

GROUNDWATER MONITORING AND MANAGEMENT

Selected contributions to an international
symposium at Dresden, GDR

COVER ILLUSTRATION Hydrogeological section of
the Elbe Valley at Dresden, GDR

TITLES RECENTLY PUBLISHED BY IAHS

Proceedings of the symposia held during the Second IAHS Assembly, Budapest, July 1986:

Modelling Snowmelt-Induced Processes
Publ.no.155 (1986), price \$40

Conjunctive Water Use
Publ.no.156 (1986), price \$48

Monitoring to Detect Changes in Water Quality Series
Publ.no.157 (1986), price \$40

Integrated Design of Hydrological Networks
Publ.no.158 (1986), price \$40

Drainage Basin Sediment Delivery. Proceedings of the Albuquerque Symposium, August 1986
Publ.no.159 (1986), price \$45

Hydrologic Applications of Space Technology. Proceedings of the Cocoa Beach Workshop, August 1985
Publ.no.160 (1986), price \$45

Karst Water Resources. Proceedings of the Ankara Symposium, July 1985
Publ.no.161 (1986), price \$45

Avalanche Formation, Movement and Effects. Proceedings of the Davos Symposium, September 1986
Publ.no.162 (1987), price \$50

Developments in the Analysis of Groundwater Flow Systems. Report prepared by a Working Group of the IAHS International Commission on Groundwater
Publ.no.163 (1986), price \$35

Water for the Future: Hydrology in Perspective
Proceedings of the Rome Symposium, April 1987
Publ.no.164 (1987), price \$50

Erosion and Sedimentation in the Pacific Rim. Proceedings of the Corvallis Symposium, August 1987
Publ.no.165 (1987), price \$55

Proceedings of the symposia held during the IUGG Assembly, Vancouver, August 1987:

Large Scale Effects of Seasonal Snow Cover
Publ.no.166 (1987), price \$42

Forest Hydrology and Watershed Management
Publ.no.167 (1987), price \$55

The Influence of Climate Change and Climatic Variability on the Hydrologic Regime and Water Resources
Publ.no.168 (1987), price \$55

Irrigation and Water Allocation
Publ.no.169 (1987), price \$32

The Physical Basis of Ice Sheet Modelling
Publ.no.170 (1987), price \$40

Hydrology 2000. Report of the IAHS Hydrology 2000 Working Group
Publ.no.171 (1987), price \$22

Side Effects of Water Resources Management. Report prepared by an IHP-III Working Group
Publ.no.172 (1988), price \$40

Groundwater Monitoring and Management. Proceedings of the Dresden Symposium, March 1987
Publ.no.173 (1990), price \$55

Sediment Budgets. Proceedings of the Porto Alegre Symposium, December 1988
Publ.no.174 (1988), price \$60

Consequences of Spatial Variability in Aquifer Properties and Data Limitations for Groundwater Modelling Practice. Report prepared by a Working Group of the International Commission on Groundwater
Publ.no.175 (1988), price \$45

Karst Hydrogeology and Karst Environment Protection. Proceedings of the IAHS/IAHS Guilin Symposium, October 1988
Publ.no.176 (1988), price \$55

Estimation of Areal Evapotranspiration. Proceedings of a workshop held during the IUGG Assembly, Vancouver, August 1987
Publ.no.177 (1989), price \$45

Remote Data Transmission. Proceedings of a workshop held during the IUGG Assembly, Vancouver, August 1987
Publ.no.178 (1989), price \$30

Proceedings of symposia held during the Third IAHS Scientific Assembly, Baltimore, Maryland, May 1989:

Atmospheric Deposition
Publ.no.179 (1989), price \$45

Systems Analysis for Water Resources Management: Closing the Gap Between Theory and Practice
Publ.no.180 (1989), price \$45

Surface Water Modeling: New Directions for Hydrologic Prediction.
Publ.no.181 (1989), price \$50

Regional Characterization of Water Quality
Publ.no.182 (1989), price \$45

Snow Cover and Glacier Variations
Publ.no.183 (1989), price \$30

Sediment and the Environment
Publ.no.184 (1989), price \$40

Groundwater Contamination
Publ.no.185 (1989), price \$40

Remote Sensing and Large-Scale Global Processes
Publ.no.186 (1989), price \$40

FRIENDS in Hydrology. Proceedings of the Bolkesjø Symposium, April 1989
Publ.no.187 (1989), price \$50

Groundwater Management: Quantity and Quality
Proceedings of the Benidorm Symposium, October 1989
Publ.no.188 (1989), price \$60

Erosion, Transport and Deposition Processes. Proceedings of the Jerusalem Workshop, March-April 1987
Publ.no.189 (1990), price \$40

Hydrology of Mountainous Areas. Proceedings of the Strbske Pleso Workshop, Czechoslovakia, June 1988
Publ.no.190 (1990), price \$45

Regionalization in Hydrology. Proceedings of the Ljubljana Symposium, April 1990
Publ.no.191 (1990), price \$45

First of New Series!

Hydrological Phenomena in Geosphere-Biosphere Interactions: Outlooks to Past, Present and Future
by *Målin Falkenmark*
Monograph no.1 (1989), price \$15

Available only from IAHS Press, Wallingford

PLEASE SEND ORDERS AND/OR ENQUIRIES TO:

Office of the Treasurer IAHS
2000 Florida Avenue NW
Washington, DC 20009, USA
[telephone: 202 462 6903]

Bureau des Publications de l'UGGI
140 Rue de Grenelle, 75700 Paris, France
[telephone: 45 50 34 95 ext. 816;
telex: 204989 igngnl f (Attn: UGGI)]

IAHS Press, Institute of Hydrology
Wallingford, Oxfordshire OX10 8BB, UK
[telephone: (0)491 38800; telex: 849365
hydrol g; fax: (0)491 32256]



Groundwater Monitoring and Management

Edited by

G. P. JONES

*Department of Geological Sciences,
University College London, Gower Street,
London WC1 6BT, UK*

Proceedings of the symposium held at Dresden, German Democratic Republic (GDR) in March 1987. The symposium was organized by the National Committee of the GDR for the International Hydrological Programme of UNESCO, in cooperation with a number of national and international bodies.

IAHS Publication No. 173

**Published by the International Association of
Hydrological Sciences 1990.**

IAHS Press, Institute of Hydrology, Wallingford, Oxfordshire
OX10 8BB, UK.

IAHS Publication No. 173.

ISBN 0-947571-51-5.

The designations employed and the presentation of material throughout the publication do not imply the expression of any opinion whatsoever on the part of IAHS concerning the legal status of any country, territory, city or area or of its authorities, or concerning the delimitation of its frontiers or boundaries.

The use of trade, firm, or corporate names in the publication is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by IAHS of any product or service to the exclusion of others that may be suitable.

The symposium organizers wish to express their gratitude to Mr Glyn Jones for taking on the duties of editor of this publication. His comprehensive and excellent work is highly appreciated.

The camera-ready copy for this publication was prepared at IAHS Press, Wallingford, by Penny Kisby, Sandra Smith, Jean Hornsby and Sue Beresford, on an Advent desktop publishing system.

Printed in Great Britain by Galliard (Printers) Ltd, Great Yarmouth.

Preface

In consideration of the increasing importance of groundwater resources for water supply, specifically for drinking water, and in view of the growing influence of human activities on the availability of groundwater resources, both in quantity and quality, the National Committee of the German Democratic Republic (GDR) for the International Hydrological Programme (IHP) of UNESCO decided to organize as a contribution to the IHP an "International Symposium on Groundwater Monitoring and Management" from 23 to 28 March 1987, in Dresden, GDR, in cooperation with a number of national institutions, in particular:

- the Institute of Water Management, Berlin,
- the Dresden University of Technology,
- the Academy of Sciences of the GDR,
- the Mining Academy of Freiberg,

and international organizations, namely:

- the United Nations Educational, Scientific and Cultural Organization (UNESCO),
- the World Meteorological Organization (WMO),
- the International Association of Hydrological Sciences (IAHS),
- the International Association of Hydrogeologists (IAH).

From the beginning, the symposium was planned as a contribution to the third phase of the IHP (IHP-III) of UNESCO, in particular to the following three projects:

Project 2.3 Role of groundwater in the hydrological cycle and in the continental water balance;

Project 2.4 Use of physical and mathematical models for studying the groundwater regime and predicting changes in quantity and quality;

Project 2.5 Interactions between groundwater and surface water including the use of mathematical models for groundwater/surface water systems.

Taking into account the objectives of these projects, the groundwater-related tasks within the Operational Hydrological Programme (OHP) of WMO, as well as recent international developments in the field of groundwater and some national demands, the objects of the symposium were to present and to discuss:

- new scientific knowledge on the whole complex of "assessment, monitoring, management and protection of groundwater resources",
- practice-orientated approaches, mathematical models and computer-aided techniques for the solution of scientific and applied groundwater problems,
- practical approaches to the protection of groundwater resources against contamination.

It was decided to include the following five themes in the scientific programme of the symposium:

- 1: Assessment of available groundwater resources
- 2: Instruments, methods, networks and observation programmes for groundwater monitoring
- 3: Mathematical modelling of groundwater flow and migration processes
- 4: Rational use of groundwater resources and their protection against pollution
- 5: Regional groundwater management systems.

In addition to the sessions on these themes, the scientific programme included a special working session on IHP-III Project 2.3, a demonstration of computer working stations, and an excursion to the lignite mining area in southeast Lusatia. At the working session on IHP-III Project 2.3, a technical report compiled by the project coordinators of the IHP National Committee of the USSR, I. S. Zektser & R. G. Dzhamalov, was presented and discussed.

A total of 109 papers from different parts of the world were submitted, pre-printed and delivered to all participants at the beginning of the symposium. The Scientific Programme Committee selected a number of papers which had generated particular interest during the symposium for inclusion in these post-published proceedings.

The local convenors of the five sections prepared introductory remarks relevant to their own section and these are included at the beginning of the sections. It is hoped that this IAHS publication will be well received by the international community of water scientists.

K.-H. Zwirnmann

*Chairman, National IHP Committee of the GDR, Schnellerstrasse 140
DDR-1190 Berlin*

S. Dyck

*Acting Chairman of the National IHP Committee of the GDR during the
Symposium*

A. Becker

Secretary, National IHP Committee of the GDR

Conclusions and Recommendations

Summarizing the results of the symposium, in particular of the discussions during its final session, the following conclusions and recommendations were drawn:

- (1) It is generally agreed that groundwater resources are of increasing importance for satisfying various water demands, in particular that for drinking water.
- (2) This is true for all regions of the Earth, for developing as well as developed countries, but in particular for climatic zones where surface water resources are absent or limited.
- (3) Due to different human impacts and influences, the availability of groundwater resources, taking account of their quantity and quality, can be more or less significantly reduced.
- (4) Continuing efforts are required for the protection of groundwater resources against exhaustion and/or pollution. The scientific basis of the related activities needs further development and it is felt that the results of research presented at this symposium represent an important contribution to achieving such a goal.
- (5) Remarkable progress has been observed in the mathematical modelling of groundwater filtration and migration processes and in applying different mathematical models to the solution of local (small-scale) and regional (larger-scale) problems of groundwater use and management.
- (6) It was emphasized that modelling needs a sound scientific basis and is essential for the investigation of the influences exerted by various human activities on the availability of groundwater resources, both in quantity and quality.
- (7) The reliability of modelling results is highly dependent on the available input information, i.e. on the available data, their quality and representivity, and on the correct description of the actual processes. This underlines the primary importance of an adequate understanding of the processes and sufficiently developed data-base systems.
- (8) In general, there is an obvious disparity between high-level mathematical models for flow and transport processes and low-level input data.
- (9) Therefore it was emphasized that monitoring systems play an extremely important role in the assessment, rational use, management and protection of groundwater resources. They have to take into account a set of complex factors such as natural, technological, economic and social factors.
- (10) In this connection, intensified efforts are needed in the development of monitoring systems, sampling and measuring instruments and techniques including remote sensing, isotope and other modern methods, i.e. for measuring concentrations of heavy metals, organic substances, hydrocarbons, pesticides etc. It was pointed out that groundtruth data are primarily required in connection with remote sensing.

- (11) The advances in investigating and understanding processes do not appear to have been as rapid as the advances in data processing and mathematical modelling. Therefore, there is an urgent need to improve our knowledge about physical, chemical and, especially, micro-biological processes in subsurface waters. This should be achieved by extending and intensifying experimental investigations in laboratories and under natural conditions and by a thorough introduction of basic knowledge of physics, chemistry, biology and system theory into the theory of both deterministic and stochastic modelling.
- (12) Models which adequately reflect the spatial variability and heterogeneity of soils and aquifers, more adequate spatial distribution functions etc. should be developed and applied. They must be capable of simulating larger scale flows including macropore flow, multiphase migration etc.
- (13) For the integrated planning and management of surface water and groundwater systems, computer-aided decision support systems are needed considering the stochastic character of the system inputs, the uncertainties and inaccuracies of natural, manmade and socio-economic processes, the contradiction between the various interest groups and the complex interactive and subjective character of the decision-making processes. Examples of the development and application of such systems have been presented and discussed during the symposium.
- (14) The increasing complexity of water use, the growing human activities endangering groundwater quality (e.g. use of fertilizers, manure, biocides in agriculture, dumping of urban and industrial wastes, wet and dry deposition) has brought about a change in the perspective of hydrology. The growing conjunctive water use and the interactions between surface water and groundwater and between water quantity and quality require that groundwater systems be considered on a broader and more complex scale.
- (15) It is felt that progress will be restricted by those scientists "digging the same hole deeper" but advanced by those taking a broader and more complex view of the problems to be solved. That means that "vertical and lateral thinking" should be well-balanced.
- (16) Academic disciplines and organizational structures within educational institutions and governmental agencies often preclude comprehensive programmes to manage groundwater resources optimally. Therefore carriers for multidisciplinary hydrologic education, research and application must be identified and encouraged by the development of institutional incentives at regional and state levels.

K.-H. Zwirnmann

*Chairman, National IHP Committee of the GDR, Schnellerstrasse 140
DDR-1190 Berlin*

S. Dyck

*Acting Chairman of the National IHP Committee of the GDR during the
Symposium*

A. Becker

Secretary, National IHP Committee of the GDR

Contents

Preface	by <i>K.-H. Zwirrmann, S. Dyck & A. Becker</i>	v
Conclusions and Recommendations	by <i>K.-H. Zwirrmann, S. Dyck & A. Becker</i>	vii

1 Assessment of Available Groundwater Resources

Preface to Section 1	by <i>S. Dyck & I. S. Zekaser</i>	3
Polycyclic aromatic hydrocarbons in spa waters of Swieradow spa and Czerniawa spa, Poland	<i>T. Babelek, J. Grochmalicka-Mikołajczk & W. Ciekowski</i>	5
Assessment of groundwater resources by computer-aided designed and operated pumping tests	<i>U. Beims & H. Mansel</i>	11
Reduced sulphur compounds in sandy aquifers and their interactions with groundwater	<i>W. Kölle, O. Strebel & J. Böttcher</i>	23
A strategy for drought mitigation using groundwater: a case study in Kolar district, Karnataka State, India	<i>C. Naganna & Y. Lingaraju</i>	31
Groundwater monitoring and management in permafrost areas	<i>Ye. V. Pinneker</i>	39
Two case studies in estimation of groundwater recharge	<i>D. C. H. Senarath</i>	45
Large-scale hydrogeological investigations for improving the completeness of sub-surface water storage assessment and for examining the impact of its development on the environment	<i>V. M. Shestopalov, Yu. F. Rudenko & V. O. Balouta</i>	57
Assessment of groundwater resources protection from the effect of acid deposition based on simple hydrogeological models	<i>W. Uhlmann</i>	65
A necessary approach to the assessment of pumping groundwater resources in coastal areas	<i>J. A. Valdes Gonzalez</i>	79
Regional cooperation of the European socialist countries in developing the fundamentals for an automated system of groundwater assessment	<i>G. G. Vartanyan, V. V. Kurennoy & K. I. Sychev</i>	93

2 Instruments, Methods, Networks and Observation Programmes for Groundwater Monitoring (Quantity and Quality) including Application of Isotopic Techniques

Preface to Section 2	by <i>J. Němec & H. Jordan</i>	101
Heavy metal transport in aquifer material: laboratory investigations and parameter estimation	<i>T. Abraham & F. Häfner</i>	103

Combined studies with uranium series disequilibrium <i>R. Gellermann, K. Fröhlich & H. Jordan</i>	113
Methodological principles for groundwater monitoring in the German Democratic Republic <i>L. Herrmann, A. Eyrich, G. Müller & G. Schreiber</i>	121
Artificial radio-tracers in groundwater flow measurements <i>J. Hulla, R. Ravinger, P. Turcek & H. Jordan</i>	131
Groundwater dating in monitoring groundwater resources <i>H. Jordan & K. Fröhlich</i>	139
Modelling of groundwater pollution by river bank filtration using oxygen-18 data <i>P. Maloszewski, H. Moser, W. Stichler, B. Bertleff & K. Hedin</i>	153
Monitoring of controlled groundwater contamination <i>V. A. Mironenko & V. G. Rumynin</i>	163
Assessing potential of groundwater replenishment on the northern Swan Coastal Plain, Western Australia <i>M. L. Sharma & B. Anson</i>	171
A new approach to the identification of vertical flow resistance of a partially penetrating river <i>Z. Shen & L. Sun</i>	183
Transport behaviour of volatile chlorinated hydrocarbons in a soil/groundwater system <i>R. Wesinger & R. Herrmann</i>	189

3 Mathematical Modelling of Groundwater Flow and Migration Processes

Preface to Section 3 by <i>P. Mauersberger & G. Matthess</i>	201
The program system GEOFIM for the digital simulation of subsurface water movement and transport <i>J. Both, S. Kaden, P. Nillert & D. Sames</i>	203
Comparing the transport of some organic micro-pollutants in a soil-groundwater system by means of a mathematical model <i>W. Durner & R. Herrmann</i>	213
Mathematical modelling of the complexation of metals and its utilization for the interpretation of physicochemical processes in natural waters <i>R. Fischer, H. Reissig, W. Gawlick & W. Reissner</i>	233
Interactive modelling of groundwater contamination <i>S. Kaden, H. J. Diersch & K. Fedra</i>	245
Modelling of interrelated water flows in the unsaturated-saturated soil-river system <i>M. G. Khublarian, V. E. Putyrskiy & A. P. Frolov</i>	255
Simulation of pollutant transport in groundwater with the random walk method <i>W. Kinzelbach</i>	265
Modelling multi-migrant systems in the case of neglectable feedback for the example of radioactive decay <i>L. Luckner, H. Mansel, D. Schäfer & W. Reissner</i>	281

Unsteady flow to a multi-aquifer artesian well	<i>G. C. Mishra & S. Chandra</i>	293
Coupled flow and advective transport simulation in multi-layer leaky aquifer systems	<i>F. Szekeley</i>	305
4 Rational Use of Groundwater Resources and their Protection against Pollution		
Preface to section 4	<i>by L. Luckner & I. Simmers</i>	317
Salt-water intrusion processes in groundwater; novel computer simulations, field studies and interception techniques	<i>H.-J. Diersch & P. Nillert</i>	319
Controlled feeding of substances in underground treatment	<i>D. Eichhorn</i>	331
Protection of drinking water resources in the GDR and the effective utilization of drinking water protection areas and drinking water reserve areas	<i>D. Kramer, W. Krüger & F. Schulz</i>	339
The role of infiltration installations with an artificially formed biogeocoenosis in protection of groundwaters against pollution and depletion	<i>V. G. Magmedov</i>	349
Scientific concepts for the assessment of groundwater protection zones	<i>G. Matthess</i>	355
Importance of vertical groundwater flow survey in connection with practical problems	<i>I. Mucha & E. Paulikova</i>	361
Monitoring and analysing water and solute transport in the vadose zone	<i>D. R. Nielsen, M. Th. Van Genuchten & W. A. Jury</i>	367
On the optimality criteria in solving optimization tasks in groundwater use and protection	<i>P. G. Petrov</i>	379
Protection of groundwater quality by biochemical treatment in the aquifer	<i>U. Rott</i>	383
Chemical pollution of the soil and groundwater in the Kingdom of Nepal	<i>C. K. Sharma</i>	391
5 Regional Groundwater Management Systems in Areas with Intensive Influences		
Preface to Section 5	<i>by S. Kaden & M. Holy</i>	401
On the methodology of developing hydrogeological forecast models for large-scale groundwater lowering and recovery models	<i>K.-D. Bilkenroth, B. Haferkorn & E. Uhlig</i>	403

Groundwater level control systems in areas adjacent to rivers <i>Z. Djankov & S. Radoslavov</i>	409
Highly accurate mathematical modelling of the process of large-scale filtration <i>J. Flisowski & O. Trzos</i>	419
Computer-aided modelling of groundwater dynamics in mining areas <i>B. Gut, F. Reichel & P.-W. Gräber</i>	425
Consideration of ecological restrictions in catchment areas by controlling the aquifer – a case study <i>T. Haarhoff & M. Kjenke</i>	433
Decision support system for open-pit lignite mining areas <i>S. Kaden, J. Michels & K. Tiemer</i>	447
Planning conjunctive groundwater and surface water development in public irrigation systems <i>K. N. Murty</i>	459
On the application of a groundwater model to the question of groundwater protection <i>K.-H. Nachtigall & E. Schekorr</i>	467
Groundwater resource management in coastal aquifers <i>A. E. F. Spink & E. E. M. Wilson</i>	475

1 Assessment of Available Groundwater Resources

**Preface to Section 1:
Assessment of Available Groundwater
Resources**

Groundwater resources can be neither developed nor managed rationally without an assessment of the quantity and quality of the water available.

The United Nations Water Conference (UNWC) of 1977 in its resolution 1, resolved that "international cooperation aimed at the strengthening of water resources assessment, particularly within the IHP of UNESCO and the OHP of WMO be keyed to the targets set by the UNWC and appropriately supported by national and international governmental and nongovernmental institutions".

In the following years UNESCO and WMO prepared the *Water Resources Assessment Handbook*, which gives a methodology for the evaluation of a country's assessment activities, and in particular its infrastructure.

