Assessment of Natural Groundwater Concentrations of Hydrogeological Structures in Germany

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1. Introduction

On 23 October 2000, the European Parliament and the Council adopted the Water Framework Directive (Directive 2000/60/EC – *WFD*), which constitutes the basic legislation for management and protection of the aquatic environment in Europe.

An "Expert Advisory Forum on Groundwater based on Article 17 of the WFD" (*EAF*) was established to propose measures of groundwater control and protection. These measures should be designed to achieve the objective of good groundwater chemical status in accordance with Article 4(1)(b) of the WFD. On their session in October 2002 EAF found that "the option to set out a list of quality standards that would be uniformly applied to all groundwater bodies throughout Europe in relation to the definition of good chemical status was withdrawn, owing to the natural variability of groundwater chemical composition and the lack of present monitoring data and knowledge". But the EAF recommends that the member states characterise the good (natural) chemical status of groundwater bodies (hydrogeological structures) in their respective countries independently.

2. Data basis of hydrogeological information in Germany

According to the Expert Advisory Forum on Groundwater (EAF), the data bases for regional hydrogeological information are on very different levels, not only in various countries of Europe but also within Germany. There are two important reasons for that situation in Germany.

Firstly, laws and directives for water are the responsibility of the individual states in the Federal Republic. Regional evaluation and measures for control and protection depend on the local state organisations.

Secondly, there are different pragmatic and scientific approaches for ground water studies existent in the old and new federal states of Germany. In the former GDR, groundwater was treated as a resource. For an exploitation of groundwater, regional exploration of a watershed was necessary. Groundwater exploitation by water works was permitted only on the basis of estimated groundwater resources. In old states of Germany, permission was already given on the basis of pumping test only, without exploration.

As a consequence of these two reasons, there exists no unified hydrogeological map for the whole country (only for the territory of the former GDR a hydrogeological map to a scale of 1:50000 is available).

No regionalisation of hydrogeological structures and their vertical profiling in the form of a hydrogeological stratification had been done, so there was no possibility of correlation of hydrogeological information across the borders of separate states.

There are no adequate systems for monitoring level and quality of groundwater in different states.

A solution for these problems is necessary not only for the characterisation of natural chemical groundwater conditions, but also in order to be able to deliver Germany's report to the EU, as required by other articles of the Water Framework Directive (WFD).

This is the reason why a method for hydrogeological mapping was prepared for the first aquifer below surface for the whole territory of Germany. (HANNAPPEL et al.) Work will be finished by the end of this year.

A group of hydrologists was assembled from all State Geological Surveys for the realisation of the tasks which were connected to the report required by the WFD. As the first step, the hydrogeological regionalisation of entire Germany was carried out by this group (figure 1) Ten main hydrogeological structures on German territory were distinguished. The first group of hydrogeological structures includes unconsolidated aquifers of Cenozoic age:

1. Unconsolidated Rocks of the Central European Basin

2. Rhenish-Westphalian Basin

3. Upper and Lower Rhine Graben

4. Alpine Foreland

The second group contains Mesozoic fissured and porous deposits:

5. Central German Sedimentary Basin

6. West and South German Sedimentary Basin

7. Alpine Folded Area

The third group comprises fissured aquifers of hydrogeological massifs:

8. West and Central German Massifs (Rhine Mountains, Harz, Pfalz Forest, and others)

9. Southeast German Massifs (Ore Mountains, Thuringian Forest, Bavarian Forest, and others)

10. Southwest German Massifs (Black Forest, Odenwald, and others)

Correlation schemes of regional aquifers and aquicludes were prepared for those major hydrogeological structures. Table 1 describes, as an example, the hydrostratigraphic units of the unconsolidated rocks of the Central European Basin which contain natural groundwater. (MANHENKE et al. 2001)

By this, the foundations for correlation of existing hydrogeological data of monitoring and exploration wells were created.

3. Methodical Approach

The solution content of groundwater is determined by a variety of factors, such as the properties of the vadose zone and the groundwater bearing rocks, as well as the hydrological and hydrodynamic conditions (see figure 2). In addition to these "natural" factors groundwater quality is affected by anthropogenic influences, e.g. land cover changes, diffuse input from agriculture and the atmosphere, and point source input (APPELO & POSTMA 1996, LfU 1996, MATTHESS 1994, DOMENICO & SCHWARTZ 1990, VOIGT 1990). Whereas the occurrence of some groundwater parameters (e.g. pesticides) is a direct indicator of human impact, most inorganic constituents may originate both from natural and anthropogenic sources. This renders 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; the latter implying that measures to decontaminate the groundwater have to be taken.

