution functions is determined by three independent parameters each (amplitude, median and variance), which have to be fitted to the observed frequency distribution using standard algorithms. As a result, the observed distribution pattern is represented by two distribution functions of known shape, which can be assigned to the natural and anthropogenic component.

Specification of natural groundwater conditions can be done by any two independent parameters characterizing the distribution function of the natural component. For the normal and the lognormal distribution, the median and the variance are the most common parameters given. However, these parameters will give not a very transparent measure to specify typical groundwater conditions. Therefore, natural groundwater concentrations are characterized by a concentration range defined by the 10% and the 90% percentiles of the concentration distribution of the natural component.

## SELECTED RESULTS

According to the procedure described above, the natural components in the investigated four groundwater typologies were identified for all 15 parameters and the ranges for natural groundwater concentrations were derived.

### Potassium

As an example, figure 4 shows the potassium concentrations in the groundwater typologies *Triassic Limestones* and *Loose Rock Sediments of the Saale Glaciation*. In both distributions only one peak at about the same concentration (~2 mg K/l) is

present. The width of the distributions, however, is quite different: the potassium concentration range in the loose rock sediments is almost twice the range in the triassic limestones.

As can be seen from the correlation coefficients ( $r^2 \geq 0,99$ ), the observed concentration distributions can be separated very satisfyingly into a natural and influenced component. As a typical behaviour, obtained also for most other evaluated hydrochemical parameters (e.g. Na, Cl, SO<sub>4</sub>, HCO<sub>3</sub>, DOC), the (lognormal distributed) natural component is dominating while the (normal distributed) influenced component contributes as a broad background.

The natural groundwater component of the potassium concentration distribution in the *Triassic Limestones* shows a relatively small scatter in the range between 0.6 and 2.1 mg K/l. This can be addressed to the lack of potassium containing minerals in this typology. An influenced component is obvious, which has also been confirmed by regional water authorities as the influence of potassium containing fertilizers. The range of the natural potassium concentrations in the groundwater of the *Loose Rock sediments of the Saale Glaciation* is broader compared to the natural groundwater concentrations in the Triassic limestones. This is a consequence of the relatively heterogeneous mineral composition of the sediments of the Saale Glaciation. The portion of the influenced component is relatively high. Here two factors are determinative: the rise of the high mineralised waters from deeper aquifers and the influence of sea water intrusion in the north and the western part of the groundwater unit.

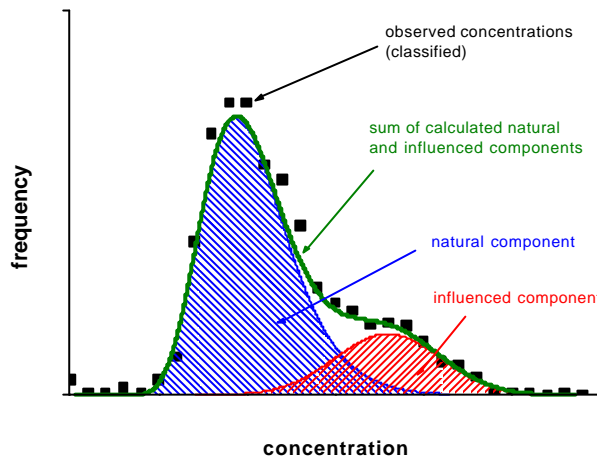


Figure 3: Basic approach of separating the natural and influenced component from an observed groundwater concentration pattern.

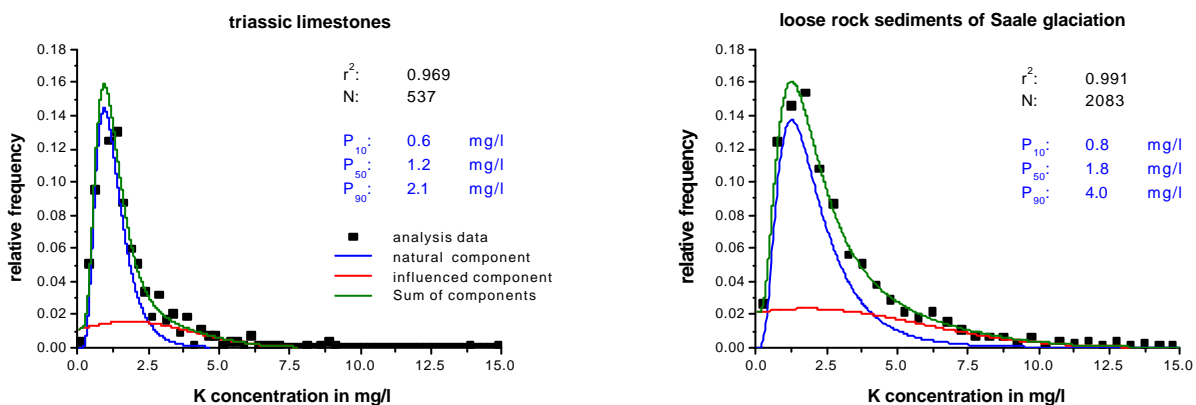


Figure 4: Observed (dots) and modelled (green) frequency distributions as well as natural (blue) and influenced (red) components of potassium concentrations in the Triassic Limestones (left) and the Loose Rock Sediments of the Saale Glaciation (right).