The definition of water resources assessment (WRA) given in the Handbook is: "Water resources assessment is the determination of the sources, extent, dependability and quality of water resources on which is based an evaluation of the possibilities for their utilization and control."

At the symposium over 21 papers were presented in this Section. These papers cover the whole spectrum of basic, regional and local water resources assessment. They were grouped as follows:

- basic groundwater resources assessment (6 papers);
- case studies for the assessment of groundwater resources assessment, mainly for the assessment of natural groundwater recharge (7 papers);
- classification of groundwater resources (4 papers);
- groundwater quality aspects (4 papers).

Computer-aided grid methods for the assessment of groundwater recharge and groundwater supply in sedimentary (loose sediments) and in hard-rock regions, demonstrate that a new quality of groundwater assessment has been reached with applied physically-based methods. Long-term means and monthly values of groundwater recharge are calculated on the basis of hydrological water balances taking into account changes of the land surface by man.

The method of continuous hydrograph separation, combined with a verification of the results of the separation procedure by water balance computations is a breakthrough with regard to the identification of runoff components and their solute transport.

The elaboration of the methodological and procedural framework of climate impact assessment should be given high priority in the assessment of groundwater resources.

Two of the papers demonstrated large scale investigations and multi-stage procedures for groundwater assessment.

Regional, system-oriented and local, project-specific case studies are important steps in the assessment of groundwater resources. Daily water

balance methods, local studies, pumping tests, forecasts of groundwater levels, procedures taking into account the dynamics of sea water encroachment in coastal areas are examples of these scales.

The formation and the assessment of groundwater resources in permafrost regions and the importance of the conservation of the natural water-heat regime was discussed in two more papers.

Four papers gave overviews on the state of classification of groundwater resources, taking into account conditions of water use and management, degree of investigation, groundwater-use classes, quality classes and hazard classes, the latter subdivided in classes of groundwater protection and of contamination hazards.

The papers dealing with groundwater quality aspects covered only some examples from this broad field: physically-based process models on groundwater accretion and nitrate leaching, effects of acid rain on soil-water and groundwater, effects of reduced sulphur compounds in sandy aquifers, occurrence of polycyclic aromatic hydrocarbons in spa-waters.

Co-convenors

S. Dyck

*Dresden University of Technology, Department of Water Sciences
Mommсенstrasse 13, DDR-8027 Dresden
German Democratic Republic*

I. S. Zektser

*Water Problems Institute, USSR Academy of Sciences
Sadovaya-Chernogyazskaya 13/3, 103064 Moscow, USSR*

Polycyclic aromatic hydrocarbons in spa waters of Swieradow spa and Czerniawa spa, Poland

**T. BABELEK,
J. GROCHMALICKA-MIKOLAJCZK**

Department of Inorganic and Analytical Chemistry, Medical Academy, 60-780 Poznan, Grunwaldzka 6, Poland

W. CIEZKOWSKI

Institute of Geotechnic, Technical University, 50-370 Wroclaw, Wybrzeze Wyspianskiego 27, Poland

Abstract Results of the qualitative and quantitative analysis of polycyclic aromatic hydrocarbons [PAH] in selected spa waters and surface waters of Swieradów spa and Czerniawa spa from the period 1983–1986 are presented. Thirteen compounds of the PAH group have been identified in waters. Results show the correlation between PAH content in spa waters and percentage of normal water. Based on these results, monitoring of PAH is recommended in underground waters especially in spa waters.

INTRODUCTION

The problem of purity of underground waters comes into prominence because of the degradation of quality of surface waters. It pertains also to spa waters which are used in drinking therapy and which should possess a high quality and a stable content of balneological important substances.

In the group of organic impurities special attention should be given to polycyclic aromatic hydrocarbons [PAH] because of their carcinogenic properties.

The occurrence of numerous organic compounds in spa waters was pointed out by Wiernadski (1933). Similarly Niewrajew (1966) analysed compounds from mineral oil in spa waters and shown their influence on the therapeutic properties of such waters. Grochmalicka-Mikolajczyk *et al.* (1984–1985) showed the appearance of six PAHs in selected spa waters in Poland.

Fresenius and his co-workers indicate the importance of monitoring of PAH pollutants in spa waters (Fresenius & Schneider, 1981; Fresenius *et al.* 1980).

From the sanitary-hygienic point of view, the WHO (1970; 1982) recommended the determination of six PAH in drinking water.

It was also shown that the content of PAH in spa waters can be used as an indicator of pollution of the water (Babelek *et al.*, 1986).

Table 1 Chemical characteristics of selected spa waters at Swieradów and Czerniawa spas

Place	Name of analysed sources	Chemical characteristics	Mineralization (mg dm ⁻³)	Percentage of normal (%)	Tritium content* (TU)
Swieradów	2 P	HCO ₃ ⁻ - Mg - Fe - Ca + F + CO ₂	2000	0	0.1 ± 1.5
	Radoczynne nr 4	Rn	55	100	38.5 ± 2.0
Czerniawa	Nr 4	HCO ₃ ⁻ - Mg - Fe - Ca + F + CO ₂	2988	11	1.8 ± 1.5
	Jan	F - Fe + Rn + CO ₂	911	87	56.0 ± 3.0

*Analyses performed at the Institute of Physics and Nuclear Technology at the Academy of Mining in Kraków.

SAMPLING AND ANALYSIS

In the period from 1983 and 1986, water samples from Swieradów and Czerniawa spas were analysed. Two samples of spa waters from two different sources in each town and also one surface water from the pond in Swieradów spa to be used as a control were selected for PAH analysis.

The chemical characteristics, percentage of normal waters and tritium content in analysed waters are shown in Table 1.

Analysis of PAH in the waters was carried out according to the method recommended by WHO and worked out by Borneff & Kunte (1969).

PAH analysis consist of three stages:

- (a) extraction with cyclohexane as a solvent and two-dimensional thin-layer chromatographic separation;
- (b) qualitative analysis: spectrofluorimetry at 77 K;
- (c) quantitative analysis: spectrofluorimetry at room temperature.

Contents of six PAH, benzo (a) pyrene, fluoranthene, benzo (g,h,i) perylene, benzo (k) fluoranthene, benzo (b) fluoranthene and indeno (1,2,3c,d) pyrene, were determined.

RESULTS AND DISCUSSION

In an earlier paper the authors described the results of the qualitative and quantitative analysis of PAH in spa waters in the Sudetes region of Poland (Babelek *et al.*, 1986). It showed abnormal amounts of PAH, especially in spa waters of West Sudetes. That was the reason why the analyses described in this paper were performed in Swieradów spa and Czerniawa spa, towns situated exactly in this region.

From 1983 to date the PAH content in spa waters in these two health resorts has been regularly determined.

Qualitative analysis after chromatographic separation revealed the presence of 13 compounds of the PAH group as shown in Table 2. All of these compounds were present in the surface water from the pond in Swieradów spa. Spa waters from Czerniawa spa contain 11 compounds and their composition is similar. In spa waters from Swieradów spa 12 compounds were identified in source Radoczynne nr 4 and 10 compounds in source 2P. The qualitative composition of PAH in spa waters samples for spring and winter was the same.

Table 3 shows the mean yearly results of the determination of the sum of six PAH for the period 1983–1986. These are the mean values of three or four results obtained every year for each source. Graphically the results are shown in Fig. 1.

The highest concentration of PAH was determined in surface water from the pond in Swieradów spa. It is an example of progressive contamination of the natural environment. An increase in the concentration of PAH in rainwater causes a growth of the amount of these compounds in surface water and consequently in underground water. The high level of PAH in surface water and also in spa waters in the Swieradów and

Table 2 PAH identified in water of Swieradów and Czerniawa spas (1985)

Place	Name of analysed sources	Analysed compounds:												
		1	2	3	4	5	6	7	8	9	10	11	12	13
Swieradów	2 P	+	+	+	-	+	+	+	+	+	+	+	-	-
	Radoczyenne nr 4	+	+	+	+	+	+	+	+	+	+	+	+	+
Czerniawa	Nr 4	+	+	+	+	+	+	+	+	+	+	+	-	-
	Jan	+	+	+	+	+	+	+	+	+	+	+	-	-
Swieradów	Surface water (pond)	+	+	+	+	+	+	+	+	+	+	+	+	+

1 anthracene 2 benzo(a)anthracene 3 benzo(b)fluoranthene 4 benzo(j)fluoranthene
5 benzo(k)fluoranthene 6 benzo(a)pyrene 7 benzo(g,h,i)perylene 8 fluoranthene
9 indeno(1,2,3,c,d)pyrene 10 coronene 11 dibenzo(a,h)anthracene 12 pyrene 13 perylene.

Table 3 Total content of the sum (ng dm⁻³) of six PAH

Place	Name of analysed sources	Year:			
		1983	1984	1985	1986
Swieradów	2 P	182	193	187	172
	Radoczyenne nr 4	-	403	170	292
Czerniawa	Nr 4	187	162	210	171
	Jan	311	258	219	244
Swieradów	Surface water (pond)	-	306	308	427

Czerniawa spas can be related with activity of power stations which are burn brown coal and which are in the vicinity of these towns. (Turoszów in Poland, most in the Socialist Republic of Czechoslovakia and Hirschfelde in the German Democratic Republic are situated exactly in West Sudetes.) Results in Tables 1 and 3 show the correlation between PAH content in spa waters and the percentage of normal water. In general, higher contents of hydrocarbons are found in spa waters containing larger amounts of normal water (sources: Radoczyenne nr 4 in Swieradów spa and Jan in Czerniawa spa).

The concentration of PAH in spa waters with lowest percentage of normal water during the period 1983–1986 was rather stable while that in spa waters with higher percentages of normal water was unstable.

Accordingly it may be supposed that surface waters after being contaminated by surface pollutants in turn contaminate spa waters with

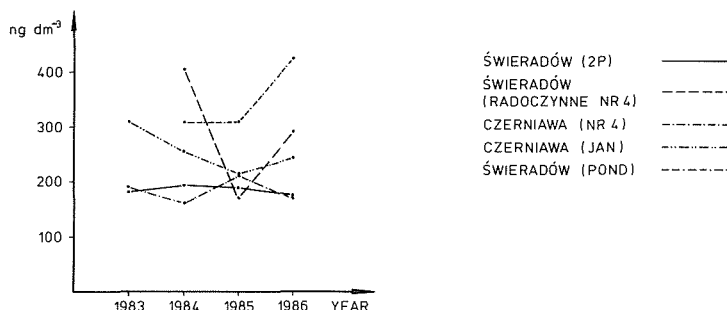


Fig. 1 Changing concentrations of the sum of six PAH in selected spa waters and surface water in Swieradów spa and Czerniawa spa (average annual values).

hydrocarbons. Based on these results it is recommended that monitoring of PAH be undertaken in groundwaters especially in spa waters.

REFERENCES

- Babelek, T., Ciekowski, W. & Grochmalicka-Mikolajczyk, J. (1986) The distribution of polycyclic aromatic hydrocarbons (PAH) content in underground waters in the Sudetes Mountain spas (in Polish). *Symposium on Hydrological Problems of Southwest Poland*. (Karpacz).
- Borneff, J. & Kunte, H. (1969) Kanzerogene Substanzen in Wasser und Boden XXVI. Routinemethode zur Bestimmung von polycyclischen Aromaten in Wasser. *Arch. Hyg. Bakt.* 153, 220.
- Fresenius, W. & Schneider, W. (1981) Organische Spurenstoffe in Heil and Mineralwässern. *Heilbad und Kurort* 33, 1.
- Fresenius, W., Quentin, K. E. & Eichelsdörfer, D. (1980) Die neuen Analysensichtlinien zur Untersuchung und Überwachung der Kurmittel. *Heilbad und Kurort* 32, 258.
- Grochmalicka-Mikolajczyk, J., Ochocka, J. & Lulek, J. (1984-1985) Untersuchungen des Gehaltes polycyclischen aromatischen Kohlenwasserstoffen (PAK) in einigen Mineralwässern. *Balneologia Polska* 28, 1-4.
- Niewrajew, G. A. (1966) Ciała organiczne w wodach mineralnych i ich znaczenie balneologiczne. *Wiad. Uzdr.* 11, 3-4.
- World Health Organization (1970) *Standard for Drinking Water*.
- World Health Organization (1982) *International Water Supply Association Congress* (Zurich).
- Wiernadski, W. J. (1933) *History of Natural Waters* (in Russian). Medgiz. Publ. House, Moscow.

Assessment of groundwater resources by computer-aided designed and operated pumping tests

U. BEIMS & H. MANSEL

Dresden University of Technology, Mommsenstrasse 13, DDR-8027 Dresden, German Democratic Republic

Abstract The paper describes an integrated system of computer-aided design, operation and estimation of pumping tests and migration tests. These methods are based on analytical and numerical solutions for the prognostic simulation and the monitoring of the flow and migration process during the experiment. For the estimation of the parameters, straight lines, type curves, search methods and interactive work on a PC are represented.

INTRODUCTION

Mathematical modelling for assessment and management of groundwater resources is worldwide the most important method for the simulation of flow and migration problems. Accurate results must, of course, be based on reliable and valid model parameters where field tests are now, as ever, the best method for the identification of such hydrological parameters as permeability (K), storage coefficient (S), leakage factor (B) or colmation factor (w) and migration parameters, dispersivity (δ) and effective porosity (n_p).

Such field methods as pumping tests, infiltration tests or the combination of both are very often difficult and time-consuming experiments. That is why a computer-aided design, operation and evaluation has a very high importance in the practical undertaking of this problem. The best method is the use of the same well and one or more observation wells for the performance of two tasks:

- (a) estimation of hydrological parameters;
- (b) estimation of migration parameters.

ESTIMATION OF HYDROLOGICAL PARAMETERS

In the process of the computer-aided design of the pumping test with a PC, the prognostic situation in the test area is calculated, based on available hydrological and geological information. The basis for this calculation is a program package of analytical solutions with superposition in space and time and consideration of different boundary conditions in accordance with equation (1):

$$s = \frac{1}{4\pi T} \sum_{i=1}^N \sum_{j=1}^M (Q_{ij} - Q_{ij-1}) \phi(r_i; t - t_{j-1}) \quad (1)$$

The function ϕ corresponds to the well-known different well functions created by:

Theis/Jacob : standard method for confined and unconfined aquifers
Hantush : leaky aquifer
Neuman/Boulton : two layered aquifer with delayed yield
Papadopoulos/Cooper : influence of well storage

The result of this calculation is the determination of

- exploitation rate Q (constant or step function),
- duration of the pumping test,
- necessary measurement times,
- beginning of the recovery period.

After beginning the test, the observation of the pumping rate and the drawdown in the well and all observation wells begins too. Once the first few measurement values exist in the memory of the computer, the computer-aided operation can start.

With pumping test plotter programs:
 semi-log, time-drawdown plot,
 log-log, time-drawdown plot,
 semi-log, distance-drawdown plot,
 type-curve plot,

the process of parameter identification begins and the parameters become more exact step by step. Now it is possible to use the program package in accordance with equation (1) a second time with the aim of correcting the pumping test with the intention of:

- minimizing the pumping test duration,
- utilizing all pumping test information.

It should mean the ability to predict better the:

- influence of boundary conditions,
- influence of well storage,
- determination of the duration of time-drawdown straight lines by delayed yield,
- determination of steady-state drawdown,
- influence of partial penetration,
- and last but not least, the determination of the beginning of the recovery process.

After finishing the pumping test, the final computer-aided evaluation of all pumping test data begins. In this case it is possible to differentiate between three methods.

Graphical-analytical method

The graphical-analytical method with the use of type-curves and straight lines is the oldest and traditional method for pumping test evaluation. Figure 1 shows the most important type-curves. Finally we have a lot of values for transmissivity and storage coefficient by the evaluation of:

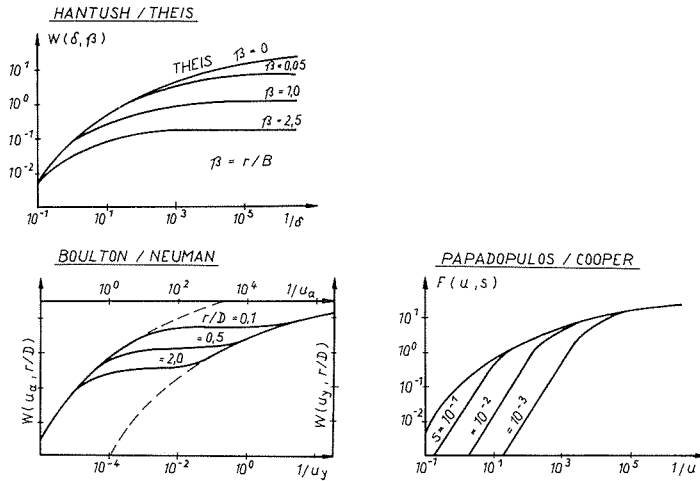


Fig. 1 Type-curves from pumping tests.

- every observation point,
- drawdown in time or space,
- drawdown or recovery.

Now it is very difficult to determine the representative system parameter set. The best method is the statistical interpretation of the parameter values.

Search method

In the last few years an iterative parameter estimation program has been developed.

The computer flow chart, shown in Fig. 2, can be described in five steps:

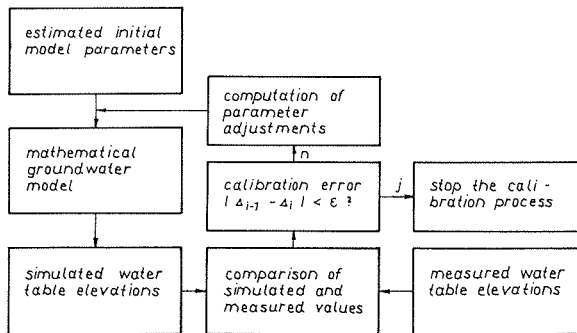


Fig. 2 Scheme of the search process.

- step 1:** select a set of initial model parameter values, based on available hydrogeological and geological information
- step 2:** these parameter values are used to compute a set of simulated water level elevations over an historic period (during the pumping test)
- step 3:** the difference between the measured and simulated water table elevations is defined as the calibration error
- step 4:** a typical example is the "least squares" performance function
- step 5:** the model parameter values are adjusted in order to reduce the calibration error

The advantages of this method are

- objectivity;
- the result is the representative parameter set by using all pumping test data;
- in step 2 all analytical solutions, different boundary conditions, single wells or well groups and constant or varying pumping rate can be used.

The program has been tested in a wide variety of applications.

The most extensive pumping test had four wells, 16 observation points, 10 steps of the pumping rate step function, and 1200 measurement times during the drawdown and recovery period.

The program uses a fast working gradient search method with a small number of necessary memory places and about 100 FORTRAN statements. However, all well-known straight-line and type-curve methods are based on many simplifying assumptions (the analytical solutions in the search method too). Very often the importance of these simplifications is not clear and the identified parameters are incorrect. That is why the following numerical method was developed.

Numerical method

Walton (1976) suggested that a computer can be used to generate a series of type-curves for each individual aquifer situation. With the increasing availability of inexpensive microcomputer systems this method is more and more advantageous.

Mucha & Paulikova (1986) developed this type of approach with their FORTRAN WELL program. The pumping test simulator WELL is a two-dimensional radial symmetrical, finite-difference model of a pumping well and the surrounding aquifer. The flexibility of the program makes it possible to analyse such characteristics of the aquifer as:

- confined/unconfined aquifer,
- isotropic/anisotropic permeability,
- layers,

- capillary fringe;
- and characteristics of the wells:
 - fully/partially penetrated wells,
 - well storage,
 - non-uniform diameter of the well,
 - non-uniform inflow into the well,
 - inflow via bottom,
 - well losses.

Discretization of the aquifer, shown in Fig. 3, is carried out in the

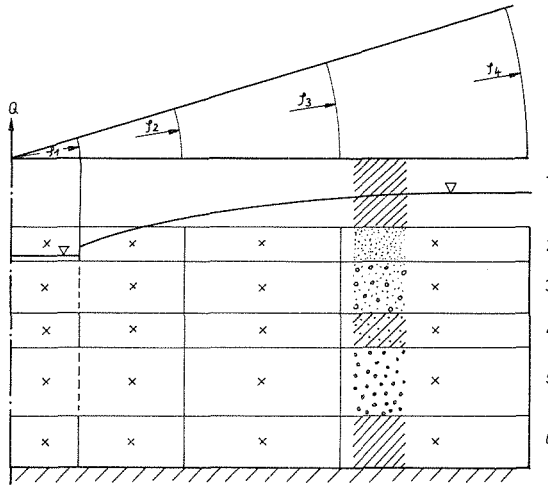


Fig. 3 Program WELL, aquifer discretization.

vertical direction by consideration of the geological stratification and the geometric characteristics of the well. The discretization in a horizontal direction begins with the radius of the well ρ_1 and increases after equation (2)

$$\rho_{i+1} = \rho_i \times 10^{0.25} \quad (2)$$

The time discretization starts from a small value Δt_1 and increases in accordance with equation (3):

$$\Delta t_{i+1} = \Delta t_i \times 10^{0.1} \quad (3)$$

Transmissivity and storage factors include horizontal and vertical conductivities, specific elastic and water table storages. The model treats the water table aquifer as a compressible system and the phreatic surface as a

moving material boundary.

The output of the program is the potential for every node-point and the well and the inflow in the well from every layer and through the bottom.

In the last few years the program WELL has been used for four tasks:

- clarification of the importance of simplifications and assumptions for different analytical well-functions,
- determination of flow and velocity conditions near differently constructed wells,
- simulation of type curves for special well and groundwater layer conditions,
- interactive pumping test evaluation.

As a consequence of this practical hydrogeological work it may be said that we have reached a new standard in pumping test analysis.

ESTIMATION OF MIGRATION PARAMETERS

In the last few years, different field methods have been developed for the evaluation of migration parameters δ (dispersivity) and n_f (effective porosity).

The dispersivity δ is a geometric characteristic of an aquifer, which determines the spreading of a stream or discrete volume of contaminant during its flow through the subsurface.

The effective porosity (n_f) describes the retardation (R_d) of a contaminant during the flow process:

$$n_f = R_d \cdot n \quad (4a)$$

$$R_d = 1 + K_d \rho/n \quad (4b)$$

where

K_d is the distribution coefficient in $\text{m}^3 \text{g}^{-1}$;
 ρ is the bulk density of the solid in g m^{-3} ; and
 n is porosity (dimensionless).