Because of the omnipresence of human influences, truly "natural" groundwater occurs at regionally limited locations at best. Especially groundwater from aquifers that are part of the

active water cycle (aquifers close to the surface) are influenced since decades and centuries by human activities, e.g. agriculture, which changed soil types or soil cover, which in turn induced changes in percolation water quality. This situation is true for more than 99% of the area of Germany. Consequently, the present solution content of groundwater samples from aquifers close to the surface rarely reflects true "natural" groundwater concentrations.

Against this background a more pragmatic understanding of the term *"natural groundwater condition"*, which considers human impact to a certain degree as inevitable, is suggested. In this paper this is done by assuming natural groundwater concentrations to be present *if the concentrations of the most important cations and anions originate from anthropogenically not significantly influenced (by fertilizers) soils and rocks of a watershed, including groundwater from areas under agricultural use or from areas where land cover changes occurred over the last centuries.* (SCHENK 2003)

This definition of natural groundwater quality 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 of 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 hydrostratigraphical units,

- aquifers in Triassic limestones (Muschelkalk),

- aquifers in Triassic sandstones (Buntsandstein),

- aquifers of unconsolidated sediments of the Saalian glaciations, and

- aquifers in Jurassic limestones (Malm),

occur throughout Germany (see figure 3) and are of high importance for water supply. For these typologies, 10 different data sets from 8 federal states (50000 groundwater samples from 19500 monitoring stations) were provided by the involved State authorities.

Before assessing natural groundwater concentrations, it was necessary to merge the individual heterogeneous data sets into one data base with a unified structure and reference to the groundwater typologies. In addition, a number of consistency checks (DVWK, 1994), e.g. the elimination of analyses with incorrect ion balances, salt effected stations, and elimination of temporal trends by median averaging had to be performed. In the end, a total of 7920

monitoring stations in the investigated groundwater typologies with one representative groundwater analysis each were used for further analysis (see figure 4).

The 15 evaluated groundwater parameters include environmental parameters (O_2, pH), summary parameters (electrical conductivity, DOC), major components (Na, K, Ca, Mg, Cl, HCO_3, SO_4), and trace substances (Fe, Mn, NH_4, NO_3). Table 2 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 is in a range between 200 and about 4900, allowing for a statistically sound analysis.

4. Methods and Results

Two statistical methods for the assessment of natural chemical conditions of groundwater were developed: the so-called *separation method* and the *selection (ranking) method*.

4.1. Separation method

The basic steps of this method are illustrated in figure 5. Starting point of the method is the frequency distribution of the observed concentrations of a groundwater parameter (represented by black dots in figure 5). It is assumed that this concentration profile can be expressed by the superimposition of two components, representing the natural and the influenced contributions. In this case the observed concentration distribution may be described by the sum of two statistical distribution functions which represent the natural and the influenced component.

The mathematical forms of the two distribution functions are not known a priori. But it can be expected that concentration patterns which are predominantly resulting from interactions with the soil or the groundwater bearing rocks may be represented by lognormal distributions, whereas 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, while 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.

The natural groundwater conditions could be described by several different sets of statistical parameters of the distribution function of the natural component. For normal and lognormal distributions, median and variance are commonly used for this purpose. However, these values are not a very perspicuous measure to characterise typical groundwater conditions. Therefore, the natural concentration ranges are specified by the 10th and 90th percentiles of the distribution of the respective component.

Table 3 shows the results for natural groundwater parameters in the composition of the four investigated aquifers. As can be seen in the table, concentrations in the aquifers significantly differ from each other, as well as the chosen distribution curves. Conclusions from electrical conductivity, magnesium and potassium should suffice as a brief example.

Electrical conductivity characterises the mineralisation of groundwater. From table 3 and figure 6 it can clearly be seen that groundwater in carbonate rocks differs from that of sand and sandstone with increased mineralisation. The reason for this is the increased quantity of soluble minerals in those rocks (carbonates, sulphate, as wells as chloride).

The observed concentration distributions are represented very well by the sum of two statistical distribution functions. The distribution patterns of electrical conductivity representing the natural groundwater condition are significantly different:

- limestone aquifer: 387…939 µs/cm

- sandy aquifer: 186…521 µs/cm

- sandstone aquifer: 50…256 µs/cm

In all aquifers the influenced component lies significantly above the natural component. The observed distribution curves of natural water in carbonate rocks correspond more or less to a normal distribution function, whereas sand and sandstone aquifers follow a typical lognormal distribution.