**Iron**

Figure 5 shows the iron concentrations in the *Triassic Sandstones* and *Loose Rock Sediments of the Saale Glaciation*. Compared to the potassium concentrations shown in figure 4 the iron concentrations show a very different behaviour. Most of the samples display very small iron concentrations in the lowest category. This distribution pattern is typical for parameters, which were almost completely removed from groundwater by redox-reactions. The same distribution type is observed for other hydrochemical parameters like Mn and NH<sub>4</sub> as well as NO<sub>3</sub> in the Loose Rock Sediments of the Saale Glaciation (see figure 6).

The iron concentrations in the (figure 5 left) show a monotonous decay of the frequencies towards higher concentrations. This behaviour is typical for an oxidized groundwater type, which is almost free ( $P_{90} < 0.1$  mg Fe/l) of solved iron (II). Although this observation can be reproduced by a lognormal distribution, a second component representing an influenced

component cannot be identified. This indicates that the iron concentrations in the groundwater are hardly influenced by anthropogenic inputs and geogenic anomalies.

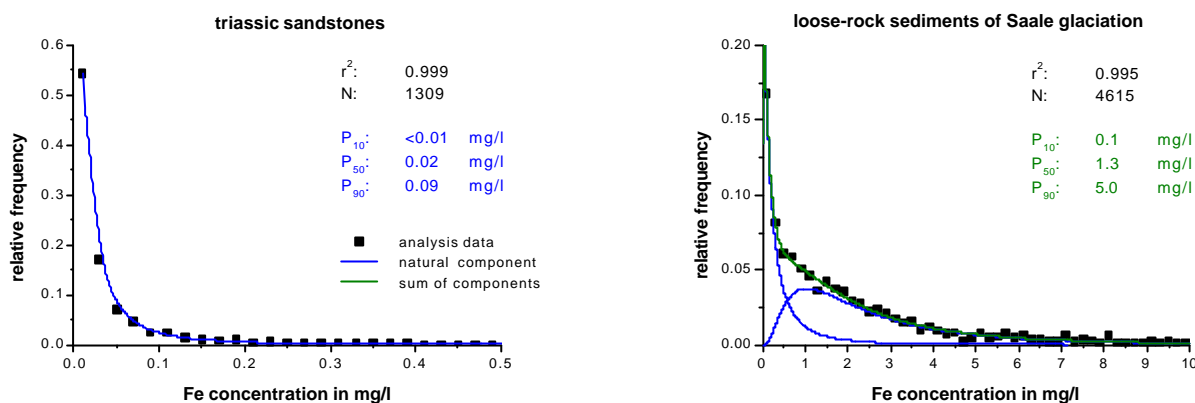


Figure 5: Observed (dots) and modelled (green) frequency distributions as well as natural (blue) components of iron concentrations in the Triassic Sandstones (left) and the Loose Rock Sediments of the Saale Glaciation (right).

Although the iron concentrations in the *Loose Rock Sediments of the Saale Glaciation* also show a monotonous decay, the iron concentrations are larger than those in the Triassic Sandstones and are the result of a different chemical situation. In this groundwater typology two components, both following a lognormal distribution, can be identified. However, none of the two components can be addressed directly to anthropogenic influences. The first component, having its maximum in the lowest concentration class, arises from oxidized groundwater zones in preferably shallow and unconfined aquifers, where almost o solved iron(II) is present. The second component, which has its maximum around 1 mg Fe/l characterizes the situation typical for reduced groundwater conditions well known for loose rock sediments. It is not allowed to classify one of these two components as being influenced and exclude it from the further assessment of natural iron concentrations. Instead, two groundwater types occur in parallel in the Loose Rock Sediments of the Saale Glaciation, resulting in a broad concentration range for the natural groundwater concentration between 0.1 and 5 mg Fe/l.

This example shows, in a more general sense, that it is urgently necessary to assess natural groundwater concentrations according to the petrography and the hydrodynamics of the groundwater typologies. Consequently, iron concentrations of 3 mg Fe/l can be considered as being "natural" in the case of the Saale aquifers. In the case of the hard rock groundwater units 3 mg Fe/l would have to be considered as "influenced".