The assumption for equation (4) is an equilibrium sorption reaction between the fluid and the soil matrix. The high importance of the field tests results from the scale dependence of δ and n_f . It means that the experiment must be done in the same area as the later prognostic simulation. The described tests are thus the only possible parameter identification methods for the following processes:

- underground water treatment,
- artificial water infiltration,
- river-bed infiltration,
- local deposits,
- underground heat/water storage.

On the other hand, field methods for estimation of migration parameters are expensive and involve time-consuming tests with a high level of technical equipment. That is why exact preparation, implementation and evaluation are particularly important.

Figure 4 shows the test schemes for which a computer-aided method was developed.

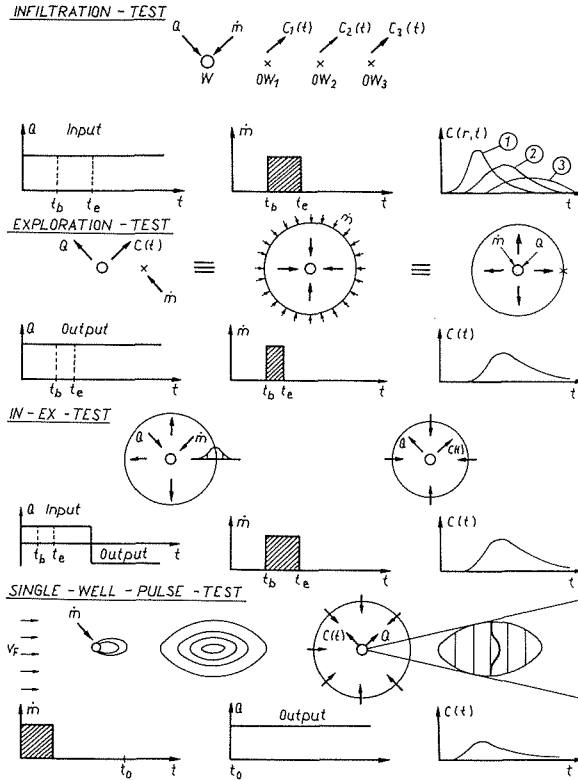


Fig. 4 Migration test schemes.

Infiltration test

Infiltration of water $Q(m^3 s^{-1})$ and the tracer expressed by a mass flow m ($g s^{-1}$) in the well and measurement of the time distribution of the concentration $C(t)$ in all observation wells.

Exploitation test

Input of the mass flow in an observation well and measurement of the concentration $C(t)$ in the exploitation water of the well.

Infiltration-exploitation test

This is a two stage test:

Stage 1: Input of water and mass flow in the well. The direction of movement layer to the well.

Stage 2: Exploitation of water from the well and concentration measurement in the discharge water. The direction of movement is from the layer to the well.

Single well pulse test

This is also a two stage test:

Stage 1: Input of mass flow in a well without water. The movement of this tracer cloud results from the natural groundwater velocity (v_f in days).

Stage 2: Exploitation of water from the same well and concentration measurement in the discharge water.

Two well test

The two well test is infiltration of water in well 1 and exploitation of the same discharge rate from well 2. Input of the mass flow in well 1 after reaching steady-state flow conditions and measurement of the concentration distribution in the discharge water. In Fig. 5, the technological scheme of this test is shown.

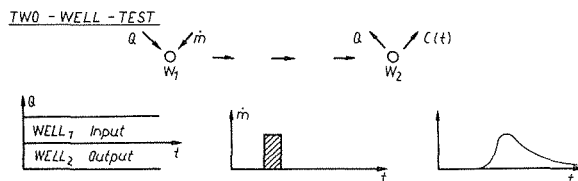


Fig. 5 Technological scheme of the two well test.

The computer-aided design assumes the mathematical description of the process. This is based as the results of the performed pumping test for the characterization of the hydraulic properties of the groundwater layer and estimated migration parameters n_f and δ . For the estimation of dispersivity (δ), the diagram in Fig. 6 can be used and for the estimation of the effective porosity (n_f), column attempts and batch attempts are a good method. Results of the calculation are the predicted concentration distribution of the tracer in the observation wells or the exploitation of a well, the possible exploitation of infiltration rate and the measurement intervals.

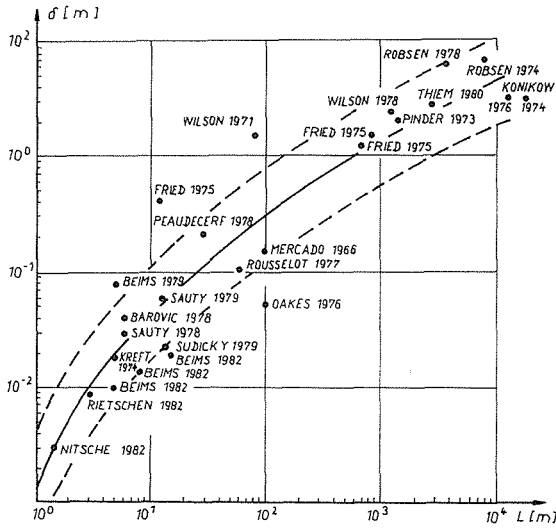


Fig. 6 Scale dependence of dispersivity δ .

For describing the migration process shown in Fig. 4, some analytical solutions and numerical schemes were tested. The most exact analytical solution of the radial diverging flow is shown in equation (5):

$$C^*(r,t) = 0.5 \operatorname{erfc} \frac{r^2 - r_0^2 - r_F^2}{(5.33 \delta r_F^3)^{1/2}} \tag{5}$$

$$r_F^2 = \frac{Q t}{\pi M n_f}$$

where

- r is the distance from the well,
- r_0 is the radius of well,
- Q is the discharge or infiltration rate,
- t is time, and
- M is the thickness of the layer.

For the numerical solution of the differential equation:

$$\delta Q \frac{\partial^2 C}{\partial r^2} - Q \frac{\partial C}{\partial r} = 2\pi M n_f r \frac{\partial C}{\partial t} \tag{6}$$

a numerical scheme was used, as created by Gray & Pinder (1976), which is characterized by the approximation of third order in time and second order in space and the minimization of effects of numerical dispersion through the use of dispersion coefficient corrections. Both these models (5) and (6) can be used for infiltration, exploitation and infiltration-exploitation tests. For the exploitation test it is possible to use this model, because it could be

shown that the results are identical for the input of this tracer in the observation well and its equivalent distribution on a circle around the well. In this case the migration process is radially symmetrical too. For the infiltration-exploitation test we get results by using the superposition rule. For describing the first stage of the single well pulse test the analytical solution of the parallel flow is used:

$$C(x,y,t) = \frac{m}{4 \pi v_f M (\delta_x \delta_y)^{1/2}} \exp \frac{x}{2 \delta_x} W(\sigma, B)$$

$$\sigma = \frac{\delta_x n_f}{v_f t} B^2 = \left[\frac{x}{2 \delta_x} \right]^2 + \left[\frac{y}{2 (\delta_x \delta_y)^{1/2}} \right]^2 \quad (7)$$

where

$W(\sigma, B)$ is the Hantush function,

m is the mass injection rate,

v_f is the groundwater velocity,

x, y are coordinates,

δ_x is the longitudinal dispersivity, and

δ_y is the transversal dispersivity.

In stage 2, the two-dimensional tracer cloud must be transformed into a migration process with radial character by differential integration about the circle and the distribution of this mass on a circle around the well analogous to the exploitation test.

We now get the concentration $C(t)$ in the exploitation water with equations (5) or (6) and utilization of the superposition principle.

The two well test supposes steady-state flow conditions and the input of a discrete mass injection rate for which Hoopes & Harleman (1967) created an analytical solution. Contrary to the four other test methods, this model describes the system conditions of the two well group (for example the two wells of a heat pump group).

For the four test methods in Fig. 4 we have developed a set of programs for the PC and the user can select the program for his special conditions. The selection of the most suitable test method depends on the advantages and disadvantages of the operation and evaluation of the test and on the situation in the test area, i.e. single well, well groups, wells with or without observation wells, and presence of infiltration water or not.

The computer-aided operation starts a short time after the beginning of the test. The main components of the migration process are measured at discrete time intervals and stored in a microprocessor. These are for example:

- flow rate,
- mass injection rate,
- conductivity,
- temperature,
- concentration etc.

After connection of the RAM with the central PC it is possible to compare

the actual situation with the calculated situation on the terminal. This is as a control of the last test period and gives the facility to adjust the test conditions and, in extreme circumstances, to stop the test. This is equal for laboratory experiments, pumping tests and migration tests too. The hardware has been tested in laboratory scale and described by Luckner & Schestakow (1986).

The methodology of computer-aided evaluation is the same as described for pumping tests and includes straight line methods, type-curves and search methods.

Straight lines, derived from equation (5), are shown in Fig. 7(a)–(c). In the cases (a) and (b) the ordinates are divided according to the Gauss error integral and in case (c) according to the inverse function of erf. The abscissa are divided normally or lognormally in space r^2 or time t . From the characteristics of these straight lines the parameters δ and n_f can be computed exactly.

For the infiltration test in Fig. 7(d), a set of type curves is shown which are calculated by analytical (equation (5)) and numerical solution (equation (6)) and drawn with dimensionless parameters $t^* = t/t_{0,5}$, C/C_{\max}

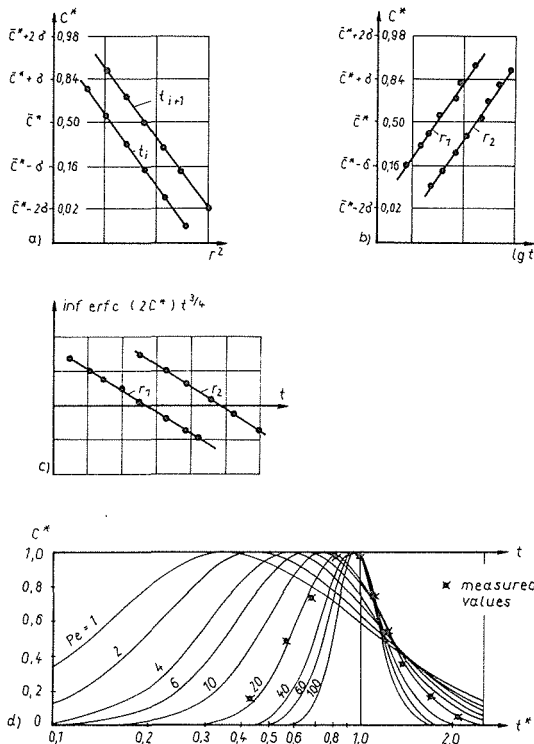


Fig. 7 Straight lines and type-curves for estimation of migration parameters.

and for different Peclet-values $Pe = r_p / \delta$, where:

t is real time,

$t_{0.5}$ is time of 50% concentration,

C is real concentration,

C_{\max} is maximum concentration,

r_p is the distance between the well and observation well, and

δ is dispersivity.

From that, the migration parameters of the test area are definable from the curve with the best fit to the real measured values.

The search methods for the parameter identification operate in accordance with the scheme shown in Fig. 2 too. The search process is observed on the monitor and after every search cycle the monitor shows:

- parameter values,
- parameter correction of the last step,
- value of the least squares sum,
- correlation function between measured and simulated parameters,
- plot of measured and simulated break-through curves.

In such a way the hydrogeologist is always able to stop the search process when necessary.

CONCLUSION

The described methods for computer-aided design, operation and evaluation of pumping tests and migration tests are summarized in

- a catalogue for pumping test evaluation, and
- a handbook for migration programs on a Sharp pocket computer.

These two books are effective in the process of investigation of the groundwater resources and are essential to obtain accurate and reliable results with predicted simulations.

REFERENCES

- Gray, W. G. & Pinder, G. F. (1976) An analysis of the numerical solution of the transport equation. *Wat. Resour. Res.* 12 (3).
- Hoopes, J. A. & Harleman, D. R. F. (1967) Dispersion in radial flow from a recharge well. *J. Geophys. Un.* 72.
- Luckner, L. & Schestakow, B. M. (1986) *Migrationsprozesse im Boden- und Grundwasserbereich*. VEB Deutscher Verlag für Grundstoffindustrie, Leipzig.
- Mucha, I. & Paulikova, E. (1986) Pumping test using large diameter production and observation wells. *J. Hydrol.* 89.
- Walton, W. C. (1976) Needed digital computer techniques for aquifer test analysis. *Ground Water* 14 (1).

Reduced sulphur compounds in sandy aquifers and their interactions with groundwater

W. KÖLLE

Stadtwerke Hannover AG, Hannover, FR Germany

O. STREBEL

Bundesanstalt für Geowissenschaften und Rohstoffe, Hannover, FR Germany

J. BÖTTCHER

Landesamt für Bodenforschung, Hannover, FR Germany

Abstract Reduced sulphur compounds participating in redox processes within aquifers are iron sulphides and native sulphur. The most important redox process is denitrification. Reaction products are gaseous nitrogen, sulphate, and ferrous iron. A complex system of kinetic interdependences, in which the activities of bacteria are involved, decides the extent of the oxidation of ferrous iron released from the iron sulphides. The reducing compounds — organic substances included — react sequentially according to their denitrification rate. Half-lives of the redox reactions range from several weeks to several decades. Trace components of sulphides may also be mobilized. Arsenic and nickel are of special interest.

INTRODUCTION

The knowledge of the quality and quantity of the reduced sulphur compounds and organic components of an aquifer material is frequently much more informative than any knowledge about the groundwater quality. Recently, much attention has been paid to components of the aquifer participating in redox processes with nitrate and oxygen. Reduced sulphur compounds play an important role in this context.

The knowledge of the stocks of these compounds is a prerequisite for the interpretation and prognosis of the quality changes in groundwater. This statement does not only refer to the main components of the water like nitrate, sulphate, and ferrous iron, but, in some cases, also to trace elements like arsenic or nickel. All of these components are essential quality parameters for drinking water and therefore of special importance.

IRON SULPHIDES

Reducing aquifers usually contain particles of organic substances like lignite, in

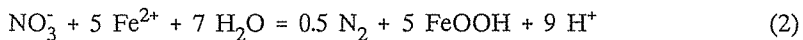
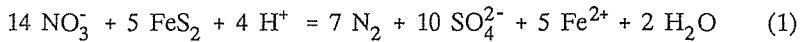
some cases in inconspicuous concentrations of less than 0.1%. However, lignite is a very slow reactant. As a consequence, minerals associated with lignite like iron sulphides usually play a dominant role with respect to the total turnover of redox processes.

Iron sulphides may occur as a component of the lignite itself but also independently as coatings on quartz particles and as crystals of metallic brightness. In some cases, pyrite can be observed as the matrix of petrified organisms.

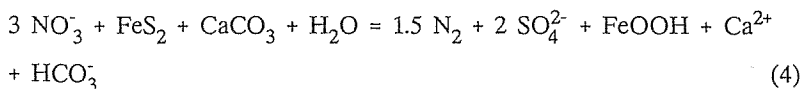
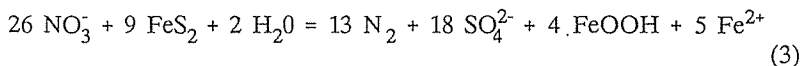
Mineralogical examinations showed that the observable iron sulphide particles mainly consist of pyrite, marcasite, or coalesced combinations of pyrite and marcasite. The iron:sulphur ratio is 1:2.

Stoichiometry of the denitrification reactions

The denitrification by iron sulphides is mediated by bacteria (Kölle *et al.*, 1983). The most important one is *Thiobacillus denitrificans* which oxidizes the sulphur component of the sulphides to sulphate. A second bacterium is able to oxidize the ferrous iron, released by the activity of the thiobacillus, to ferric iron with nitrate as the electron acceptor. The corresponding equations are the following:



It is important that both bacteria (both reactions) compete for the available nitrate. When the nitrate is used up, the turnover of both reactions becomes zero. The concentration of ferrous iron at this point of the process is a function of the reaction rate of (2) (k_2) related to that of (1) (k_1). In addition, the equations show that the first reaction step consumes, and the second step produces hydrogen ions. Thus, equations (1) and (2) can be combined in such a way that the process is balanced with respect to hydrogen ions. The resulting equation (3) characterizes the situation in unbuffered aquifers, idealized with respect to possible external influences on the hydrogen ion balance. The presence of a sufficient amount of calcium carbonate within the aquifer favours reaction (2) because there is a sink for the hydrogen ions exceeding the balance. According to equation (4) the resulting groundwaters are approximately free from ferrous iron.



A scheme of these interdependences is presented in Fig. 1.

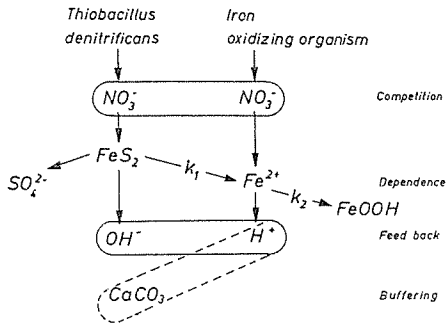


Fig. 1 Pattern of interdependences of denitrification reactions.

It follows from these interdependences that the oxidation of ferrous iron according to reaction (2) is used for "back titration" of the system to a constant pH (in most cases between 6.1 and 6.6). Thus, the pH value is extremely constant, whereas the concentration of ferrous iron is extremely sensitive to external influences.

Stock of reactive sulphur compounds

Kölle *et al.* (1985) defined a sulphate formation capacity (SFC) of aquifers in kg sulphate per m^3 of sediment material. The SFC is based on the real turnover of iron sulphides during incubation experiments with sediment material, which is exposed to an aqueous nitrate solution. Thus, well crystallized sulphides of low reactivity are not included in the SFC results.

Additional information originates from the conventional analytic determination of the total sulphur of aquifer material. The results represent the "theoretical maximum SFC", as Strebél *et al.* (1985) pointed out. Figure 2 shows, as an example, the SFC-depth functions of the Fuhrberg basin near Hannover at three locations.

The difference between the SFC and the theoretical maximum SFC is due to sulphides of low reactivity. It is questionable if there are any sulphide components having a real long-term stability. Even if they oxidize in the presence of high concentrations of nitrate or even oxygen with a very low rate, they may be responsible for some essential water quality phenomena, especially the concentration of sulphate and traces of ferrous iron.

A very rough estimation for the Fuhrberg aquifer shows that the stock of reactive reduced sulphur compounds, based on results of SFC incubation experiments, is sufficient for a period of denitrification lasting several hundred years.

However, any conclusions from laboratory SFC data on the real behaviour of reduced sulphur compounds in the aquifer are uncertain. It is for example, at present impossible to describe the denitrification as a sequential process which is controlled by the actual reactivity of the available

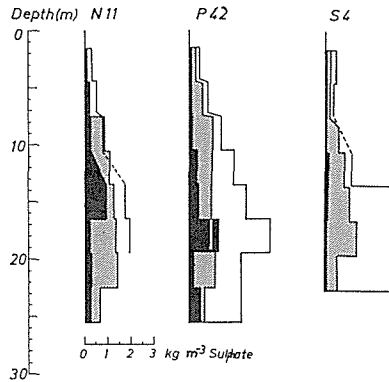


Fig. 2 SFC-depth functions for the Fuhrberg aquifer; SFC of lignite: black; SFC according to the incubation experiments: hatched; theoretical maximum SFC: outer line.

residual components. This situation is not adequate with respect to the general importance of long-term prognosis.

Kinetic aspects

Böttcher *et al.* (1985) estimated the kinetic parameters of the denitrification process in the Fuhrberg aquifer. It can be described as a first order reaction with a half-life of about two years. However, this is an actual result which is restricted to the present conditions existing in the Fuhrberg aquifer.

Many factors are of importance for denitrification kinetics, e.g. pore water velocity, solute transport conditions etc. Additionally, more detailed information about those properties of the stocks of reducing compounds which influence the kinetics should be available. Since iron sulphides are concerned, information is needed about their chemical and mineralogical identity, their particle size or surface: volume ratio, their crystal quality, and finally their concentration and distribution within the aquifer, which are accessible by prospecting activities.

It is important to realize that these kinetic aspects do not refer only to the process of working off a given stock of compounds by oxidation, but also to the kinetic competition of different reactions: even minor changes of the reaction rates may change the concentration of ferrous iron dramatically. Considerable effects are also to be supposed in the context of well deterioration.

Chemical and mineralogical identity It is important to distinguish between native sulphur and sulphidic components, as is pointed out later. Extraction of the aquifer samples with organic solvents and analysis of the extracts for sulphur is the usual method.

A magnetic separation covers pyrrhotite and magnetite, and sulphur

analysis of the magnetic components gives information about the pyrrhotite content. The decomposition of pyrrhotite by acids and analysis of the originating hydrogen sulphide is a classical method, based on the insolubility of pyrite and marcasite under the experimental conditions. However, according to the experience available to date pyrrhotite is of minor importance in most aquifers.

As a first approach to the problem, it seems to be adequate to operate with native sulphur on the one hand and the total minus native sulphur on the other hand. The latter criterion represents pyrite and marcasite with sufficient precision, according to the existing experience.

Particle size The denitrification by iron sulphides according to equation (1) is a surface reaction. Thus, it should be useful to know the reactive surface of iron sulphides per volume of the aquifer. Because of sulphide coatings on quartz particles and the occurrence of porous sulphide aggregates, results based on particle size distribution are questionable. As a consequence, we try to find specific surface reactions which give quantitative information about the surface area of the sulphides. Techniques of this kind are quite common for the characterization of adsorbents.

Crystal quality There are considerable differences in the quality of the crystal lattice of iron sulphides which may influence their chemical (biological) reactivity. This problem, as well as other detailed mineralogical characterizations should be investigated at least after solving the particle size problem.

Deterioration of wells

Denitrification by iron sulphides leads to nitrate concentrations of less than 0.1 mg l^{-1} , if the reaction time is sufficient. Groundwater containing ferrous iron from reaction (1) and intermediate nitrate concentrations of more than about 0.7 mg l^{-1} should not be abstracted from its reaction milieu because reaction (2) is able to proceed still after abstraction until the nitrate is used up. The consequences are depositions of hydrous ferric oxide ("ochre formation") in wells and raw water pumps and pipes.

