The role of hydrochemical data for water resources management

Abstract

Hydrochemical parameters of water resources are often seen as a descriptive property: Major ion and trace element concentrations, organic pollutant loads, anorganic contaminants, natural and artificial radioactive substances, concentrations of dissolved gases can be analysed and compared to national or international standards for water quality (WHO, National or European Drinking Water Regulations). Often the use of hydrochemical data is not carried much beyond this scope. The hydrochemical composition of water, however, is the result of know physical, chemical and hydrologic principles. Hydrochemical parameters reflect the flow paths in the hydrologic cycle, e.g. conditions in the recharge area. Quantitative parameters of hydrological systems can be estimated based on hydrochemical data such as residence time of water in the aquifer. Hydrochemical data can also be used to infer mixing relationships, to estimate flow paramters and to analyse flow in complex systems. By presenting examples of increasing complexity the use of hydrochemical data for water resources management is demonstrated. For the use of hydrochemical data principles of best simplicity, reproducibility and efficiency must hold as for hydrological methods using physical measurements (discharge, water level). A general framework is presented how hydrochemical data can be included in groundwater modeling projects, evaluation of spring vulnerability, sustainability assessment. In conjunction with modeling approaches of the physical system, hydrochemical methods may provide new insights into contaminant transport and fate or natural attenuation. Future applications are seen in the analysis of hydrologic system resilience and adaptation times to climate change.

Methods

The applications of hydrochemical data for understanding hydrological systems can be grouped loosely in 5 approaches: Each group of applications is based on specific assumptions regarding the behaviour of hydrochemical substances:

- Classification methods (CMs) have been at the very beginning of hydrochemical analysis. They still provide basic information on the type of hydrological system and allow to distinguish shallow, fresh and deep groundwater systems
- End Member Mixing Analysis (EMMA) is based on classification methods and is among the most commonly used approaches, in general applied for two end members. EMMA can be extended to 3 or more end members using the methodology of compartment modeling (that is extensively used in pharmaceutical applications and for radiation protection), but issues of uncertainty and multi-finality arise. In combination with inverse modelling this approach provides means for quantitative assessment of flow systems.
- Enrichment Analysis (EA) provides simple means of controlling the enrichment of substances compared to an original input. This can be done for conservative indicator substances, but also compared to mixing ratios or for hydrochemical fingerprints.

- Thermodynamic modeling (TM) indicates the degree of equilibration of systems. The applicability of this method is limited by parameter identification problems, uncertainty and multi-finality. However, it has interesting new applications for isotope fractionation kinetics and in soil physics.
- Residence time analysis (RTA) - this group encompasses a wide range of methods. Some are based on variable (seasonally fluctuating, increasing, CFCs, Krypton-85) some on constant input functions (Sodium-22, Carbon-14). Common to all methods is the need for a concept model of mixing (model identification e.g. Piston Flow, complete mixing or convection-dispersion model) and a procedure for parameter identification (fitting, inverse modeling).

The use of time series or of hydrochemical evolution along flow paths are not explicitely mentionned as they rather represent sampling strategies that can be applied to all methods.

Case Studies

Each group of applications is presented with a case study.

Case study for classification: Upper Rhine River water supply near Karlsruhe

The first necessity in complex groundwater systems is to understand the hydrogeologic structure. This should be done based on stratigraphic data and sound geological mapping - where this is possible. Often, however, indiscrimante drilling through different aquifers, complex conditions and lack of data prevent such a 'perfect' approach. In this case water classification can be used. The example is taken from a water supply area near Karlsruhe. The different water types are identified based on major ions, isotopes and physical parameters.

End Member Mixing Analysis

This approach is based on the principles of conservative behaviour of the elements used for EMMA. This means: all non-conservative elements need to be disregarded. Often stable isotopes, chloride, sometimes Mg, Sulphate can be used. The example of the identification of snow-melt contributions to runoff in the Dreisam Catchment is used.

Enrichment Analysis

Enrichment analysis is often made for Chloride. In Central Europe and Western Europe it does not make much sense. The sample principle can be used for Trace Element Fingerprints. An example of identifying inflow from the basement of the Black Forrest into the Upper Rhine Valley is presented.

Thermodynamic modelling

TM seems to be complicated and often is. The art of applying TM lies in the simplification. If hydrological system can be simplified to one or few dominating processes TM is very powerful in describing sorption, precipitation. It can even be used for the analysis of complete systems (acidification research). An example of contaminant transport from Bad Krozingen to one of the main water supply boreholes of Freiburg is used.

Residence Time Analysis

Residence Time Analysis is an old but growing area of research. Credibility of results is a key issue, therefore only multi-parameter approaches are presented and discussed. An example of system analysis of springs in Switzerland is presented.

Summary and conclusions

Hydrochemical methods can not solve problems and provide assessments alone. However, without quantitative hydrochemical methods, physical modeling approaches may fail. In combination with other approaches they may be used to identify systems, validate results, provide parameters for system dynamics and dominant processes. The following pyramid of methods is proposed: geological (topology and structure define the space and framework) physical (water levels in the geological structure must be satisfied), chemistry (solutes must match) and isotopes (origin and age must match) is proposed. In some cases the results of these different methods will differ: often this is not a methodological flaw but a hint to insufficient system identification. All hydrological systems are strongly under-determined: we have much more variables than equations. Therefore hydrochemical methods provide additional dimensions for finding better solutions for the description and modeling of such systems.

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