### Nitrate

Compared to the other groundwater parameters evaluated in this study, nitrate is an exception. The geogenic fraction of nitrate in groundwater is low. The reason for this is that all nitrate minerals are very water soluble, so that in the course of geological history no nitrate rocks were formed from which nitrate could be solved by circulating water. The most important source of nitrate in groundwater are fertilizers and to a minor extent atmospheric nitrate inputs. Many studies have shown, that nitrate concentrations above 5 mg  $\text{NO}_3/\text{l}$  are a reliable indication of anthropogenic influences.

In some groundwater typologies however, nitrate can be degraded to molecular nitrogen by microbial controlled redox-reactions. If a groundwater is largely free of dissolved oxygen, certain micro organisms are able to satisfy their oxygen demand by reducing nitrate. An important prerequisite for this reaction is the presence of organic carbon compounds or pyrite ( $\text{FeS}_2$ ) in the aquifer acting as reducing substances. As could be shown by the example of the iron concentration distributions, this hydrochemical groundwater condition may occur in the Loose Rock Sediments of the Saale Glaciation. Figure 6 shows the observed nitrate concentrations distributions in the groundwater typologies Jurassic Limestones and Loose Rock Sediments of the Saale Glaciation. The nitrate concentrations in the *Jurassic Limestones* cover a wide range between 0 and about 75 mg  $\text{NO}_3/\text{l}$ . Two widespread components may be identified, each showing a maximum above 10 mg  $\text{NO}_3/\text{l}$  and 90% percentiles above 30 mg  $\text{NO}_3/\text{l}$ . from this distribution pattern it can be concluded that the groundwater in this groundwater typology is ubiquitously influenced by anthropogenic nitrate inputs to a degree, which makes it impossible to identify a natural component. Instead, the observed nitrate concentrations may be regarded as an orientation range for "typical occurring" nitrate concentrations in this groundwater typology.

For the nitrate concentrations realized in the *Loose rock sediments of the Saale Glaciation* only one lognormal distribution can be identified. As most of the samples fall into the lowest class it may be tempting to conclude that the groundwater in these aquifers is almost free from anthropogenic nitrate inputs, thus representing "natural" groundwater concentrations. However, this interpretation is misleading. Due to denitrification processes in reduced aquifers, it may be possible that a groundwater appears to be almost nitrate free, although the nitrate inputs with the percolation water were high. Hence, the

range of nitrate contents in the Loose Rock Sediments of the Saale Glaciation reflects on the hydrogeochemical conditions in the aquifer, which result in “natural” nitrate concentrations between 0,001 and 0,1 mg/l.

		Sediments of the Saale glaciation		Jurassic Limestones		Triassic Limestones		Triassic Sandstones	
		10%	90%	10%	90%	10%	90%	10%	90%
el. conductivity	µS/cm	<b>186</b>	<b>521</b>	387	704	637	939	50	256
O <sub>2</sub>	mg/l	<b>0,2</b>	<b>4,6</b>	6	11	3	10	5	11
PH		<b>6,0</b>	<b>7,8</b>	7,1	7,7	7,0	7,5	6,8	7,7
DOC	mg/l	<b>0,8</b>	<b>5,0</b>	0,3	1,3	0,4	1,2	0,3	1,6
Ca	mg/l	<b>29</b>	<b>143</b>	69	126	99	154	7	29
Mg	mg/l	<b>3</b>	<b>30</b>	4	37	17	50	2	23
Na	mg/l	<b>6</b>	<b>24</b>	1,3	6,3	3,0	9,2	2	16
K	mg/l	<b>0,8</b>	<b>4,0</b>	0,3	1,9	0,6	2,1	1,3	3,6
NH <sub>4</sub>	mg/l	<b>&lt;0,01</b>	<b>0,5</b>	<0,01	<0,01	<0,01	<0,01	<0,01	<0,01
Fe	mg/l	<b>0,1</b>	<b>5,0</b>	<0,01	0,15	<0,01	0,1	<0,01	0,1
Mn	mg/l	<b>0,04</b>	<b>0,64</b>	<0,01	<0,01	<0,01	0,01	<0,01	<0,01
HCO <sub>3</sub>	mg/l	<b>150</b>	<b>426</b>	278	380	287	446	6	96
Cl	mg/l	<b>9</b>	<b>43</b>	5	37	9	49	4	17
SO <sub>4</sub>	mg/l	<b>4</b>	<b>68</b>	13	32	30	147	5	58
NO <sub>3</sub>	mg/l	<b>&lt;0,01</b>	<b>0,1</b>	-	-	-	-	3	34