Measures resulting in a decrease of the nitrate input into the aquifer or in an increase of the residence time (available reaction time) that are necessary to successfully avoid deposition include: reducing of nitrate leaching from agricultural lands, increase of the distance between wells and areas with high nitrate input, shortening of the well filters and positioning them as deep as possible, and finally operation of the well at a low capacity.

SULPHUR

The previous sections of this paper neglected the additional occurrence of sulphate reduction which is possible in aquifers containing particulate organic

substance like lignite, if the reaction time is considerably longer — or the aquifer considerably deeper — than necessary for denitrification alone. Sulphate-reducing aquifers have been able to accumulate mineral stocks of a considerable complexity. The most interesting component is native sulphur.

Sulphur was discovered in aquifer material of a waterworks at Nordhorn. Some samples of this material revealed high SFC values but contained no sulphide phases detectable under a microscope. This was interpreted as the presence of sulphur particles of a few micrometres in diameter as they are stored by sulphur bacteria. Extraction of these samples with organic solvents confirmed this supposition. Organic substances, including hydrocarbons, were also extracted.

Native sulphur could be detected in the depth range from 15 to 70 m below surface with a maximum concentration of 0.75 g kg^{-1} at 21 m below surface. Iron sulphides occurred only below 32 m.

This aquifer should be used for the subterraneous water treatment for iron and manganese removal. This method implies a periodic change of the well operation; during an infiltration period, oxygen-containing water is introduced into the aquifer, and during an extraction period a groundwater free of iron and manganese can be obtained. The extraction:infiltration ratio is, in many cases, about ten. However, the change of participating volume of the aquifer from a reduced into an oxidized state makes it necessary to "burn out" the reducing components, previous to any subterraneous treatment activity. In the case of Nordhorn the influenced zone of the well is treated by infiltrating a sodium nitrate solution of about 200 mg l^{-1} nitrate. This procedure is more effective than the use of water with only about 9 mg l^{-1} of oxygen.

During this work interesting information about the kinetic behaviour of the different stocks of reducing compounds could be obtained under the conditions of the Nordhorn aquifer. The native sulphur denitrifies with a half-life of about 50 days. This rate is considerably higher than that of iron sulphides, which is probably an effect of the uniform distribution and the small particle size of the native sulphur and not of the chemical differences between sulphur and sulphides.

Table 1 represents an attempt to characterize the different stocks of the Nordhorn aquifer according to their kinetic behaviour. Nitrate is "harvesting" the different stocks sequentially according to the half-life of the denitrification reactions involved.

TRACE COMPONENTS

Natural minerals may contain impurities. In some cases the impurities play a more important role as a resource for industrial processes than the basis mineral. In the case of pyrite, nickel, cobalt, and arsenic are able to occupy positions in the crystal lattice of pyrite. Copper and zinc (and a series of other metals) contribute as separate mineral phases to the impurities of pyrite.

In groundwaters characterized by denitrification processes with iron

Table 1 Stocks of reducing compounds of the Nordhorn aquifer and their approximate half-lives of denitrification

<i>Stock of reducing substance</i>	<i>approximate half-life</i>
<i>Native sulphur</i>	<i>weeks</i>
<i>Iron sulphides</i>	<i>years</i>
<i>Lignite</i>	<i>10–100 years</i>

sulphides as reactants, nickel, cobalt, arsenic, and zinc were observed in some cases in remarkable concentrations. These groundwaters usually contain also ferrous iron. Thus, the trace components may occur in the finished drinking water or in the iron oxide precipitation of the treatment plant.

Koppers (1985) reported difficulties in the Netherlands originating from the arsenic content of iron oxide sludges of groundwater treatment plants. Above a maximum permissible concentration of 50 mg kg⁻¹ (related to the dry residue) the sludge has to be considered as a chemical waste. The maximum concentration observed to date is 3100 mg kg⁻¹, which may possibly be interpreted as an effect of a comparatively low iron concentration of the raw water. High concentrations in sludges above 1000 mg kg⁻¹ have been stated also for cobalt, copper, and zinc. Nickel was obviously not analysed.

The advantage of the elimination of trace components from the water leads to the disadvantage of obtaining a chemical waste as a reaction product. About 50% of the Dutch waterworks are affected by this problem, especially with respect to arsenic.

Nickel is an element of a high mobility, or low tendency to be eliminated by adsorption on, or co-precipitation with, iron oxides. The European standard for drinking water of 50 µg l⁻¹ can easily be exceeded, if minerals of the aquifer are releasing nickel.

To date, two treatment plants in the northern region of Germany are known to have some problems with nickel. However, the treatment plant of the waterworks of Fuhrberg is eliminating some nickel. It is interesting to compare (Table 2) the trace components of the Fuhrberg sludge with those of the Berkhof sludge, because these two plants are using practically the same aquifer but differ significantly in the treatment conditions, especially the pH

Table 2 Trace components of the Fuhrberg and the Berkhof sludge (mg component per kg iron, as Fe)

<i>Plant</i>	<i>pH</i>	<i>As</i>	<i>Se</i>	<i>Ni</i>	<i>Zn</i>
<i>Fuhrberg</i>	8.8	72	< 1	225	740
<i>Berkhof</i>	7.3	144	1	< 25	120

during iron removal. The analyses were carried out by the DVGW-Forschungsstelle at Karlsruhe with samples of December 1985. The results are related to the iron content of the sludge for eliminating a dilution effect caused by co-precipitated calcium carbonate in the Fuhrberg sludge. Further investigations should be directed to the pH influence on the mobilization of trace components from the aquifer and their immobilization during water treatment measures.

Acknowledgements It is gratefully acknowledged that part of these investigations has been supported by the Deutsche Forschungsgemeinschaft and part by the Ministerium für Forschung und Technologie.

REFERENCES

- Böttcher, J., Strebel, O. & Duynisveld, W. H. M. (1985) Vertikale Stoffkonzentrationsprofile im Grundwasser eines Lockergesteins-Aquifers und deren Interpretation (Beispiel Fuhrberger Feld). *Z. Dt. Geol. Ges.* 136, 543-552.
- Kölle, W., Werner, P., Strebel, O. & Böttcher, J. (1983) Denitrifikation in einem reduzierenden Grundwasserleiter. *Vom Wasser* 61, 125-147.
- Kölle, W., Strebel, O. & Böttcher, J. (1985) Formation of sulphate by microbial denitrification in a reducing aquifer. *Wat. Supply* 3, 35-40.
- Koppers, H. (1985) Wasserwerksschlamm—ein zusätzliches Problem für die Versorgungsunternehmen in den Niederlanden. *Gas- und Wasserfach* 126, 513-518.
- Rohmann, U. & Sontheimer, H. (1985) Nitrat im Grundwasser, Ursachen-Bedeutung-Lösungswege. DVGW-Forschungsstelle am Engler-Bunte-Institut der Universität Karlsruhe (TH).
- Strebel, O., Böttcher, J. & Kölle, W. (1985) Stoffbilanzen im Grundwasser eines Einzugsgebietes als Hilfsmittel bei Klärung und Prognose von Grundwasserqualitätsproblemen (Beispiel Fuhrberger Feld). *Z. Dt. Geol. Ges.* 136, 533-541.

A strategy for drought mitigation using groundwater: a case study in Kolar district, Karnataka State, India

C. NAGANNA

School of Earth Sciences, Bangalore University, Bangalore 560 056, India

Y. LINGARAJU

Department of Mines and Geology, Government of Karnataka, Bangalore, India

Abstract Karnataka, one of the southern states of India, has an area of 192 204 km²; of this nearly one third is constantly affected by drought. Based on various factors responsible for causing drought conditions, the Kolar district has been identified as one of the chronically drought prone areas. Reviewing different drought mitigation strategies that are in vogue in India, one finds that there is a dominance of irrigation and associated dryland agricultural programmes. These measures involve only the utilization of surface water. Through an analysis of the physiographic and geological conditions in the state, a new strategy is proposed to use the groundwater which is likely to be flowing along the east-west running lineament connecting the western water surplus areas to the water deficit areas of the east. To test this hypothesis a small basin in Kolar district was selected. Refining the lineament map already prepared by ground check within the basin selected, a number of sites were located along these lineaments. The average yield of these wells is 4 to 5 times higher than the average yield of the wells in the basin outside the lineament. Since some of these lineaments cut the water divide and extend up to the water surplus west, it is inferred that there is a flow of water across the water divide from the west and by properly managing the supply of water from these wells situated on the lineament, a permanent solution can be worked out for drought mitigation.

INTRODUCTION

The water resources in India depend on the monsoons, 70% of which occur during the monsoon season (June–November). Besides this, there are large tracts of land depending entirely on localized showers for their water needs. While there is sufficient shift in the period of the more dependable monsoons, the localized showers are totally undependable. This will completely upset the rather rigid agricultural programme of the Indian farmer resulting in situations coming under the definition of drought. Drought in

general may be defined as a "lack of rainfall" sufficiently large, and for a sufficiently long period, as to effect adversely plants, water supply for domestic purpose, operation of power etc. Drought, though essentially a meteorological phenomena, can be of three categories, (a) meteorological drought, a situation when the actual rainfall is significantly less than the climatologically expected rainfall; (b) hydrological drought, associated with the depletion of surface water, consequent drying up of lakes, river, reservoirs etc (a hydrological drought may result if meteorological drought is sufficiently prolonged); (c) agricultural drought, when soil moisture is inadequate to support a healthy growth of crops to maturity.

Past records show that drought conditions have existed in India since the eleventh century, some of which were very severe. Bhatia (1967) has systematically worked out drought periods in India since 1799. From this study it is evident that fairly severe drought conditions have occurred in India in some parts of other, once in two to five years. In Karnataka, the south-eastern and middle interior are the regions which are often affected (Fig. 1).

A review of the action of the Government for the past 30 years can only indicate some major and minor irrigation projects coming into being in the chronically drought-prone areas. Except for the Tungabhadra project, whose waters can flow into less than 5% of the chronically drought affected areas of Karnataka, the other projects are not designed to overcome the drought conditions. The minor irrigation projects in the area appear to have been undertaken more by way of providing employment to the local population during drought, rather than as a real mitigation strategy. Consequently, recurrence of drought has become a regular feature. The present study is intended to focus the attention of the planners on the possible mitigation strategies which are more permanent in nature by selecting an area for the case study (Fig. 1).

DROUGHT PRONE AREAS KARNATAKA

Drought prone areas of Karnataka have delimited on the basis of annual rainfall, rainfall variability, soil moisture characteristics, annual potential evapotranspiration, water surplus and index of aridity (Barai & Naganna, 1978). The drought-affected, north-south zone comprising 111 taluks in Bijapur, Belgaum, Gulbarga, Raichur, Chitradurga, Tumkur and Kolar districts with less than 700 mm annual rainfall lie in eastern part of the State (Fig. 1). This zone can be further delimited into four zones of drought intensity as, moderate, large, severe and disastrous drought conditions.

STUDY AREA

The Kolar region covering Kolar district was selected as the study area, mainly because according to the classification of drought in Karnataka it has moderate drought, with semiarid conditions and is subjected to dryness. Kolar, Gulbarga, Raichur and Bijapur districts in Karnataka are the only

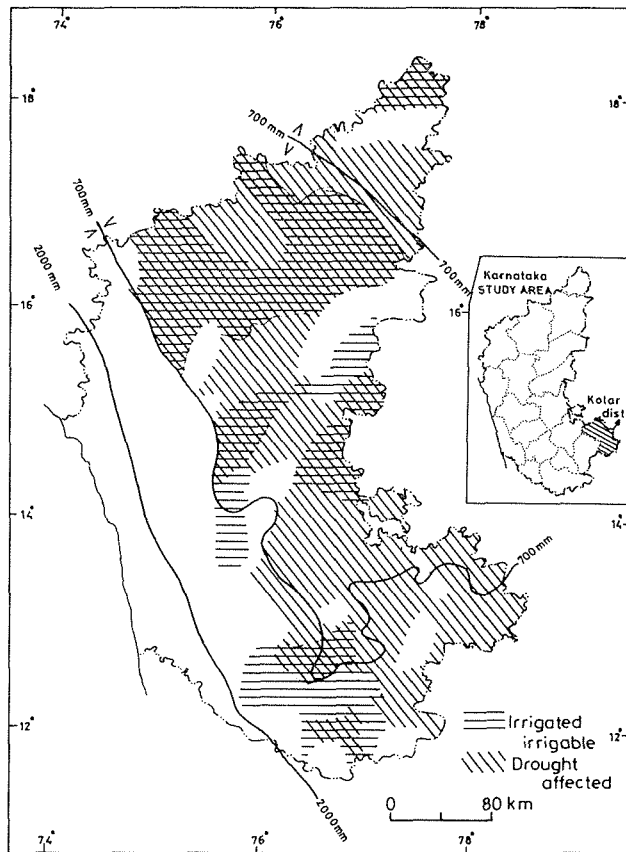


Fig. 1 The drought situation in Karnataka State, southern India.

drought-affected areas which do not have an assured supply of water by an of the means of surface irrigation. While the contemplated massive river valley projects in the Krishna River basin can bring some relief to the drought affected areas in the northern districts of Karnataka, there appears to have been no major attempt made to mitigate the drought condition in Kolar district. Kolar in 1980 had only 2–3% of the normal annual rainfall of 730 mm. In such a drought-affected area, an effective drought mitigation strategy needs to be evolved so that some assured supply of water is made available. Kolar district is situated between $12^{\circ} 46'$ and $13^{\circ} 58'$ N and $77^{\circ} 21'$ and $78^{\circ} 35'$ E, with an area of 8236.5 km².

GEOLOGY

Geologically the area is composed of crystalline complex of Precambrian age.

The rock types are gneisses of varying grain size and gneissosity, intrusive granites, various types of schists formed by metavolcanics and metasediments, younger basic dykes etc. The areas has suffered repeated tectonic disturbance and the famous gold mines which are known to be the deepest in the world are situated at the contact between the granitoids and the schists. Due to tectonic disturbance there are fractures, joints, faults, shear zones, and lineaments are very well developed. A prolonged weathering has created a thick mantle of soil representing A, B, C horizons in many places sometimes extending to tens of metres.

PHYSIOGRAPHY

The Kolar district is dotted by numerous hills and peaks of varying heights, particularly in the north. The principal chain of mountains is Nandidurga Range with the peak at 1617 m. Other peaks include Kalauardurga, Bharmagiri, Harahereshwarabetta and Divigiri. Further east is another range of hills of lower elevation forming a chain to the west of Kolar town. A third low line of hills lies to the south of Bangarpet.

There are no perennial rivers in Kolar. Most channels are small and carry water only in the rainy season. Three important rivers are the Palar, South Pennar and North Pennar. Several of the tributaries to these rivers have their origins in the district and flow in different directions.

CLIMATE

The average rainfall of the district is 730 mm, about 70% of its occurring during the southwest monsoon. September–October usually records the highest rainfall; which is also associated with thunderstorms. These were wide variations in rainfall recorded over a 50-year period. In 11 out of 50 years rainfall was less than 80% of the normal. Though the district as a whole did not record two consecutive years with rainfall less than 80% of the normal, such occasions are known at individual stations.

Temperatures indicate a rise from March to May, recording the highest of 40°C. With the advance of the southwest monsoons, temperature decreases till September–October. The withdrawal of the southwest monsoon records the lowest temperatures in December with 25°C (maximum) and 20.6°C (minimum). Relative humidity is high in the southwest monsoon period.

STRATEGIES FOR DROUGHT MITIGATION

A number of strategies have been suggested for drought mitigation in India, many of which are sociological. However, Bali (1979), Rao Ranganathan (1979) and Ramarmurthy (1979), have suggested some physical methods. Mr K. L. Rao, who as the Minister for Irrigation, Government of India in 1971,

had plans to bring the surplus waters of the River Ganga to be linked with rainfed rivers of the south by pumping the water over a head of 550 m using 7×10^6 kW of power. This has remained only as a plan. The other methods suggested are very general in nature, suggesting interbasin transfer of surface water and no one has considered the possibility of using the groundwater except the author (Naganna, 1979), who proposed a hypothesis which required testing.

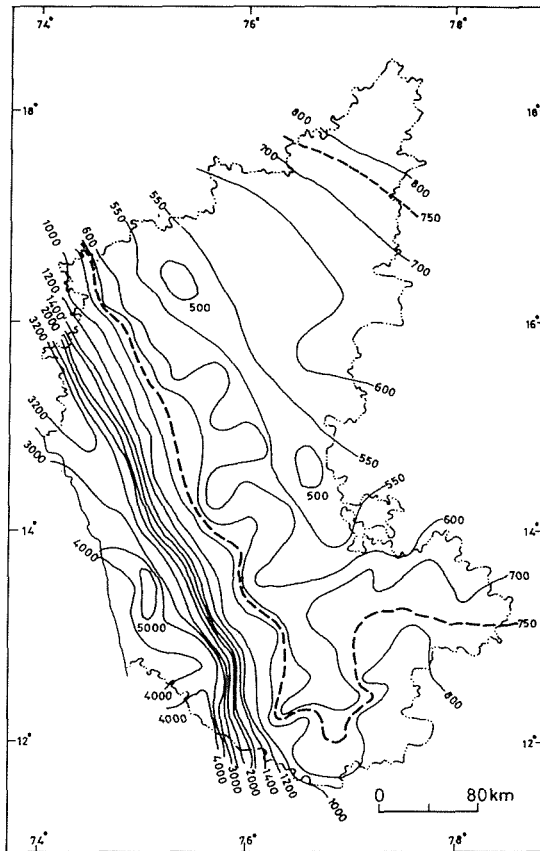


Fig. 2 Average annual rainfall (in mm) in Karnataka State, southern India.

UTILIZATION OF GROUNDWATER FLOWING THROUGH DEEP SEATED LINEAMENTS : A HYPOTHESIS

Naganna (1979) has hypothesized that there is a western belt lying along the western coast of Karnatak comprising of high mountains of the Western

Ghats. This region receives very heavy rainfall ranging from 1000 to 4000 mm and this Ghat forms the water divide for the east and west flowing rivers (Fig. 2). Further, as confirmed by the exploratory work in Kudremukh, Bababudan and Kemmangundi, and further north in Belgaum, there is a thick weathered mantle providing sufficient media for the formation of a subsurface water reservoir. During the non-rainy season water from the subsurface water body through effluent seepage is discharged and flows as baseflow in all the rivers. This accounts for the discharge of groundwater wherever the water table intersects the surface.

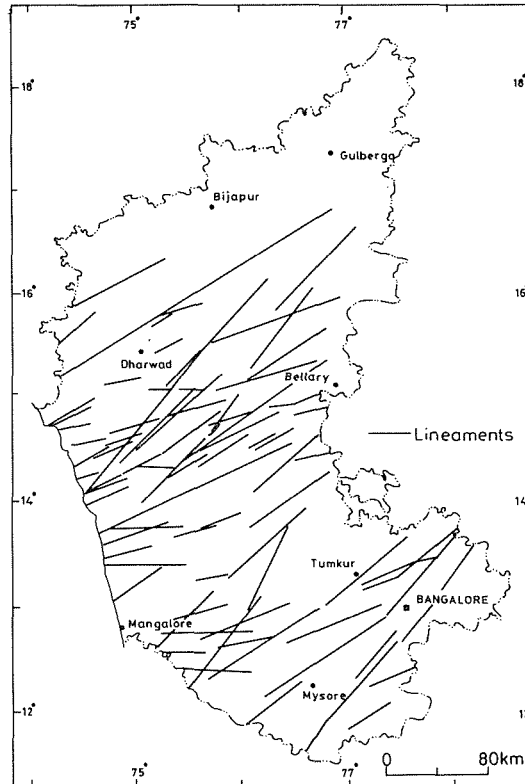


Fig. 3 East-west major lineaments in Karnataka State, southern India.

The existence of east-west running lineaments in Karnataka is established by the study of Landsat image though their exact location on the ground is yet to be established in many places. These lineaments are found to exist all along Karnataka from north to south (Fig. 3) and must be transporting groundwater from the surplus western region to the east.

CASE STUDY

In order to verify the above hypothesis, the Palar basin in Kolar district was selected. By a close examination of the satellite imageries, the lineaments present in the basin were demarcated on the map. Location of these

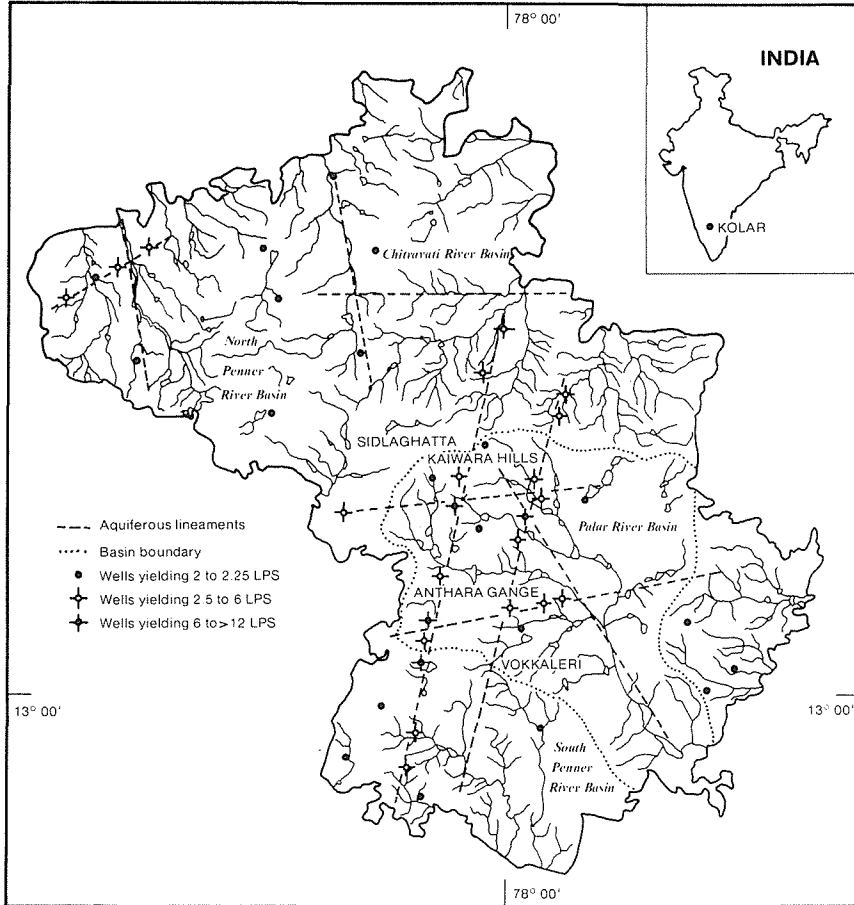


Fig. 4 Map showing river basins of the Kolar district with aquiferous lineaments across the basin divides.

lineaments on the ground was made by a detailed geological and geophysical investigations involving resistivity profiling across the suspected lineaments on the ground. The linear extent of each one of these lineaments was traced by both geological and geophysical investigations. Further, by depth probes through electrical resistivity, sites were located along the lineaments. Bore holes were sunk to depths ranging from 50 to 80 m. Yield tests were

conducted in all the wells located along the lineaments. These details are indicated in Fig. 4. In this, there are wells yielding 2 l s^{-1} to more than 12 l s^{-1} . A number of bore holes also exist outside these lineaments and yield tests were conducted in these wells and the average yield was noted to 4 to 5 times less than the minimum yield noticed in the wells sunk along the lineaments, with lower rate of recuperation. Further, it is also noticed that these lineaments cut across the water divide of the basin and some of them can be traced up to far western region of the State, where there is a surplus water storage in the subsurface.

