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Edited by
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Groundwater Geochemistry

A Practical Guide to Modeling of Natural and Contaminated Aquatic Systems

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With 76 Figures and a CD-ROM

Springer

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Foreword

To understand hydrochemistry and to analyze natural as well as man-made impacts on aquatic systems, hydrogeochemical models have been used since the 1960's and more frequently in recent times.

Numerical groundwater flow, transport, and geochemical models are important tools besides classical deterministic and analytical approaches. Solving complex linear or non-linear systems of equations, commonly with hundreds of unknown parameters, is a routine task for a PC.

Modeling hydrogeochemical processes requires a detailed and accurate water analysis, as well as thermodynamic and kinetic data as input. Thermodynamic data, such as complex formation constants and solubility products, are often provided as data sets within the respective programs. However, the description of surface-controlled reactions (sorption, cation exchange, surface complexation) and kinetically controlled reactions requires additional input data.

Unlike groundwater flow and transport models, thermodynamic models, in principal, do not need any calibration. However, considering surface-controlled or kinetically controlled reaction models might be subject to calibration.

Typical problems for the application of geochemical models are:

- speciation
- determination of saturation indices
- adjustment of equilibria/disequilibria for minerals or gases
- mixing of different waters
- modeling the effects of temperature
- stoichiometric reactions (e.g. titration)
- reactions with solids, fluids, and gaseous phases (in open and closed systems)
- sorption (cation exchange, surface complexation)
- inverse modeling
- kinetically controlled reactions
- reactive transport

Hydrogeochemical models are dependent on the quality of the chemical analyses, the boundary conditions presumed by the program, theoretical concepts (e.g. calculation of activity coefficients) and the thermodynamic data. Therefore it is vital to check the results critically. For that, a basic knowledge about chemical and thermodynamic processes is required and will be outlined briefly in the following chapters on hydrogeochemical equilibrium (chapter 1.1), kinetics (chapter 1.2), and transport (chapter 1.3). Chapter 2 gives an overview on standard hydrogeochemical programs, problems and possible sources of error for modeling, and a detailed introduction to run the program PHREEQC, which is used in this book. With the help of examples, practical modeling applications are addressed and specialized theoretical knowledge is extended. Chapter 4 presents the results for the exercises of chapter 3. This book does not aim to replace a textbook but rather attempts to be a practical guide for beginners at modeling.

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