Distribution curves for magnesium are presented in figure 7. The figure shows that not only the shapes of the curves for natural water in sand and sandstone are similar, but the concentration as well:

- sand 3…30 mg/l

- sandstone 2…23 mg/l

In comparison with these, water in Triassic carbonate rocks has an increased magnesium content of 17…50 mg/l.

magnesium concentrations in Jurassic carbonate rocks exhibit an interesting distribution. There are two clearly distinguished maxima. The two statistical distribution functions reveal petrographical differences within the Jurassic limestone in Germany: the degree of dolomitisation of the Jurassic limestone increases from west to east. Accordingly, magnesium concentration rises. Therefore we suggest to distinguish two different types of natural groundwater for Jurassic carbonate aquifers for these two different parts of Germany.

The ranges of natural potassium concentration (figure 8) in groundwater of carbonate aquifers are significantly narrower and lower than those in sandstone:

- carbonate rocks: 0.3…2.1 mg/l

- sandstone: 0.8…4.0 mg/l

In all aquifers the influenced component lies significantly higher than the natural component. This can be explained by diffuse input from fertilisation or sewage water.

sodium, calcium, Chloride, Sulphate, and Dissolved Organic Carbon exhibit similar distribution curves as those of potassium.

4.2. Selection Analysis

At first sight, the statistical method of selection is a more pragmatic approach. It starts with the construction of a histogram for every measured parameter in the investigated aquifer.

The next step comprises the exclusion of all analyses where the concentration of any parameter is higher than the 95th percentile of the frequency distribution. During the third step, all analyses are excluded where nitrate content exceeds 10 mg/l.

After that second selection the 80% confidence interval is determined for the remaining analyses (by taking the interval from the 10th to the 90th percentile).

The determined confidential intervals for every groundwater component can be represented graphically using "box plots" (see figure 10). Table 4 shows the 10th and 90th percentile for every component of the investigated aquifers.

For the unconsolidated rocks of the Saalian Glaciation of Northern Germany, an improved selection method was tested using not only monitoring nets, but also exploratory and production wells. After preliminary selection, as described above (ionic balance, nitrate > 50 mg/l, etc.), about 15000 analyses remained and were statistically analysed with regard to:

- the position of the well in the hydrodynamic system and

- depth interval of sampling

Histograms for every component were constructed for different hydrodynamic positions:

- direct recharge areas

- indirect recharge areas

- transit areas

- discharge areas (lowlands)

After that sequential selection of so-called types of influence was carried out (figure 9). At first all analyses of mineralised water of discharging deep water were selected. They occur only in transit and discharge areas and are characterised by a chloride content of above 1452 mg/l (determined from the 95th percentile) and a ratio of equivalent concentrations of sulphate and chloride of less than 1.

For the remaining analyses of those two areas histograms were constructed anew.

During the second step analyses of water which indicate fertilisation influence on chemical components were selected. The 95th percentile served as criterion for the respective hydrodynamic areas. These critical concentrations differ among different hydrodynamic conditions (table 5). For example, the following concentrations of nitrate were identified as influenced:

- in recharge areas higher than 10 mg/l,

- in transit areas higher than 1.7 mg/l,

- in discharge areas higher than 4.1 mg/l.

In the same way water other influence types are distinguished:

- organic type

- acidification influence on account of atmospheric precipitation

- sulphate type

- diffuse influence by anthropogenic factors

After these selections, about 50% of the initial analyses quantity remained as characteristical of natural groundwater, which is summarised in the table 6.

Comparison of the results shows that the differentiated and the simple analyses of the unconsolidated aquifers in the Central European Basin *do not differ significantly*.

Contrary to this conclusion, distinct sampling depth intervals show significant differences, as is illustrated by the box plots in figure 10.

For the majority of groundwater components a change in depth is observed, moreover very often differently in recharge and discharge areas. For example, hydrogen carbonate concentration and electrical conductivity decrease with depth in discharge areas, but increase in recharge areas.

Oxygen Content and Sulphate in both hydrodynamic structures decrease with depth, as does Manganese content, which is also significantly higher in discharge areas than in recharge, at comparable depths. The latter effect is the result of reduction processes in discharge areas, which also characterise the ammonium distribution.

Therefore, conclusion was proposed that for a more detailed description of natural chemical groundwater composition in Central European aquifers, it is necessary to distinguish separate depth intervals for investigation:

- down to 10 m below surface,

- 10…25 m,

- 25…50 m,

- deeper than 50 m.

5. Conclusions

- Identification of natural groundwater composition for four aquifers was carried out, which comprise a total of 7900 monitoring wells.

- Two methods were developed to separate natural from modified groundwater composition.

- Typical intervals of natural groundwater components of the investigated aquifers were distinguished.

- The intervals which were found using those two methods, correlate well (see table 6).

- For the unconsolidated aquifers of the Central European Basin, it is reasonable to establish natural groundwater quality ranges for different depth intervals.

The LAWA working group made a decision to determine natural groundwater composition for all regional aquifers in all hydrogeological structures by these two methods.

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