CONCLUSION

From this it could be concluded that the best drought mitigation strategy would be to locate the deep seated east-west lineaments which connect the water surplus of the Western Ghat region to the eastern chronically drought-stricken belt on the ground by detailed geological investigation and to sink deep boreholes to tap the water flowing along the lineaments. Yield tests conducted in these wells show a fair degree of consistent supply of water with a steady rate of recuperation. Therefore, proper management of this water can serve as a permanent drought mitigation strategy.

Acknowledgements The second author is indebted to the Director of the Department of Mines and Geology, Government of Karnataka, and the Karnataka Government for providing deputation to undertake this study.

REFERENCES

- Bali, J. S. (1979) Watershed management to fight droughts. In: *Proc. International Symposium on the Hydrological Aspects of Droughts* (Souvenir, New Delhi), 61-65. IIT, New Delhi.
- Barai, D. C. & Naganna, C. (1978) Criteria for delimiting drought prone areas - A case study in Karnataka. *Vignana Bharathi* 4 (2), 88-103.
- Bhatia, S. S. (1967) A new measurement of agricultural efficiency in U.P., India. *Econ. Geogr.* 43 (3), 244-260.
- Naganna, C. (1979) Delimiting drought prone areas, in Karnataka and a mitigation strategy. In: *Proc. International Symposium on the Hydrological Aspects of Droughts* (Souvenir, New Delhi), 486-493. IIT, New Delhi.
- Ramamurthy, V. (1979) Drought mitigation strategy through weather modification. In: *Proc. International Symposium on the Hydrological Aspects of Droughts* (Souvenir, New Delhi), 67-75. IIT, New Delhi.
- Rao Ranganathan, V. (1979) Drought mitigation measures for drought prone areas in Andhra Pradesh. In: *Proc. International Symposium on the Hydrological Aspects of Droughts* (Souvenir, New Delhi), 494-501. IIT, New Delhi.

Groundwater monitoring and management in permafrost areas

YE. V. PINNEKER

Institute of the Earth's Crust, 664033 Irkutsk, USSR

INTRODUCTION

With respect to its relation to permafrost, groundwater may be subdivided into the following types (Tolstikhin, 1941): suprapermafrost, intrapermafrost (including talik water), and subpermafrost (Fig. 1). For groundwater quality and resources management under "usual" conditions it is mainly the water-salt regime to be regulated, while in the case with permafrost the water-thermal regime is to be observed as well. What are the characteristic features of such management?

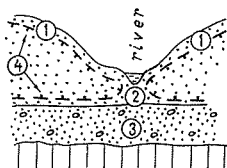


Fig. 1 Diagram showing interrelationship between groundwater and permafrost rock: 1 - suprapermafrost water of the active layer; 2 - intrapermafrost water of taliks; 3 - subpermafrost water; 4 - permafrost rock boundary.

The main feature consists in taking into account the water-thermal equilibrium which has formed over centuries in the "rock-water" system and which is conditioned by subzero temperatures (Melnikov & Tolstikhin, 1974). Disruption of this equilibrium will lead to serious consequences; once started, it will continue as a "chain reaction", on the one hand causing qualitative changes in groundwater (including its pollution) and, on the other hand influencing the resources and dynamics (depletion, freezing of filtration paths). Here is a simple example; a tractor track, once left on the virgin surface of permafrost, will some time later provide a channel for surface water infiltration leading to the degradation of both seasonally freezing and permafrost soil and its disintegration.

Preservation of the natural water-thermal regime is a necessary condition for construction work. A building is constructed on piles so there can be a thermoinsulation "air pillow" between the building itself and the permafrost soil under it (Fig. 2). The same condition is necessary in the case of technogenic influence on groundwater, or otherwise there will be a drastic change in the

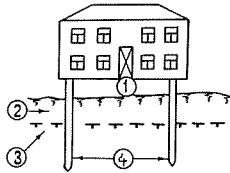


Fig. 2 Construction on piles in permafrost: 1 - "air pillow; 2 - active layer; 3 - upper boundary of permafrost rock; 4 - piles.

qualitative-quantitative state of the geological environment and, primarily of its most mobile component — groundwater.

The main distinction of criolite-zone groundwater, as compared to non-permafrost areas, is the localization of fresh groundwater, firstly, within the bounds of the suprapermafrost water-bearing horizon, secondly, among taliks (under river-beds or along tectonic faults) and, thirdly, to the upper subpermafrost stratum. Let us consider the changes of groundwater quality and resources with respect to these three sections of the geological profile.

TECHNOGENIC INFLUENCE ON GROUNDWATER QUALITY

The seasonally thawing layer is the most sensitive to the industrial activity of man; this is possibly why it is called the "active layer". In the suprapermafrost water-bearing horizon even seasonal freezing-thawing leads to the accumulation of dissolved substances through their extraction from rock. Periodical freezing-thawing precipitates the reduction of a substance to a solution at approximately twice the usual rate.

Therefore, if the pollutants find their way into this layer they are more rapidly concentrated than diluted. Waste product infiltration is of particular ecological harm in industrial and residential areas, where lack of power and low suprapermafrost water-bearing horizon drainage (both of these features are characteristic of alluvial plains) lead to the gradual accumulation of pollutants in the summer. As a result, instead of being a fresh water supply, the water-bearing horizon becomes a malodorous accumulator of waste matters. Furthermore, an increase in suprapermafrost groundwater mineralization leads to a lower stability of the ground, particularly of the active layer. A similarly negative change of the water-thermal regime may be attributable to irrigation, drag test ground thawing or possible water mains and sewage system leakages under buildings. In point of fact, this is where peculiar hydrogeothermal anomalies occur which not only bring about deterioration of groundwater quality but also reduce the stability of the ground.

As a rule, rivers and streams in permafrost territories freeze in the winter, so that the suprapermafrost water-bearing horizon serves as a major water supply for most nearby residential areas. Here the previously mentioned regularities of the technogenic influence are the basis for groundwater quality

management.

The usual practice, especially in cities, is to use for water supply the talik and subpermafrost water which is not so much subject to qualitative changes. Nevertheless, even along taliks, signs of pollutant infiltration can be observed (along river-beds and under lakes, along tectonic faults). Being channels of intensive interaction between groundwaters and surface waters they act as discharge sinks for groundwater in the summer when they also are transformed into pollutant sources. During exploitation of the intra- and subpermafrost water-bearing horizons, the thermodynamic situation often becomes artificially changed which leads to disruption of the water-bearing horizon isolation and the merging of fresh groundwater with upconing mineral water.

ICING FORMATION CONTROL

With respect to their genesis, icings are subdivided into the following groups: groundwater (or spring) icings, surface water (very often river) icings, and mixed icings. Icings are groundwater which has come out on the surface and frozen near the emergence point. River icings are also connected with the activity of groundwater because they form during that very period when rivers are fed exclusively by underground resources. So, icings occur on the surface which makes it impossible to consider them as groundwater, but they cannot be regarded as surface water either, for the contained water is temporarily excluded from the surface volume. Tolstikhin (1974) calls icings "the intermediary" between surface waters and groundwaters. They function as regulators and redistributors of groundwater during its transition into surface water.

Icings very often fix taliks and occur in the lower parts of slopes or valley basins, stretching along tectonic fault zones, valley slopes and river banks. Their size and thickness vary within a wide range. Sometimes they are over 10 km² in area, extending over tens of kilometres and having a thickness of 15–40 m. Many icings remain all the year round.

While beyond permafrost areas groundwater emergence poses no serious danger for engineering activity, icings make the situation far more difficult since they exercise a destructive influence on any sort of construction, especially when they occur unexpectedly in the process of building. Mentioning the Baikal-Amur railroad as an example, it can be pointed out that icings occur there along embankments (Pinneker & Pisarsky, 1977). The construction of the latter increases icing formation as the result of changing the direction and even the interception of the underground flow which occurs through slope cutting (Fig. 3(a)), drainage gutters digging (Fig. 3(b)) and soil packing, the latter leading to water-bearing horizon freezing (Fig. 3(c)). The mentioned technogenic influence has one other consequence — those springs and wells which might well have been serving as the only fresh water supply points stop functioning and go out of use. Sometimes in cities situated in permafrost areas, this may result in a drastic change of the hydrodynamic regime, the progressing icing formation can paralyse traffic, destroy buildings etc.

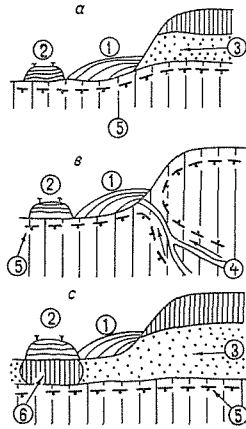


Fig. 3 Icing formation: a – slope cutting and drainage of water-bearing horizon of layer type; b – as the result of fault emergence drainage with the help of gutters; c – as the result of the freezing and interception of the suprapermafrost water-bearing horizon through the packing of soil under the embankment.

To prevent the above-mentioned and other negative consequences, icing control practices should observe the regularities of icing formation and conform to the water-thermal regime which has formed over centuries. Icing control methods are divided into active and passive ones. The latter provide for the inspection of icings and their removal by cutting. The active methods are far more effective; they are aimed at eliminating the causes of icing formation. Namely, it is the interception of the groundwater flow with the help of drainage devices, the warming of water-diverting devices, and the installing of so-called permafrost belts which are placed from the ground surface across the groundwater flow in front of the protected site.

The best choice of a method depends on the icing origin. Figure 3, for example, shows icings that seem to be quite identical at first sight, though they are very different in their genesis. This requires different methods for their prevention. Dealing with large icing formations, or icings fed by deep waters may often require sophisticated combinations which include drainage and diversion devices as well as permafrost belts.

In Siberia, railroad construction has increased the number and sizes of icings two-fold compared with the period prior to construction. That means that apart from knowing the causes, icing formation control requires prediction of areas liable to icings and creation of the appropriate installations to prevent them.

Finally, it should be pointed out that the nature of icing formation began to be considered by scientists at the turn of the century during the construction of the Trans-Siberian railroad. The regularities of icing formation were first discussed by Lvov (1916) who considered ways of combatting it.

GROUNDWATER EXPLOITATION MANAGEMENT

If the given permafrost rock has considerable thickness, groundwater exploitation might involve difficulties connected with its possible freezing within the well. Practical experience has suggested concrete requirements which ensure the smooth running of intake operations (Baskov & Tolstikhin, 1967). One of the most important requirements is to initially provide a secure talik around the well. This is done either by constant pumping or artificial heating of the water. Either way it must be observed that the controlled heat exchange between the well and the water containing rock does not exceed or go below a certain critical limit ensuring maintenance of the talik around the well.

To lessen the danger of the intake well freezing, one should by all means seek to reduce heat absorption by the aquifer and at the same time stabilize the heat output of the well. This can be achieved through reducing the diameter, when the velocity of the water moving through it increases. Choosing the optimum pumping intensity (which means the optimum thermal regime) will make artificial heating unnecessary. Even so there will be no 100% certainty that in the event of an emergency stoppage (pump breakdown, electricity supply failure) the water in the well will not freeze. That is why artificial heating is strongly recommended for groundwater intake operations in permafrost regions. Heating of shallow small-diameter wells is done by pouring in hot water; more often a special cable is used which functions in the heat element regime (Fig. 4).

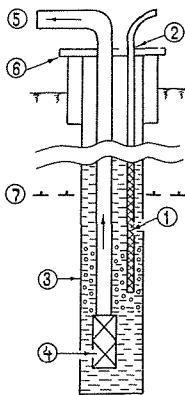


Fig. 4 The groundwater well: 1 - cable heat element; 2 - cable input; 3 - filter column, 4 - pump; 5 - rising main; 6 - well head; 7 - lower permafrost boundary.

Intensive seasonal groundwater exploitation in winter time, when surface water freezes, may result in the partial depletion of the water-bearing horizon. In this case it is artificially replenished with the necessary amount of surface

water in the summer (Kalbin, 1960). The three-year long trial operations in the Kolyma River basin aimed at testing this technique of groundwater intake, proved the efficiency of such a method of groundwater monitoring and management.

REFERENCES

- Kalbin, A. I. (1960) *Permafrost and Hydrogeology of the Soviet Northeast*, tr VNII-I, v.XVIII. Magadan.
- Baskov, Ye. A. & Tolstikhin, O. N. (editors) (1967) *Groundwater of Yakutiya as Water Supply*. Nauka, Moscow.
- Lvov, A. V. (1916) *Prospecting and Trials of the Water Supply Sources in the Western Section of the Amur Railroad in Conditions of Permafrost Soils*. Irkutsk.
- Melnikov, P. I. & Tolstikhin, N. I. (editors) (1974) *General Permafrost Study*. Nauka, Novosibirsk.
- Pinneker, Ye. V. & Pisarsky, B. I. (1977) *Groundwater in the Baikal-Amur Railroad Zone*. Nauka, Novosibirsk.
- Tolstikhin, N. I. (1941) *Groundwater of the Lithosphere Permafrost Zone*. Gosgeoizdat, Moscow/Leningrad.
- Tolstikhin, O. N. (1974) *Iceings and Groundwater in the Soviet Northeast*. Nauka, Novosibirsk.

Two case studies in estimation of groundwater recharge

D. C. H. SENARATH

Department of Civil Engineering, University of Moratuwa, Sri Lanka

Abstract A water balance technique is used to estimate groundwater recharge. Actual evapotranspiration is estimated using potential evaporation data and considering the nature of vegetation and existing soil moisture conditions. The unknown parameters used in the technique can be established by comparing computed values of streamflow with gauged streamflow. The estimated values of recharge can be confirmed by feeding these values to a flow model of the aquifer. The techniques of recharge estimation are demonstrated by considering two specific aquifers, the Chalk aquifer of Essex in southeast England and the sand aquifer of Mannar Island in Sri Lanka.

INTRODUCTION

Development of groundwater schemes has received considerable attention in recent years in many parts of the world, particularly in providing drinking water supplies. However, in many such instances, the expansion of groundwater development has not been preceded or accompanied by systematic studies to evaluate the resource potentials of the respective aquifers.

In order to derive the optimum benefit from a groundwater scheme, a proper resource study has to be carried out. But unlike surface water processes, much of groundwater activity takes place unseen by the human eye, in the strata that lie below the ground surface. Measurement and monitoring of groundwater flow is therefore extremely difficult. As a result, it has often been necessary to make several simplifying assumptions in evaluating the resources of an aquifer (Fernando, 1973), because much of the data that is required for a systematic study has not been available. When data are available, it is no longer necessary to resort to doubtful assumptions and reliable studies involving refined techniques can be carried out.

To achieve a detailed understanding of the processes that take place in an aquifer, a model of the aquifer can be developed. Groundwater recharge is an essential component of such models and therefore must be estimated before the development of a groundwater model can be attempted.

A water balance study is a method that can be used to obtain an accurate estimation of groundwater recharge. This paper describes two specific case studies in the use of the water balance method to estimate groundwater recharge. The first case study refers to the Chalk aquifer in Essex, southeast England, and the second case study refers to the sand

aquifer of the island of Mannar, Sri Lanka. In both cases, the aquifer had already been developed at the time of study which was carried out to find a solution to a specific problem that had emerged in connection with the utilization of the aquifer.

ESTIMATION OF RECHARGE BY THE WATER BALANCE METHOD

As the entire recharge is primarily derived from precipitation, a reliable record of precipitation representative of the surface area feeding the aquifer is essential for estimating recharge. It must be noted that some confined aquifers may derive their recharge from the ground surface far remote from the area of abstraction and in such situations, the precipitation records that are used must correspond to the area that feeds the aquifer and not the area that directly overlies the aquifer. A surface water balance is carried out taking into account the components such as evapotranspiration, interflow, stream runoff, baseflow and groundwater recharge. There are many techniques for carrying out the surface water balance (Rushton & Ward, 1979; Senarath & Rushton, 1984). The essential features of these methods is that a daily balance is evaluated starting from precipitation for each day. The daily value of potential evaporation is estimated either from an empirical or semi-empirical formula such as Penman's formula (Penman, 1949) using meteorological data or using pan evaporation data. However, if the latter are used, a multiplying factor has to be incorporated in order to correct for the scale effect of the pan and heat transfer from the sides of the pan.

The actual evapotranspiration corresponding to each day is estimated from potential evaporation taking into account the type of vegetation covering the area and the residual moisture content of the soil. A variety of models have been devised for estimating actual evaporation from potential evaporation. In one of these models (Rushton & Ward, 1979) it is assumed that as long as the soil moisture deficit (in relation to the moisture content at field capacity) is less than a certain value known as "root constant", evaporation takes place at the potential rate, the water required for this purpose in excess of precipitation being removed from soil moisture storage, thereby increasing the soil moisture deficit. The value of the root constant is a function of the type of vegetation, those with deeper roots having higher values of root constant. When the soil moisture deficit is in excess of the root constant, it is assumed that the soil moisture is unable to contribute readily to evapotranspiration and therefore only a small fraction F (about 10%) of potential evaporation is removed from soil moisture storage. It is also assumed that recharge of the aquifer is possible only when the soil moisture deficit is completely nullified, bringing the soil to field capacity condition. Any water that infiltrates when the soil is in this condition is assumed to percolate down to the water table and this component is regarded as groundwater recharge.

Using a method similar to that outlined above to represent soil moisture balance, a simple model may be devised to represent the overall water balance of an entire catchment (Senarath & Rushton, 1984). Such a model would consist of components such as precipitation, evapotranspiration, surface runoff,

interflow, groundwater recharge, baseflow and stream runoff. The peripheral components of such a model would be precipitation, potential evaporation, actual evaporation, groundwater recharge and stream runoff (Fig. 1). The distribution of flow along the various paths is specified in terms of coefficients whose values may be established on the basis of field values of some of the components of the model. Often it is possible to compare the values for stream runoff given by the model with the corresponding values obtained by streamgauging.

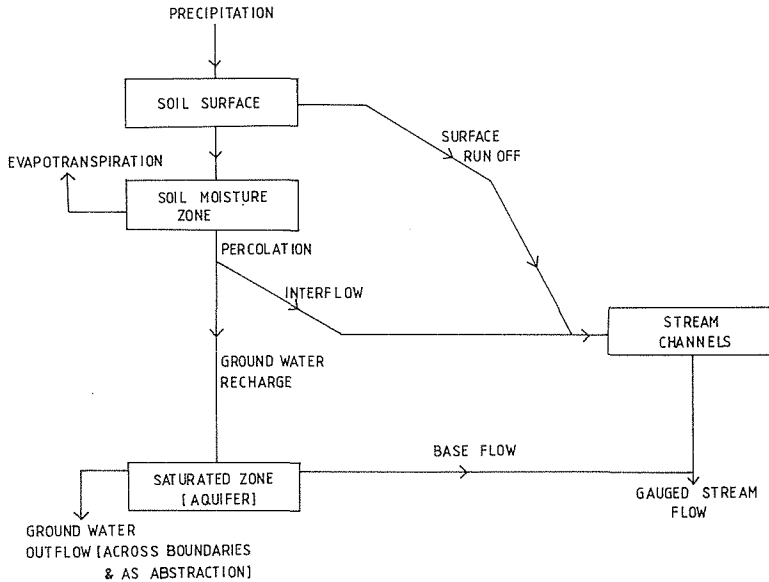


Fig. 1 A typical flow path system in a catchment.

Thus, the data required for estimation of recharge are precipitation, potential evaporation, and stream runoff together with information regarding the topography, geology and vegetation of the catchment area. Additional groundwater data such as well hydrographs can be extremely useful in confirming the results of estimated recharge. Since the factors affecting processes such as evaporation change rapidly, the time step for calculations should not be large. In practice, a time step of one day gives good results.

ESTIMATION OF RECHARGE OF THE CHALK AQUIFER OF ESSEX

The study area

The area that is considered includes the headwaters of the rivers Chelmer, Pant and Colne in Essex, England (Fig. 2). Geologically, the region lies on

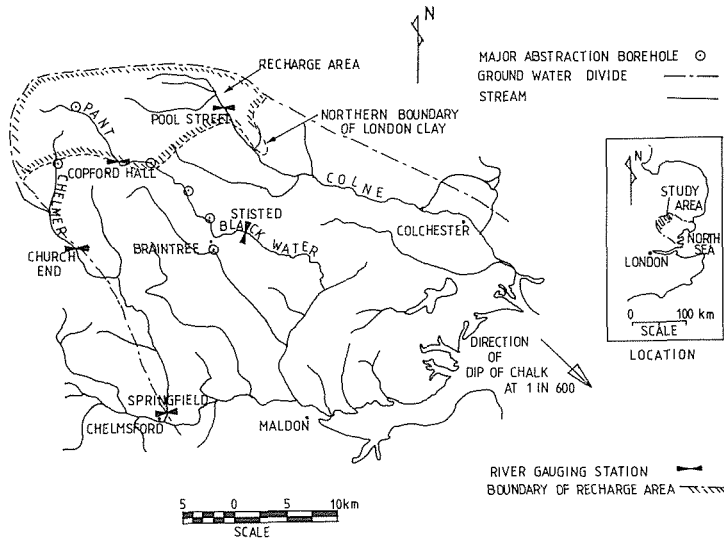


Fig. 2 Map showing the recharge area of the Essex Chalk aquifer.

the northern limb of the London basin. The chalk occurs at depth throughout the area and is overlain by the Lower London Tertiaries and London Clay. The London Clay has a consistently low permeability, and the volume of flow through it is small.