Table 2: Natural groundwater concentration ranges in the groundwater typologies

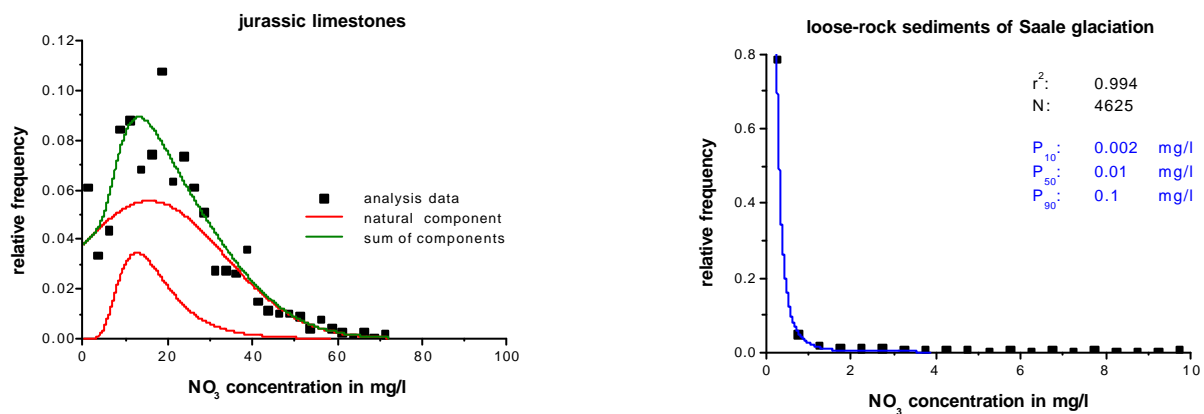


Figure 6: Observed (dots) and modelled (green) frequency distributions as well as natural (blue) components of nitrate concentrations in the groundwater typologies Jurassic Limestones (left) and Loose Rock Sediments of the Saale Glaciation (right).

## DISCUSSION AND CONCLUSIONS

Natural groundwater concentrations were defined using ten data sets, which were heterogeneous with regard to the spatial and temporal distribution of the sample data as well as the purpose of the basic sampling programme of the monitoring network in the different Federal States. These data sets were joined together in a uniform data base and referenced to the four groundwater typologies investigated here. As the frequency distributions of the individual parameters turned out to be homogeneous in each of these groundwater typologies, it was concluded that the basic procedure, i.e. the separation of heterogeneous groundwater analyses according to petrographical and hydrodynamical properties of aquifers, is a suitable starting point to assess natural groundwater concentrations.

The basic approach of separating the natural and influenced component from observed groundwater concentration distributions based on statistical distribution functions was applied consistently to all 15 investigated groundwater parameters in the investigated groundwater typologies. Table 2 summarizes the concentration ranges of the natural groundwater concentrations for all groundwater typologies and all parameters.

Table 2 shows that for some parameters the assessed natural groundwater concentration ranges are almost identical in the four typologies. The redox parameters Fe(II), Mn(II) and NH<sub>4</sub>, for instance, show in all hard rock groundwater typologies concentration ranges between 0.01–0.1 mg/l and for DOC ranges between 0.3 and 1.6 mg/l. As these concentration ranges occur on the basis of a similar chemical situation (oxidized groundwater), this indicates that in further investigations no differentiation according to the groundwater typologies would be necessary for these parameters.

For most other parameters, however, the natural groundwater concentration ranges differ considerably amongst the investigated groundwater typologies, reflecting the different properties of the vadoze zone and the groundwater bearing rocks as well as the hydrological and hydrodynamic conditions. The Calcium and Magnesium concentrations for instance do not only show (the expected) differences between the limestones and the clastic sediments, but also considerably differences between the jurassic and the triassic limestones. For these two typologies the results can be explained by the “natural” degree of dolomitisation.

The pilot study showed that natural groundwater concentrations should not be defined based on fixed threshold values as being “valid for the whole groundwater“. Instead, the results study showed the importance to assess natural groundwater concentrations according to individual groundwater typologies. Because of the promising results of the pilot study, the *Working Group of the Federal States of Germany on Water Problems (LAWA)* recommended the extension of this study in 2003 towards all groundwater typologies in Germany not considered so far. In this sense, this study contributes to the definition of the “good groundwater chemical status” according to the requirements of the EC WFD.

## REFERENCES

- Kunkel, R., Hannappel, S., Voigt, H.-J., Wendland, F. (2002): Die natürliche Grundwasserbeschaffenheit ausgewählter hydrostratigrafischer Einheiten in Deutschland.- Endbericht eines FuE-Vorhabens im Rahmen des Länderfinanzierungsprogramms „Wasser und Boden“ der Länderarbeitsgemeinschaft Wasser (LAWA). 97 S.
- LfU (1996): Grundwasserüberwachungsprogramm. Landesamt für Umweltschutz Baden-Württemberg, Karlsruhe, 2. Ed.
- Schenk, V. (2001): Natürliche Grundwasserbeschaffenheit. Stellungnahme des PK „Natürliche Grundwasserbeschaffenheit“ an den DVGW, Bergheim.