In the upper region of the catchments, the London Clay is not present. Drift deposits of glacial sands and gravels overlain by boulder clay cover much of the area. Because of the impermeable nature of the London Clay, recharge to the aquifer is possible only in the area in which the London Clay is absent. In many of the river valleys in this region, the glacial sands and gravels are exposed and the boulder clay cover is absent. A typical cross section of the recharge area is shown in Fig. 3.

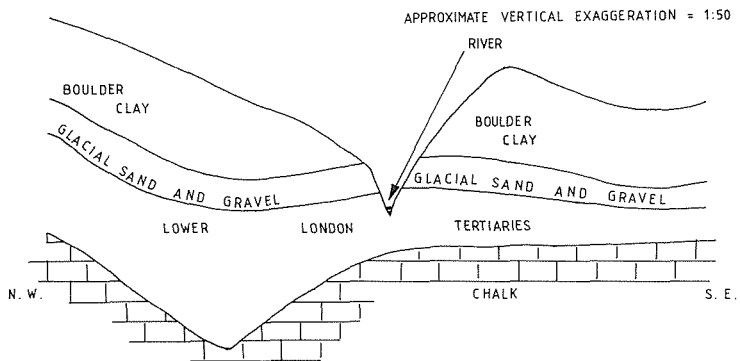


Fig. 3 Generalized geological section of the recharge area of the Essex Chalk aquifer.

Estimation of recharge

The estimation of recharge of the above aquifer was carried out as a part of an overall study of the aquifer including development of a flow model to investigate a sharp decline in the piezometric levels of the area around Braintree (Fig. 2). The method of water balance outlined above was applied to this aquifer. Precipitation records and potential evaporation based on Penman's formula obtained from the Meteorological Office, Bracknell, Berkshire, UK, were used. The data covered the eight-year period from 1970 to 1977. Initial estimates based on model parameter values established for other catchments in the UK (Rushton & Redshaw, 1979) yielded recharge values of the order of 70 Ml day^{-1} which when fed into a flow model of the aquifer produced groundwater heads which were far in excess of observed groundwater heads. This revealed the necessity to establish the values of parameters by calibration against suitable field values for the particular catchment.

Calibration of the model

In the components of the model shown in Fig. 1, some of the paths such as those of surface runoff and interflow involve a "delay" as regards the flow that takes these paths. Hence it was necessary to incorporate delay parameters in these paths. The technique of incorporation of delay parameters is described in Senarath & Rushton (1984). The parameters whose values are to be established by calibration are the distribution coefficients which govern the distribution of flow along different paths; and delay parameters which govern the "shape" of the hydrograph along each path.

Calibration was done on the basis of comparison between the streamflow hydrograph produced by the model with the corresponding hydrograph obtained by streamgauging. A trial and error procedure was adopted. The comparison was done by visual examination of the corresponding hydrographs as well as by evaluation of an objective function to measure the degree of overall agreement between calculated and gauged streamflow (Senarath, 1981; Senarath & Rushton, 1984).

Results

The results of 12 different computations for various combinations of parameters are shown in Tables 1 and 2. The value of the objective function is expressed as a percentage, 100% indicating perfect agreement between computed and gauged stream runoff. The values of the objective function are evaluated for the total quantities of computed and gauged streamflow for the entire eight-year period of calculation.

The high recharge value given by computation number 8 indicates that if water does not find its way to the streams, a large quantity of water ($79.65 \text{ Ml day}^{-1}$) is available for recharge. However, if the aquifer is unable

Table 1 Computed parameter values for the Chalk aquifer of Essex

Computation no.	Distribution coefficients:			Duration (days):				
	To soil moisture zone	Direct through boulder clay	Overland flow to boulder clay	Chalk recharge from gravels	Chalk recharge from valleys	In boulder clay	In gravels	In overland flow
1	0.95	0.10	0.40	0.10	0.10	180	60	12
2	0.80	0.10	0.40	0.10	0.10	180	60	3.0
3	0.95	0.20	0.40	0.10	0.10	180	60	3.0
4	0.95	0.10	0.20	0.10	0.10	180	60	3.0
5	0.95	0.10	0.40	0.20	0.10	180	60	3.0
6	0.95	0.10	0.40	0.10	0.20	180	60	3.0
7	0.75	1.0	0.0	1.0	0.0	0.0	0.0	3.0
8	0.95	1.0	0.0	1.0	1.0	0.0	0.0	3.0
9	0.95	0.40	0.40	0.10	0.10	180	60	3.0
10	0.95	0.10	0.50	0.10	0.10	180	60	3.0
11	0.95	0.10	0.40	0.05	0.10	180	60	3.0
12	0.95	0.35	0.40	0.10	0.10	180	60	3.0

Table 2 Results of computations for the Chalk aquifer of Essex

Computation no.	Annual mean recharge (Ml day ⁻¹)										Overall mean recharge (Ml day ⁻¹)	Value of objective function (%)
	1970	1971	1972	1973	1974	1975	1976	1977	1977	1977		
1	18.11	12.94	10.35	2.87	17.39	18.93	7.24	19.15	13.37	98.60		
2	20.52	16.34	11.81	7.46	17.84	20.79	8.67	21.57	15.63	79.56		
3	18.51	13.50	10.71	3.00	17.63	19.88	7.16	20.08	13.81	99.16		
4	16.70	10.90	9.04	2.52	16.34	15.72	7.33	16.02	11.82	96.36		
5	23.02	16.91	13.38	3.65	22.10	24.73	8.93	25.05	17.23	96.64		
6	30.78	21.45	17.33	4.88	29.63	31.33	12.66	31.69	22.47	90.20		
7	88.91	40.54	34.18	2.16	50.79	65.39	27.18	73.24	47.80	89.36		
8	127.90	62.40	59.00	7.50	127.00	93.50	62.70	97.22	79.65	19.80		
9	19.33	14.62	11.43	2.95	18.12	21.78	6.99	21.93	14.64	99.72		
10	18.81	13.96	11.00	3.05	17.91	20.53	7.20	20.71	14.15	99.59		
11	15.65	10.96	8.83	2.48	15.04	16.03	6.40	16.20	11.45	96.15		
12	19.16	14.39	11.29	2.95	18.03	21.38	7.04	21.54	14.47	99.99		

to accept this water, it would result in lesser recharge, the excess water being forced to flow to the streams. Considering the value of the objective function, the most probable value of recharge corresponds to computation number 12 which gives a recharge figure of $14.47 \text{ Ml day}^{-1}$. The flow model of the aquifer (Rushton & Senarath, 1983) indicated that even this value of recharge is too high for the early period of development of the aquifer in the early part of the present century. The physical explanation for this phenomenon is that in the early period of development of the aquifer, the high piezometric heads prevented acceptance of all the available recharge resulting in some it being rejected to find its way to the streams. However, with the development of the aquifer, when the piezometric heads declined, more of the available recharge was accepted by the aquifer. This demonstrates the interesting fact that for recharge to be effective, it must not only be available but the aquifer must be in a condition to accept it.

ESTIMATION OF RECHARGE OF THE SAND AQUIFER OF MANNAR

The study area

The island of Mannar is situated along the northwest coast of Sri Lanka and is about 260 km north of Colombo (Fig. 4). The extent of the island is approximately 128 km^2 . The area is generally flat and is constituted of coastal plains except for the sand dune ridges rising along the axis of the elongated island. The area is devoid of any surface streams.

Geomorphologically, two contrasting formations are present namely, lagoonal deposits and wind-blown sand deposits. The low elevation areas consist mainly of lagoonal deposits while the higher elevations are occupied by

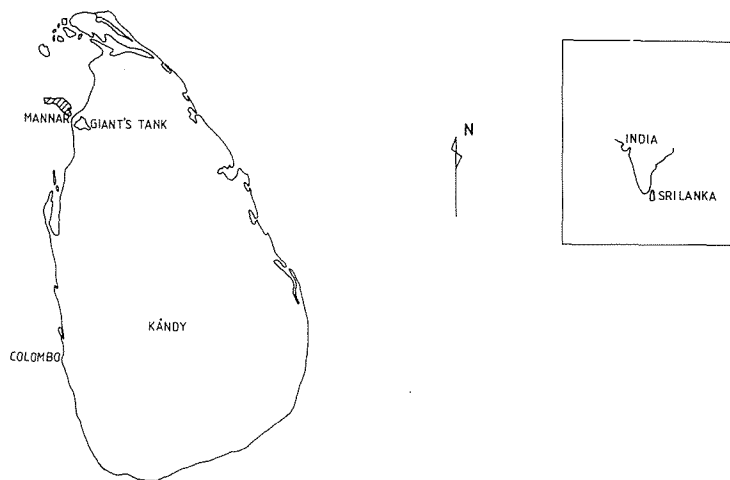


Fig. 4 The study area of the Mannar sand aquifer.

wind-blown sand deposits. These Quaternary deposits which together have a maximum thickness of about 20 m are underlain by Miocene limestone followed by secondary deposits of Jurassic sandstone and the Precambrian basement which is encountered at a depth of about 250 m (Rao, 1984).

Climate of the study area The Mannar Island falls into the semiarid climate area and receives a mean annual precipitation of about 975 mm. The maximum and minimum mean monthly precipitation are 240 mm corresponding to the month of November and 5 mm corresponding to the month of July respectively.

The temperature in the area ranges from a minimum of 23°C to a maximum of 35°C. The nearest pan evaporation measuring station is at Giants' Tank which is about 30 km southeast of Mannar Island. The climate at Giant's Tank is similar to that at Mannar Island and it is assumed that the pan evaporation values of Giant's Tank are applicable to Mannar Island. The average monthly pan evaporation values for Giant's Tank for the 20-year period from 1954 to 1973 range from 125 mm corresponding to the month of December to 178 mm corresponding to the month of June.

Hydrology There is a large number of shallow dug wells spread throughout the island each of which supplies the domestic requirements of individual homes. The overall abstraction from these wells however, is insignificant compared to the abstraction from deeper boreholes constructed and maintained by the National Water Supply and Drainage Board, Sri Lanka. These provide a water supply to about 20% of the population. The total abstraction from these wells amounts to about 860 m³ day⁻¹. A study was undertaken to estimate the additional abstraction that could be safely implemented to augment the existing supply. This study was primarily based on an estimation of the recharge that reaches the aquifer.

Estimation of recharge

The method of consideration of water balance in this study was based on the following:

- (a) The values of daily precipitation were obtained from records maintained by the Department of Meteorology, Sri Lanka. The period of study consisted of the eleven years from 1972 to 1982.
- (b) The values of pan evaporation recorded at Giant's Tank gave consistently lower values compared to those given by Penman's formula, the difference being about 14%. (Giant's Tank was the pan evaporation measuring station closest to Mannar Island and was considered to be representative of the evaporation at Mannar Island.) In order to arrive at a conservative estimate for recharge, the higher values of evaporation, i.e. those given by Penman's formula were used.
- (c) Direct runoff out of a catchment represents the surface runoff that leaves the catchment through the surface boundaries. This component usually enters the streamflow that leads water out of the catchment. In

the case of Mannar Island, since the upper stratum of the catchment is highly permeable and since there are no significant surface streams, direct runoff out of the catchment is small. The component direct runoff was therefore taken as a small percentage of the daily precipitation. Three values were tried in the computations: 0%, 5% and 10%.

- (d) Soil moisture balance was carried out on a daily basis using the concept of root constant (Rushton & Ward, 1979). The calculations were initiated around the beginning of December when the soil moisture deficit in any year is likely to be zero due to northeast monsoonal rains which are effective in Mannar. The calculations were terminated also at a similar date so that the net increase in soil moisture storage for the period of calculations could be assumed to be zero.

Root constant is a parameter that depends on the type of land use in the catchment area. Grindley (1969) suggests values of root constant for different types of vegetation in the UK ranging from 12.5 mm for rough grazing to 200 mm for woodland. In a study of the northwest limestone aquifer of Vanathavillu, Sri Lanka (Lawrence & Dharmagunawardene, 1981), the following values of root constant were used:

- (i) annual crops such as paddy and grassland: 50 mm;
- (ii) coconut and mango: 150 mm;
- (iii) forest cover: 300 mm.

The estimates of recharge for the limestone aquifer of Vanathavillu based on the above values for root constants have been confirmed by flow models (De Silva, 1986). Vegetation in Mannar Island consists mainly of randomly distributed palm (palmirah) trees and small shrubs. Therefore, considering the values suggested above, the root constant for this area is probably in the region of 100–150 mm. In the present study, a series of values ranging from 50 to 150 mm were tried in different computations, bearing in mind that higher values give more conservative estimates for recharge.

- (e) Outflow through the aquifer boundaries was calculated from Darcy's equation, based on estimated values of permeability and thickness of the aquifer and hydraulic gradient at the aquifer boundary, which was evaluated from data on water table elevation.

For Mannar Island, the boundary length (perimeter) is 70 km, the average thickness is 7.75 m and the water table gradient towards the boundaries is 0.0035. Based on a number of pumping test results, the average permeability was estimated as 10.2 m day⁻¹. Corresponding to these values, the outflow through the boundaries works out as follows:

$$\begin{aligned} \text{Discharge} &= \text{area} \times \text{permeability} \times \frac{dh}{dl} \\ &= 70 \times 1000 \times 7.75 \times 10.2 \times 0.0035 \\ &= 19\,367 \text{ m}^3 \text{ day}^{-1} \end{aligned}$$

The area of Mannar Island is 128 km². Therefore, the outflow of 19 367 m³ day⁻¹ is equivalent to

$$\frac{19367 \times 10^3}{128 \times 10^6} \times 365 = 55 \text{ mm}$$

over the catchment per year.

Results

The results of recharge estimates for 30 different computations based on different combinations of values of parameters are shown in Table 3. The recharge values given are the averages per year computed for the entire study period.

It is seen that the most stringent conditions for recharge are imposed in computation number 19 corresponding to the maximum values of direct runoff fraction, root constant and factor F (factor F represents the fraction of moisture needed for evaporation taken from the soil when the soil moisture deficit exceeds the root constant). The annual mean recharge in this case is 93 mm, which is 10.34% of annual precipitation. The least stringent condition corresponds to computation number 13 which gives an annual mean recharge

Table 3 Results of computations for the sand aquifer of Mannar Island

Computation no.	Direct runoff fraction of precipitation	Root constant (mm)	Factor F	Mean recharge (mm year^{-1}):	
				Gross	Net
1	0	100	0.10	184	116
2	0.10	100	0.10	128	60
3	0	50	0.10	189	121
4	0	100	0.10	167	99
5	0	100	0.10	184	116
6	0	150	0.10	145	77
7	0	50	0.10	253	185
8	0	50	0.20	182	114
9	0	150	0.20	140	72
10	0	100	0.20	159	91
11	0	150	0.05	149	81
12	0	100	0.05	202	134
13	0	50	0.05	287	219
14	0.10	100	0.10	130	62
15	0.10	150	0.10	98	30
16	0.10	50	0.10	189	121
17	0.10	50	0.20	129	61
18	0.10	100	0.20	112	44
19	0.10	150	0.20	93	25
20	0.10	150	0.05	102	34
21	0.10	150	0.05	152	84
22	0.10	50	0.05	224	156
23	0.05	100	0.10	158	90
24	0.05	150	0.10	121	53
25	0.05	50	0.10	221	153
26	0.05	50	0.20	155	87
27	0.05	100	0.20	134	66
28	0.05	150	0.20	115	47
29	0.05	150	0.05	126	58
30	0.05	150	0.05	180	112

of 287 mm which is 31.9% of mean annual precipitation. Comparing the results with previous studies in a similar climatic and vegetative area (Lawrence & Dharmagunawardene, 1981) in which the recharge estimates have been confirmed by flow models, the most appropriate parameter values for the present study are most likely those assumed in computation number 24 which gives a mean annual recharge of 121 mm which is 13.45% of the mean annual precipitation.

It may be noted that in this case, no direct calibration of the model was possible but the results have been subsequently confirmed by means of a flow model.

CONCLUSIONS

The two examples described in this study have demonstrated that simple water balance techniques can be adopted for estimating groundwater recharge. An essential requirement in these methods is that reliable records of precipitation and evaporation must be available, together with sufficient information about the topography and geology of the catchment. Reliable data on streamflow are required for purposes of calibration. The estimates of recharge can be finally confirmed by means of flow models.

Acknowledgements The author is grateful to the University of Moratuwa, Sri Lanka, and the National Water Supply and Drainage Board, Sri Lanka, for the facilities provided and data supplied in carrying out the investigations described in this paper.

REFERENCES

- De Silva, V. W. (1986) Investigation of resources of a limestone aquifer using a digital technique. M.Eng. Thesis University of Moratuwa, Moratuwa, Sri Lanka.
- Fernando, A. D. N. (1973) *The Groundwater Resources of Sri Lanka*. Publication of Ministry of Power and Highways, Sri Lanka.
- Grindley, J. (1969) The calculations of actual evaporation and soil moisture deficit over specified catchment areas. *Hydrol. Memo no. 38, Met. Office, Bracknell, Berkshire, UK*.
- Lawrence, A. R. & Dharmagunawardene, H. A. (1981) *The Groundwater Resources of the Vanathavillu Basin*. Groundwater Division Publication, Water Resources Board, Colombo 7, Sri Lanka.
- Penman, H. L. (1949) The dependence of transpiration on weather and soil conditions. *J. Soil Sci.* 1.
- Rao, K. V. R. (1984) *Groundwater Investigation for Community Water Supply in Mannar Island*. Publication of National Water Supply and Drainage Board, Ratmalana, Sri Lanka.
- Rushton, K. R. & Redshaw, S. C. (1979) *Seepage and Groundwater Flow. Numerical Analysis by Analog and Digital Methods*. John Wiley and Sons, Wiley Interscience Publications.
- Rushton, K. R. & Senarath, D. C. H. (1983) A mathematical model study of an aquifer with significant dewatering. *J. Hydrol.* 62.
- Rushton, K. R. & Ward, C. (1979) The estimation of groundwater recharge. *J. Hydrol.* 41.
- Senarath, D. C. H. (1981) Regional groundwater flow simulation using a numerical model including aquifer dewatering and recharge estimation. PhD Thesis, University of Birmingham, UK.
- Senarath, D. C. H. & Rushton, K. R. (1984) A routing technique for estimating groundwater recharge. *Ground Water* 22.

Large-scale hydrogeological investigations for improving the completeness of subsurface water storage assessment and for examining the impact of its development on the environment

V. M. SHESTOPALOV, YU. F. RUDENKO & V. O. BALOUTA

Academy of Sciences Ukrainian SSR; Institute of Geological Sciences, Section of Hydrogeological Problems, Kiev, USSR

Abstract The experience of large-scale hydrogeological investigation with the purpose of increasing the reliability of subsurface water storage assessment as well as estimating the impact of its recovery on the environment is generalized. The intensification of water recovery leads to a gradual complication of modelling the geological water-exchange system as well as to increasing problems concerning social and economic impact of the water-economic complex and more reliable prediction of this impact. Methodology and results concerning proved subsurface water storage estimation are given, as well as ecologic and social-economic problems treated by means of a simulation model. As an example, the simulation model of the Rowno industrial region is considered.

GENERAL

The experience of Soviet hydrogeological research work has demonstrated that large-scale subsurface water assessments aimed at industrial and urban water supply have been typically repeated many times.

For all this, modelling representations of a geological water-exchange system on the basis of progressive account of subsurface water formation distinctions under natural and disturbed conditions are becoming increasingly sophisticated.

During the period of increasing recovery, problems concerning the social and ecologic impacts of the water-economic complex are becoming more and more complicated along with an increase in requirements for their reliable prediction.

Retrospectively, this process may be divided into a number of stages:

- (a) Simplified schematization of hydrogeological conditions; proven subsurface water storage assessment by means of analytical methods with considerable "reserve of strength" of a solution through underestimation of some parameters and sources of the storage formation.
- (b) Utilization of computer simulation methods permitting simulation of the

features of hydrogeological conditions to a large measure. Given some small experience of usage, simulation makes it possible to solve non-stationary epignostic problems which influence reliable estimates of subsurface water recharge formation sources under field conditions and, hence, a more complete evaluation of proven subsurface water storage.

- (c) Model sophistication aimed at complete revelation of the formation sources of proved storage, evaluation of the influence of subsurface water recovery on the environment, working out proposals for a complex of measures with the aim of the most judicious utilization of the environment under conditions of optimum subsurface water recovery.

An initial research stage was typical for the 1960s and 1970s, a period when costs of prospecting and exploration depended on the necessity for obtaining the most accessible information which enabled development of the so-called "rigorous" computation pattern. Assessment of proved subsurface water storage by means of such patterns led to an underestimation of the storage evaluated and an overestimation of the area of affected land, as well as the impact of recovery on the environment.

Increasing needs for potable water and its limited storage, a need to explain the influence of subsurface water recovery on the environment, as well as increasing need for care of the utilized lands require a more complete account of the factors controlling subsurface water storage. These facts were supported by intensive adoption of computer simulation methods in hydrogeological research work.

The more complete investigation, concerning conditions and factors of proved subsurface water storage formation incorporates the study of a number of aspects:

- (a) the main hydrogeological parameters, plotted on a map;
- (b) boundary conditions which directly influence proved subsurface water storage formation;
- (c) factors and conditions which indirectly influence proved subsurface water storage formation.

The principal consideration in interpolation and extrapolation of the results of filtration tests in the field derived from restricted areas is to reveal the genetic aspects of the parameters obtained. Thus when plotting on a map the subsurface water levels for both water table and for confined aquifers we can disclose the extent of the modern topographic influence on the piezometric surface, as well as those deviations caused by specific geological conditions of the interconnected aquifer system.

With progressive geological exploration in an area we can adopt the results of mapping for more substantial interpolation and extrapolation of the results of field tests.

The principal considerations in obtaining a reliable solution by means of the network analyser is its balancing taking into account all the main subsurface water storage formation factors as well as a lack of discrepancies against formation generalities attributed to individual factors. A network analyser has to be balanced successively:

- (a) under conditions of the natural flow pattern;

- (b) under conditions of the flow pattern influenced by field tests;
- (c) under field conditions in non-stationary or, if possible, in a stationary definition of a problem.

The need for more reliable estimates of the influence of subsurface recovery on the environment leads to a growing requirement for programmes and methodology in research work. First of all, there is a necessity for the more detailed study of the influence of recovery on the state of the upper part of the geological environment and biosphere in general.

The influence may be investigated by means of more detailed study of the conditions of water exchange in a system of aquifers with surface recharges and discharges in terms of:

- (a) increasing the extent and nature of the purposeful field researches;
- (b) careful study and mapping of all the factors using stored data as well as field data;
- (c) wide application of the analogy method adopting the data received for other similar producing fields;
- (d) by means of solving a series of inverse simulation problems after developing the problem set-up for simulation.

APPLICATION

Subsurface well-fields near Rowno are situated at the edge of the Volin-Podolian artesian basin within the limits of the west slope of the Ukrainian Shield. This area is characterized by westward deepening of the basement rocks, which are monoclinaly overlapped by faulted Upper Proterozoic and sedimentary deposits (Polessian, Volinian and Valdai series) as well as Lower Palaeozoic (Cambrian, Silurian) and Mesozoic and Cenozoic (upper Cretaceous, Neogene and Quaternary) sedimentary rocks. Aquifers related to Upper Cretaceous marl and chalk deposits, to Kanilov and Nagornian suites of the Volinian series, as well as to Gorbachev deposits of the Volinian series are of practical importance in the area considered. The last two are isolated from one another by low permeability Berstovets effusive deposits (the upper part of the Valdai series) and by Yarishev terrigenous rocks (the lower part of the Valdai series).

The aquifer related to the marl and chalk deposits is not very thick (up to 20–40 m) and is localized within the limits of the Ustie and the Gorin rivers.

Due to monoclinial bedding, Kanilov and Nagornian deposits appear beneath Mesozoic rocks like submeridionally-oriented belts ranging from 3 to 8 km wide. A wedging-out boundary of these beds is situated 10 km east of Rowno. At the valley of the Ustie River, the aquifers are most permeable and tapped for water supply. Because of the lack of continuous water-confining layers, the aquifers related to marl and chalk deposits as well as to Kanilov-Nagornian beds may be considered as a common water-bearing formation.

The aquifer related to the Gorbachev beds, which is widespread in the area considered, was the main subject of inquiry in the region of investigation.

The wedging-out boundary of this aquifer is essentially westward from the course of the Gorin River and is nearly parallel to its valley. The maximum water permeability of the aquifer ($700\text{--}3000\text{ m}^3\text{ day}^{-1}$) is observed in the valley of the Gorin River. As long as sinking of the aquifer is increasing, water permeability is becoming substantially lower with values in the vicinity of Lutsk of $1\text{--}2\text{ m}^2\text{ day}^{-1}$ provided that the Gorbachev beds occur at a depth of 2000 m.

With reference to this general pattern, we can note the increase of permeability in the river valleys and its decrease in the watershed areas.

The area under investigation may be divided into two regions with different recharge conditions and subsurface water storage in the Gorbachev aquifer:

- (a) valley of the Ustie River with water sources in operation in the vicinity of Rovno;
- (b) valley of the Gorin River where detailed exploration was carried out.

The recharge conditions of the proved subsurface water storage in the vicinity of Rovno are governed by such main factors as:

- (a) water permeability of the aquifer in the area of borehole siting as well as on a strip between the Ustie River and the valley of the Gorin River, which may be considered as a zone of subsurface water transit from a possibly drainage area towards the water sources;
- (b) vertical hydraulic communication between the Gorbachev aquifer and overlying aquifers and surface water;
- (c) volume of the natural resources and subsurface water storage in the area in question, including a zone, where the Gorbachev beds pass directly under Mesozoic and Cenozoic sedimentary rocks.

Recharge conditions of proved subsurface water storage in the vicinity of the Gorin River are substantially different from those discussed above. Wedging-out of the low-permeability beds of the Berestovets tuffs in close proximity to exploration areas, means that the Gorbachev aquifer appears as a wide strip, and is overlapped directly by water-bearing Cretaceous and Quaternary deposits.

Discharge of the aquifer related to the Gorbachev beds takes place under natural conditions as well as by means of vertical leakage through the Berestovets tuff rock mass. Under such conditions the main drainage effect is connected with the valley of the Gorin River, where multiple swamped areas are widespread along the river course. But, it follows from the information available, that the river course is isolated from the aquifers by low-permeability flood-plain sediments ($K = 0.1\text{ m day}^{-1}$) and hydraulic continuity between subsurface and surface waters is very poor.

An inverse non-steady problem based on the Gorbachev aquifer recovery near Rovno and on a cluster test-pumping operation at the Goshcha exploratory site was solved by means of the simulation method. The RC-type net integrator was employed for simulation and the problem was solved in terms of drawdown.

The examination of the vertical hydraulic communication between the Gorbachev aquifer and overlying water-bearing strata was the main goal of the inverse problem treatment. Flow through the separating layer

represented by the Berestovets tuffs (this flow accounts for up to 97% of the total some 25 years after initial operation of the water source) governs the recharge of proved subsurface water storage related to the Gorbachev aquifer. The accuracy of the estimation of K_o is of prime importance, since errors in the other hydrogeological parameters do not contribute significantly to the predicted results. The second aim is to derive the most reliable estimation of underground water storage.

It should be emphasized that the possibility of withdrawing the required volume of water was demonstrated without sufficient estimation of its influence on the environment or of the impact of the designed water sources on other water-development projects (for example, on irrigation and drainage projects). These considerations, as well as the growing need for potable subsurface water produced the need for a more complete account of the recharge sources for the proved subsurface water storage, and improvement of the geofiltration model as well as the problem set-up for simulation.

In the first stage of a solution, the geofiltration medium was thought of as being three-layered with two separate beds involved. Both aquifers, related to Quaternary and Neogene sediments, were provided for, as distinct from the preceding model, and the problem was solved in heads.

A simulation aimed at determining the model sensitivity with reference to the change in the hydrogeological parameters preceded the inverse problem solving. The recharge effects due to water infiltration, water conductance ratios, elastic and gravitational water losses, as well as permeability of the separating beds on groundwater level behaviour in water-bearing formations related to Quaternary, Upper Cretaceous and Upper Proterozoic deposits were investigated for steady and non-steady conditions.

The values of the specified infiltration recharge and, to a lesser extent, that of filtration resistance in the separating beds exerted a principal influence on the variations in the water balance.

Realization of all solutions was accomplished on a digital electronic computer EC-1033 and adopting the program complex "MIF", developed by V. M. Livshitz. By means of this complex, a set of equations may be solved either according to explicit, or to non-explicit schemes. In the first case, it uses an explicit absolutely stable Defourt-Frankel scheme, but in the second case a solution is obtained by means of a component-wise upper relaxation iterative method (modified Gauss-Zeidel method).

It may be emphasized that the longer the period of epignosis and the more pronounced the disturbance amplitudes, then the more validated the model will be.

In view of these considerations, an accuracy of agreement between model and natural functions was determined, first of all, as a result of inverse epignostic non-steady problem treatment. It can be emphasized, however, that filtration parameters, which are estimated as a result of the inverse problem treatment, must satisfy steady state as well as non-steady-state problem statements.

As was found by calculation, flow from overlying aquifers is the main source of recharge to the proved underground water storage in the water-bearing formation related to the Upper Cretaceous sedimentary rocks,

Table 1 Steps for proved subsurface water storage assessment with the treatment of ecological as well as social and economic problems related to the simulation model of the Rowno industrial region

	I step	II step	III step	IV step
(1) Structural models (a) Under natural conditions	Main aquifers are separated one from another. Upper aquifer is hydraulically connected with the Ustie River; hence the upper is semiconfined, but the lower one is unconfined on a plane. The upper aquifer is recharged at the expense of laterat water influx.	Main aquifers interact one with another through low-permeable layers as well as with rivers. Aquifers are recharged at the expense of laterat water influx.	Quaternary aquifer is discerned separately. All the water-bearing layers are hydraulically connected one with another through low-permeable beds as well as with the rivers. Aquifers are recharged at the expense of precipitation seepage and water exchange from adjacent aquifers.	Geofiltration model is complicated with allowance for changing the value of infiltration recharge in time and as well as according to thickness of a zone of aeration and for including the variability of the water level during the year. Information about water chemistry and rock mechanics concerning water with different chemical composition as well as exogenic processes on the earth surface and at depth under natural conditions are also considered.
(b) Under production conditions	Formation of proved subsurface water storage of the upper main aquifer arise from subsurface flow as well as from interception of the lowest flow of the Ustie River.	Formation of proved subsurface water storage of the main aquifer arise from inherent subsurface flow as well as from partial interception of the lowest flow of the Ustie River. Formation of proved subsurface water storage of the main aquifer arise from natural resources as well as from additional water influx from the overlying aquifer.	Formation of proved subsurface water storage of the main aquifers arise from natural resources of the water exchange system in general as well as from partial interception of the Ustie River flow.	Formation of proved subsurface water storage of the upper producing aquifer arise from natural resources of the system as a whole as well as at the expense of the Ustie and the Gorin rivers.

Table 1 continued

	I step	II step	III step	IV step
(2) Methods of model implementation	Calculations through analytical methods.	Analog simulation with RC-networks in finite differences.	Digital computer EC-1033 simulation in finite differences.	Digital computer EC-1045 simulation.
(3) Treatment of ecological as well as social and economic problems	Not considered.	An approximate estimate to consider the possibility of shaft well dewatering at country settlements at the riverside area of the Gornj River was made.	The influence of reservoir complemented at the Gornj River on underflooding of adjacent areas was estimated and as alternative way of water supply which proved to be unprofitable due to economic indexes, recommendations concerning the additional water supply of small settlements in connection with shaft well dewatering were given.	To investigate in what manner subsurface water chemistry is influenced by precipitation chemistry, including the complex of the most substantial physical and chemical processes in the unsaturated zone. To study the variation in water chemistry conditions, which gives rise to remobilizing of the pollutants elutriated before as well as to repeated aquifer pollution. To define the sources of substantial subsurface water pollution and to work out recommendation, concerning their localization including economic and social estimates. To locate the areas on the earth's surface which are subjected to soil slip danger as well as to karst phenomenon due to increasing subsurface water recovery.

the Upper Proterozoic Kanilov-Nagornian deposits as well as to the Gorbashev aquifer. In the case of the Gorbashev aquifer, the value of flow from the Kanilov-Nagornian beds as well as from Quaternary and marl and chalk deposits to the above-mentioned water-bearing formation is practically sufficient to maintain the design water intake capacity. Clastic storage is not of great significance. It was brought to light that surface water from the Gorin and from the Ustie rivers contributed to the generation of recharge to the aquifer within the limits of the cone of depression and constituted approximately 30% of the total water intake capacity.

By means of inverse problem solving, it was shown that water table depressions derived from the simulation model for the Rowno subsurface water fields matched fairly well with the field data aimed at generating a flow pattern. It was confirmed also by results of a retrospective simulation after putting into operation a set of new wells in the monitoring well pattern, as well as by matching the cones of depression in the Quaternary aquifer calculated through simulation with those estimated on the basis of water table depression in the wells between different time intervals of operation.

On this basis it is believed that the filtration parameters and the boundary conditions chosen for computation are substantially adequate. It follows that the problem to be solved for the impact of growing water extraction on hydraulic conditions in the water fields may be simulated with sufficient reliability. The main research steps and extended description of the considerations involved are shown in Table 1.

Recommendations aimed at minimizing adverse effects connected with extensive subsurface water extraction have been derived on a basis of results obtained.

Assessment of groundwater resources protection from the effect of acid deposition based on simple hydrogeochemical models

W. UHLMANN

*Dresden University of Technology, Water Sciences Division,
Department of Soil and Groundwater Sciences, Mommsenstrasse 13,
DDR-8027 Dresden, German Democratic Republic*

Abstract Starting from the thermodynamic concept of the multiphase "subsurface" system and hydrogeochemical models of low-mineralized natural waters (concept of conservative and non-conservative components, charge balance equation) the terms acidity and alkalinity, acidification and buffering, are explained for soil- and groundwaters on a uniform basis. Taking these explanations as a basis, the most important heterogeneous buffer systems are described and analysed. This is used to assess the degree of protection of subsurface water resources against the influence of acid depositions which depends on their hydrogeological conditions.

INTRODUCTION

Recently the anthropogenic contamination of the atmosphere has become one of the most serious environmental problems. The nuclear weapon tests in the open atmosphere in the 1950s and 1960s made evident the close interconnection between atmospheric precipitation and terrestrial water resources including groundwater. The so-called "acid rain" is the most spectacular manifestation of extensive air pollution in Europe and North America. It is mainly caused by the emission of acid-forming gases such as sulphur dioxide (SO_2) and nitrogen oxides (NO_x) which occur in large quantities during the combustion of organic energy-producing raw materials (coal, lignite, oil, natural gas etc.) in power stations, industry, households and in various technological processes. When coming into contact with the soil surface, they are converted into strong acids. Ammoniac emanations, which are mainly the result of intensive agriculture, entail a nitrification of ammonium (NH_4^+) and even the acidification of soils and waters.

Since the 1960s and 1970s, when the negative impacts of air pollution on the environment were reaching immense magnitudes in terms of acidified lakes and rivers and extensive damage to forests, interest in the problem of "acid rain" has remarkably increased. In humid climatic areas, precipitation is the main source of groundwater recharge, so that the problem of possible changes in the chemistry of soil water and groundwater resources due to contaminated precipitation becomes more important.

IMPORTANCE OF ATMOSPHERIC DEPOSITION AS A SOURCE OF GROUNDWATER CONTAMINATION

Instead of "acid rain", the term "acid atmospheric depositions" should be used. It includes not only wet, i.e. precipitation, but also dry deposition and the adsorption of gases, acids and all acidifying substances.

In historic terms, soil acidification caused by intensive cultivation (agriculture, fertilization, forestry etc.) has played an important role for a much longer period than environmental acidification due to atmospheric depositions. The most significant processes resulting in acidification are

- the capacity of plants for selective nutrient uptake, particularly of basic components (so-called extraction of bases) connected with a permanent biomass export by harvests;
- utilization of physiologically acid fertilizers, e.g. ammonium sulphate $[(\text{NH}_4)_2\text{SO}_4]$, ammonium nitrate $[\text{NH}_4\text{NO}_3]$, urea $[\text{CO}(\text{NH}_2)_2]$ etc.

The importance of atmospheric depositions as a potential source of groundwater contamination can be derived from the following special features:

Spatial scale During the past decades, air pollution has developed and extended to be of regional character, with an impact on soil water and groundwater resources occurring in the form of diffuse contamination. In this case protective measures are made difficult and often impossible.

Time scale In Europe, the beginning of extensive air pollution can be linked to the industrialization during the second half of the nineteenth century. From that time, emissions have been continuously increasing with a jump appearing in the 1950s and 1960s of our century. Consequently, in spite of a relatively low density of pollutants, the long-term effect may entail lasting changes in aquatic systems.

Damage caused by extensive and prolonged air pollution mainly occurred in regions which, due to long distances from the sites of emissions, were considered to be reliably protected such as mountainous areas and forests including their water resources.

THE THERMODYNAMIC MULTIPHASE SUBSURFACE CONCEPT

The soil-water and groundwater zone can be described as a multiphase "sub-surface" system (hydrogeochemical system) (Luckner & Sestakov, 1986), where soil air and soil water are nonmiscible fluid phases and the rock matrix represents the fixed solid phase. These phases are separated by interface. When the phases consist of several components, the term "mixphases" is used.

The reactions proceeding within the single phase (so-called internal phase reactions) are also designated as homogeneous, and the interactions between two phases (exchange phase processes) as heterogeneous processes. Among the latter, the exchange between the soil air and water phases and between the water and mineral phases is particularly relevant.

The difference between the multiphase "subsurface" system and terrestrial surface waters is mainly given by:

- the high density of the solid phase (capacitative factor);
- the large interface of phases, i.e. internal specific surface of the rock matrix (geometric factor);
- the relatively long residence time of the fluid in the subsurface (kinetic factor);
- the often high alkalinity of the solid phases (geochemical factor).

Therefore, when compared with precipitation and surface waters, soil-waters and groundwaters show a different response to anthropogenic influences. In general, one can start from the higher natural protection of groundwater resources. However, experience shows that the self-purification capacity of the subsurface is not inexhaustible, and decades may pass between cause and effect of a contamination event.

THE ACID-BASE CONCEPT OF SOIL-WATER AND GROUNDWATER RESOURCES

Differentiation between the pH value as a measure of the activity of hydrogen ions in aqueous solutions and the acidity as the gross acid load of a water body compared with a defined standard (reference value) is essential for the assessment of acidification process. There is no *a priori* correlation between acidity and the pH value; waters of the same acidity may have extremely different pH values and *vice versa*.

The pH value is defined as the negative common logarithm of the activity of hydrogen ions:

$$\text{pH} = -\log(\text{H}^+) \quad \text{with } (c_i) = [c_i] \cdot \gamma \quad (1)$$

Starting from the fundamental charge balance equation of low-mineralized aqueous electrolytic solutions in molar units:

$$\left\{ \begin{array}{l} [\text{Na}^+] + [\text{K}^+] + [\text{H}^+] + [\text{NH}_4^+] + \\ 2[\text{Ca}^{2+}] + 2[\text{Mg}^{2+}] + 2[\text{Fe}^{2+}] + \\ 3[\text{Fe}^{3+}] + 3[\text{Al}^{3+}] + \dots \end{array} \right\} = \left\{ \begin{array}{l} [\text{HCO}_3^-] + [\text{NO}_3^-] + [\text{HS}^-] + \\ [\text{Cl}^-] + [\text{R-COO}^-] + [\text{H}_3\text{SiO}_4^-] + \\ [\text{OH}^-] + 2[\text{SO}_4^{2-}] + 2[\text{CO}_3^{2-}] + \dots \end{array} \right\} \quad (2)$$

the chemical definition of the acidity and alkalinity (Stumm & Morgan, 1970; Stumm *et al.* 1983) for the aqueous phase is obtained after separating the components into conservative and non-conservative (Drever, 1982), and the only consideration of the most important ions as follows (Fig. 1):

$$\text{Aci} = 2[\text{SO}_4^{2-}] + [\text{NO}_3^-] + [\text{Cl}^-] + \dots - [\text{Na}^+] - [\text{K}^+] - 2[\text{Ca}^{2+}] - 2[\text{Mg}^{2+}] \quad (3)$$

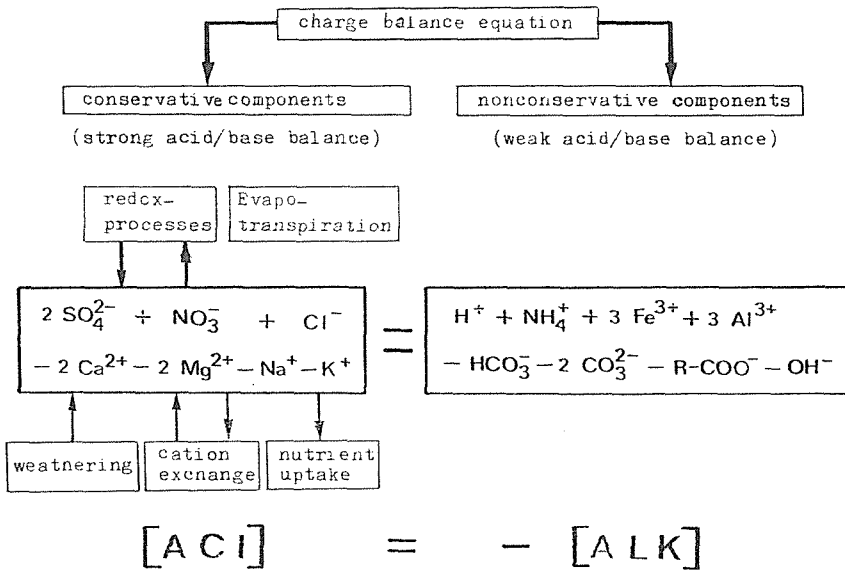


Fig. 1 The acid-base concept of fresh waters.

$$\text{Alk} = [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{R-COO}^-] + [\text{OH}^-] + \dots - [\text{NH}_4^+] - [\text{H}^+] \quad (4)$$

Contrary to conservative components, the non-conservative components in the system under consideration consist of unstable compounds, i.e. they are dependent on external thermodynamic parameters (temperature, partial gas pressure etc.) and internal parameters (concentration of other non-conservative components: acidity and alkalinity, respectively, etc.). The following relationship exists between acidity and alkalinity:

$$\text{Aci} = -\text{Alk} \quad (5)$$

An analysis of equations (3) and (4) reveals that the former represents the balance of dissociated anions of strong acids and the cations of strong bases, while the latter represents the balance of anions of weak acids and of cations of weak bases, respectively. Consequently, the acidity (or alkalinity) represents a difference of conservative parameters (equations (3)) and is again a conservative parameter. In contrast, the concentration of hydrogen ions and the pH value, respectively, are non-conservative parameters:

$$\text{pH} = f(\text{Aci}; T; p; c \dots) \quad (6)$$

Therefore, the pH value and other non-conservative parameters are unsuited to the quantitative description of an acidification state. But its changes are an important sensitivity measure of the geo-chemical contribution to the

influence of acidification.

After Stumm *et al.* (1983), the acidification of aquatic systems should be understood as a large-scale natural titration reaction. This process can be reconstructed on the basis of equations (3) and (4) if it can be formulated in the following form:

$$Aci = f(H^+) \quad (7)$$

If Aci and Alk are equal, i.e.

$$Aci = Alk = 0 \quad (8)$$

the aqueous phase does not contain any strong acids or bases. The pH value in accordance with this state is also called the reference value (Stumm *et al.*, 1983). For atmospheric precipitation a reference value of pH = 5.65 is defined which can be derived from the equilibrium state of the two-phase air-atmospheric humidity system and an atmosphere of ideal purity with $pCO_2 = 3.5$ and only neutral salts.

It is appropriate to define a reference value for soil waters and groundwaters which is in accordance with the heterogeneous equilibrium state of the multiphase soil air-soil water-rock matrix system. However, the following aspects are the reason that this concept comes across with some methodical difficulty:

- a polymictic mineralogical composition of most rocks (i.e. the rock itself consists of several phases);
- intense seasonal variations of soil water content and gas regime in the unsaturated zone (i.e. variable contributions of the fluid phases);
- thermodynamic non-equilibrium state between the water and the rock matrix;

and others.

In addition, in their natural and uninfluenced equilibrium state, most of the hydrogeochemical multiphase systems are alkaline with $Alk > 0$. From this point of view, it is more advantageous to use the differences of the theoretical equilibrium state reference value rather than the absolute values for acidity and alkalinity, respectively; these are called excesses of the acid or base (Aci_{ex} ; Alk_{ex}).

In conformity with Steinberg & Lehnhardt (1986), the anthropogenic acidification of the environment is defined as follows: acidification of geoecological compartments is understood as the reduction of their acid buffer capability, measurable as an increase in acidity or decrease in alkalinity, and their possible consequences for water quality (e.g. reduction of the pH value, aluminium mobilization, cation leaching).

The self-purification capacity of terrestrial water resources against acidification is determined by their acid buffer capability.

Buffering of an aqueous solution should be understood as its capability to counteract pH value changes after the addition of a strong acid or base (i.e. an equivalent increase in acidity and alkalinity, respectively).

The classic definition of buffer processes was essentially restricted to acid

and base buffering in the single-phase "water" system as, for instance, in the hydrogen carbonate buffer system of surface waters. However, it has to be extended for the multiphase "surface" system, where the following heterogeneous buffer reactions (Ulrich, 1981) should be taken into account:

- carbonate solution,
- alumino-silicate weathering,
- ion exchange,
- aluminium mobilization,
- ferrous mobilization etc.

In addition, the acid-base metabolism is decisively influenced by redox processes (Fig. 2).

HETEROGENEOUS BUFFER SYSTEMS IN THE SOIL-WATER AND GROUNDWATER ZONE

In a rough approach the carbonate buffer system complies with the following simplified charge balance equation:

$$A_{ci,ex} = [H^+] + 2[Ca^{2+}] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] \quad (9)$$

Assuming a carbonate equilibrium, the calcium carbonate content in the pore solution is limited by the solubility product for calcium carbonate K_1 and can be substituted in equation (9) as follows:

$$(Ca^{2+}) = K_1 / (CO_3^{2-}) \quad (10)$$

In actual thermodynamic conditions (open or closed system depending on the soil air CO_2), equation (9) is specified and solved in accordance with the example mentioned above. These computations confirm the general experience that carbonate soils and limestones, respectively, are actually the most effective natural buffer medium. As long as there is carbonate in the soil and rock matrix which is accessible to weathering, even intense acid inputs will not result in essential changes of the equilibrium pH. However, there is an essential increase in the weathering rate in terms of dissolved calcium which entails an increasing hardness in soil-waters and groundwaters.

In exchange buffer systems, the cation exchange play a dominating role. The equivalence of exchange between dissolved and sorbed components is required as a basic feature of ion exchangers. For such systems, the same balance equation may be formulated for the aqueous phase in cation exchange systems as equation (9) as in the following case:

$$A_{ci,ex} = 2[Ca^{2+}] + [H^+] - [HCO_3^-] - 2[CO_3^{2-}] - [OH^-] \quad (11)$$

As an example, the binary equilibrium for exchange between calcium and hydrogen ions reflects the correlation between the saline (alkaline) and hydrolytic (acid) occupation of the CEC:

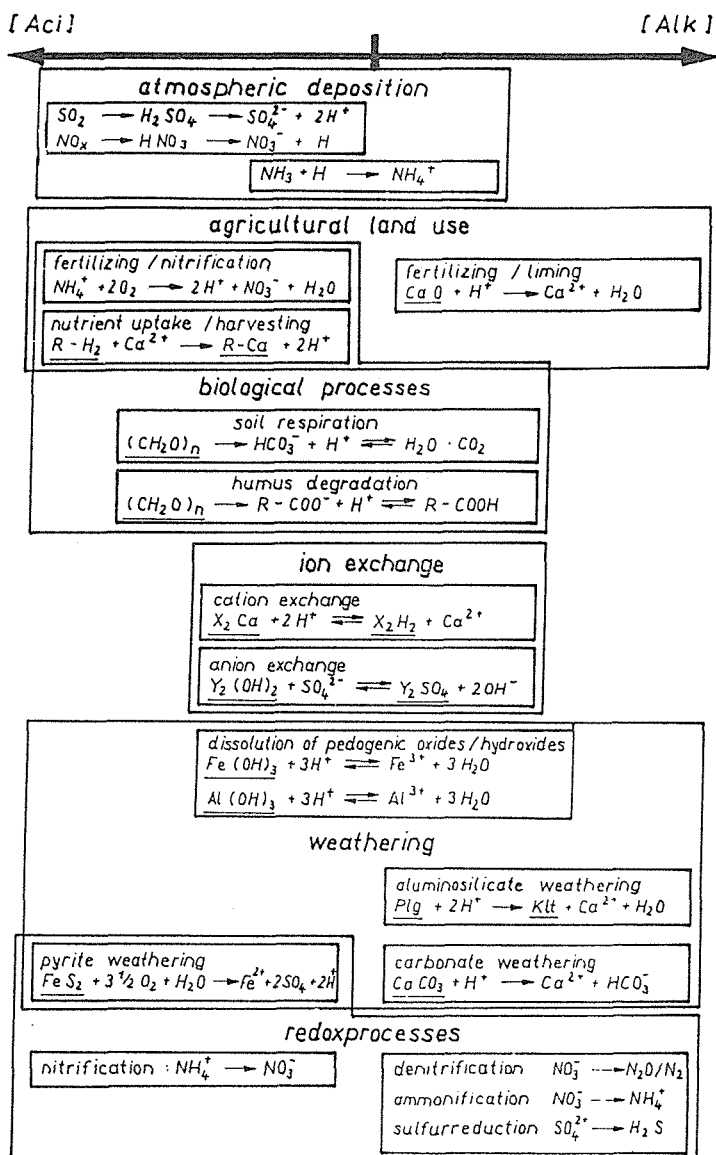


Fig. 2 The important acid-base reactions in soils and groundwater.



The following equilibrium correlation (Kokotov, 1986) is the result of a thermodynamic approach to binary cation exchange in accordance with the

mass action principle, where the molar concentration of the participating components has been taken into account and the activity coefficients of both sorbed and aqueous components have been neglected:

$$\frac{[\text{Ca}^{2+}]}{[\text{H}^+]^2} = K_{\text{Ca,H}} \frac{X_2\text{Ca} \cdot n_0 w}{X\text{H}^2 \cdot \rho_0} = K_{\text{Ca,H}} \frac{N_{\text{Ca}} \cdot n_0 w}{2 \rho_0 \text{CEC} (1 - N_{\text{Ca}})^2} \quad (13)$$

where

$$\begin{aligned} K_{\text{Ca,H}} &= \text{equilibrium constant;} \\ N_{\text{Ca}} &= \text{base saturation of the exchange} = 2 \cdot X_2\text{Ca}/\text{CEC} \\ X_2\text{Ca} &= \text{sorbed portion (mol kg}^{-1}\text{);} \\ \text{Ca}^{2+} &= \text{dissolved portion (mol m}_w^{-3}\text{)} \\ \text{CEC} &= \text{total cation exchange capacity (moleq kg}^{-1}\text{)} \\ \rho_0 &= \text{bulk density (kg m}_R^{-3}\text{);} \\ n_0 &= \text{porosity (m}_w^3/\text{m}_R^3\text{) and} \\ w &= \text{relative water content (0 ... 1).} \end{aligned} \quad (14)$$

The following mass balance equation holds for calcium and all other conservative components:

$$m_T = m_{\text{sorb}} + m_{\text{aq}} \quad (15)$$

$$\text{Ca}_T = X_2\text{Ca} \cdot \rho_0 + [\text{Ca}^{2+}] n_0 w \quad (16)$$

where Ca_T = total calcium content (mol m_R^{-3}) in a representative elementary volume (R) of the subsurface. Calcium fixed in mineral structures is not considered here; this is part of the carbonate or silicate buffer systems.

Solution of the equation system (11), (13), (14) and (16) and the appropriate sensitivity analysis reveal that the buffer capacity is dependent on the absolute value of the exchange capacity CEC rather than the base saturation N_{Ca} . The latter is essentially determined by the content of dissolved calcium Ca in the soil solution. Considering the binary equilibrium of exchange for aluminium-calcium, Reuss (1983) arrived at a similar conclusion, where the aluminium content of the soil solution is largely determined by the gibbsite equilibrium state described below. In the case of very low pH values, $\text{pH} < 4.2$, i.e.

$$3[\text{Al}^{3+}] > [\text{H}^+]$$

aluminium rather than hydrogen ion content is an indicator of acidification.

The chemical relationships shown here confirm the fact that significant changes in the pH value of the exchange buffer system caused by anthropogenic acidification are to be expected for fresh soil-waters and groundwaters, with low mineralization levels ($M < 300 \dots 500 \text{ mg l}^{-1}$).

Due to kinetic (very low weatherability) and thermodynamic features (previous achievement of other geochemical thresholds of solubility, e.g. for calcium carbonate), no equilibrium is obtained between primarily aluminosilicates and the pore solution of aluminosilicate buffer systems.

Silicate weathering gains significance as a buffer system is irreversibly released and, consequently, the aqueous phase alkalizes.

Starting from the latest scientific findings regarding silicate weathering, a pseudo-linear kinetics for the release of alkaline cations can be assumed for sufficiently long periods of time ($t > 1$ month) to be as follows:

$$\frac{d}{dt} \left\{ \frac{[\text{cation}]^{Z+}}{Z} \right\} = a^* \cdot k^* \quad (17)$$

which is characterized by two important factors:

(1) Geometric factor a^* ($\text{m}_R^2/\text{m}_R^3$) where

$$a = A \cdot f / (V \cdot n_0 \cdot w), \quad (18)$$

correlating the specific contact surface between the reacting solid phase portion ($A \cdot f$) and the corresponding water volume ($V \cdot w \cdot n_0$) (Table 1), where A = internal wetted particle surface of a defined soil-rock volume (V) and f = relative portion of the reacting mineral fraction in the total area.

Table 1 Geometric factor a^* of different aquatic systems (with $f = 1$)

Medium	$\log(a)$
Surface waters	
Standing waters	< 0
Running waters	0 ... 2
Soil waters and groundwaters	
Fissured rocks	3 ... 6
Sands; gravels; sandstones	8 ... 12
Silts; loams; clays	> 12

(2) Kinetic factor k^* ($\text{moleq m}^{-1} \text{ s}^{-1}$) where

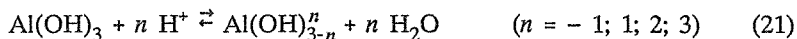
$$k^* = k \cdot (\text{H}^+)^m \quad (19)$$

whose dimensions is between 10^{-14} and 10^{-8} $\text{moleq m}^{-1} \text{ s}^{-1}$, where k = mineral specific constant and m = dependent parameter with $0 < m < 1$. According to Stumm *et al.* (1983), $m = 0.4$ holds for many silicates. The charge balance equation for a system with the alumino-silicate buffer will be a time-dependent function for all nonconservative and of all those conservative components which are released by weathering:

$$\text{Aci}_{\text{ex}} = [\text{H}^+]_t + k^* a^* t - [\text{HCO}_3^-]_t - 2[\text{CO}_3^{2-}]_t - [\text{OH}^-]_t \quad (20)$$

Thus, the buffer capacity of aluminosilicates is essentially dependent on their weathering rate and, with similar external conditions, on the residence time of the water within the system. From this aspect the clear differences in the buffer capacity of surface- and groundwaters and, in the latter case, of groundwaters in fissured and porous media can be derived. The aluminosilicate buffer is very common in nature; however, it will only gain importance in carbonate-free, low-exchange substrates. In extremely slow weathering reactions such as in quartzites, granites and gneisses, mainly homogeneous buffer reactions (e.g. the hydrogen carbonate buffer) will be effective in the systems.

With high acid loads, such systems are shifted to the aluminium buffer which is mainly effective through the dissolution of pedogenic aluminium oxides and hydroxides (gibbsite, for instance) and clay mineral weathering (e.g. kaolinite). Experience has shown that this system can be described with sufficient accuracy by means of the dissolution balance of gibbsite in water followed by multi-stage dissociation:



According to the mass action law, each partial reaction can be described by a thermodynamic equilibrium constant:

$$K_n = \frac{\text{Al(OH)}_{3-n}^n}{(\text{H}^+)^n} \quad (22)$$

The charge balance equation of an idealized system gibbsite-pore solutions is:

$$\text{Aci}_{\text{ex}} = [\text{H}^+] + 3[\text{Al}^{3+}] + 2[\text{AlOH}^{2+}] + [\text{Al(OH)}_2^+] - [\text{Al(OH)}_4^-] - [\text{OH}^-] \quad (23)$$

where the last two terms can be neglected to give an acid regime ($\text{pH} < 5$). In the strongly acid regime ($\text{pH} < 4.2$), the aluminium buffer gains importance and plays a significant role in topsoil layers and surface water. Not least due to the toxicity of aluminium to plants and animals, this regime is of ecological relevance.

Relationships analogous to the aluminium buffer can be derived for the iron buffer which is represented by the dissolution of pedogenic ferrous oxides and hydroxides. Since iron mobility in aquatic systems is dependency on numerous other parameters (redox and organic conditions etc.), only a relative quantification of this process is possible. As a measurable quantity, iron dissolvable in dithionate or oxalate is taken as basis. In the subsurface, the ferrous buffer is only reached in cases of extreme acidification (due to pyrite weathering, for instance).

Under natural conditions several homogeneous and heterogeneous buffer

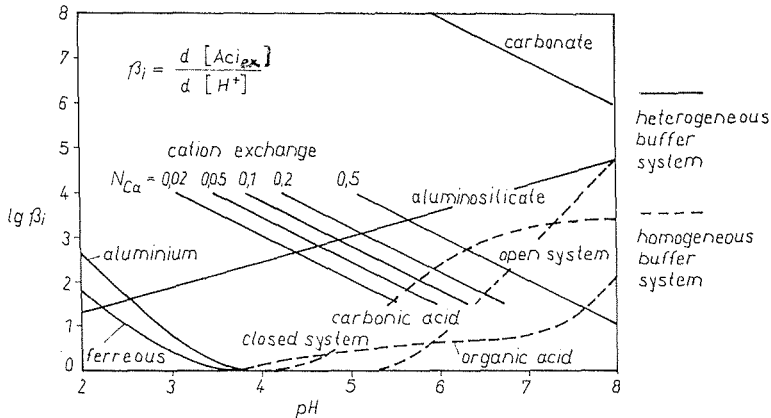


Fig. 3 The relation between heterogeneous buffer systems and the chemical composition of pore solutions in soils and groundwater.

processes often show a parallel effect, where the most intensive one is decisive for hydrochemical conditions (Fig. 3). The buffer intensity parameter B (buffering) enables a quantitative comparison of different hydrogeochemical buffer systems (i):

$$B_i = \frac{d [Aci_{ex}]}{d [H^+]} \quad (24)$$

It is appropriate to designate the complementary quantity $1/B_i$ as acidification sensitivity; from the chemical point of view it represents the increase in free hydrogen ions under the addition of strong acids. To make the mathematical approach more convenient, should drop the logarithmic description as used by Stumm & Morgan (1970), for instance (Fig. 4).

CHANGES IN GROUNDWATER CHEMISTRY UNDER THE INFLUENCE OF ANTHROPOGENIC ACIDIFICATION

The higher acidity of soil waters intensifies weathering or exchange processes in carbonate and exchange buffer systems (limestones, marls, sandstones rich in lime and clay, loess soils etc). The mineral load is particularly increased under the effect of calcium and magnesium, for example, by an increasing hardness of the groundwater.

Among the anions, sulphate and nitrate are increasing, partly at the expense of hydrogen carbonate and carbonate ions. As a consequence, long-term acidification processes in sufficiently buffering media can be identified by an increase in the correlation

soil matrix	soil solution	4	5	6	buffer processes	base saturation ¹⁾
	SO ₄ ²⁻ H ⁺ Fe ³⁺ SM NO ₃ ⁻			pH	ferrous Fe(OH) ₃ + 3H ⁺ = Fe ³⁺ + 3H ₂ O	N _{Ca} < 0,1
	NO ₃ ⁻ H ⁺ Al ³⁺ SO ₄ ²⁻				aluminium Al(OH) ₃ + 3H ⁺ = Al ³⁺ + 3H ₂ O	N _{Ca} < 0,2
	NO ₃ ⁻ Ca ²⁺ SO ₄ ²⁻ K ⁺ H ⁺ HCO ₃ ⁻				cation exchange X ₂ Ca + 2H ⁺ = X ₂ H ₂ + Ca ²⁺	0,1 < N _{Ca} < 0,9
	HCO ₃ ⁻ K ⁺ Mg ²⁺ Ca ²⁺				aluminosilicate Plg + 2H ⁺ → Klt + Ca ²⁺	0,8 < N _{Ca} < 1,0
	Ca ²⁺ HCO ₃ ⁻				carbonate CaCO ₃ + H ⁺ = Ca ²⁺ + HCO ₃ ⁻	N _{Ca} ≥ 1,0 ²⁾

1) in relation to the CEC-total
2) including the free carbonate content

Fig. 4 The buffer intensity of various heterogeneous and homogeneous hydrochemical systems (parameters:

- (1) organic acid: $pK = 4.5, m_o = 10^{-4} \text{ mole l}^{-1}$;
- (2) carbonic acid — open system: $pCO_2 = \text{open system: } pCO_2 = 3.5$;
- (3) carbonic acid — closed system: $m_{c2} = 10^{-3} \text{ mole l}^{-1}$;
- (4) alumino-silicate: $k = 10^{-12} \text{ mole m}^{-2} \text{ s}^{-1}, a^* = 10^6, t = 6 \text{ months}$;
- (5) cation exchange: $n_o = 0.2, w = 1.0, K = 10^8, \text{CEC} = 5 \text{ meq/100g}, N_{Ca} \text{ values are given in the figure}$;
- (6) carbonate: $pCO_2 = 3.5$).

$$R = \frac{2\{[Ca^{2+}] + [Mg^{2+}]\}}{[HCO_3^-] + 2[CO_3^{2-}]} \quad (25)$$

This is even possible with minor changes in the pH value or in cases, where a medium-term series of measurement did not reveal any changes (Jacks, 1984; Nordberg, 1985).

Most of the metamorphic rocks (gneisses, quartzites, schists) magmatites (granite, basalt, porphyries) as well as carbonate-free and low-clay sediments (sandstones, quartz sands) can be assigned to aluminosilicate buffer systems. In these systems, homogeneous buffers (hydrogen carbonate buffer) will be effective over shorter periods and, in connection with a longer rock contact, silicate weathering will be effective as a buffer process. With heavy acid loads the system will be shifted to the aluminium buffer. Depending on the degree of acidification, essential differences may occur in the chemistry of the corresponding groundwaters. If the marine components (Na⁺, Cl⁻) are

balanced, the following stages of acidification can be differentiated (Krieter & Haberer, 1985):

- (a) without acidification: $2\{[Ca^{2+}] + [Mg^{2+}]\} = [HCO_3^-]$;
- (b) pH > 5.0: $2\{[Ca^{2+}] + [Mg^{2+}]\} = [HCO_3^-] + 2[SO_4^{2-}]$;
- (c) pH = 4.0 ... 5.0: $2\{[Ca^{2+}] + [Mg^{2+}]\} = 2[SO_4^{2-}]$;
- (d) pH < 4.0: $[H^+] + 3[Al^{3+}] + 2\{[Ca^{2+}] + [Mg^{2+}]\} = 2[SO_4^{2-}]$.

The schematic variants of classification indicate that a reduction in the relationship between the total hardness and sulphate or nitrate:

$$R = \frac{2\{[Ca^{2+}] + [Mg^{2+}]\}}{2[SO_4^{2-}] + [NO_3^-]} \quad (26)$$

reflects very clearly the long-term influence of acidification along with an often significant decline in the pH value and, under special circumstances, a complete disappearance of hydrogen carbonate.

By means of several springs in the Middle and Lower New Red Sandstone, Puhe & Ulrich (1985) proved the influence of atmospheric deposition on the chemistry of groundwaters, where the springs were clearly assigned to emission-influenced and emission-protected sites. The causal connection between the geological substrate (crystalline rocks, interstitial aquifers etc.) and acidification has been established by Fauth (in *Materialien*, 1984) by means of water mapping covering the total area of the Federal Republic of Germany.

Where not all synergistic and antagonistic phenomena are assessable, the following phenomena have to be considered as having possible contamination potential due to acid atmospheric depositions for groundwater resources

- increased solubility of autochthonous and allochthonous metals and other trace substances in the case of a reduced pH value;
- higher mobility of the group of substances mentioned by an input of complex-forming substances (SO_4^{2-} , F^- and others);
- increase in the mineralization and hardness of water.

Therefore, a long-term reduction in the drinking water quality cannot be excluded. In extreme cases expensive treatment may become necessary for drinking water supplies.

In addition, negative impacts of acidified soil- and groundwaters on metallic subsurface installations (pumping wells, water pipes etc.) and concrete structures (e.g. foundations) have to be expected.

Some catchments in central European low mountain areas are already heavily charged, and except for the subsurface no buffer media are

effective any more. The exhaustion of this buffer is already appearing on the horizon and will entail a radical aggravation in the situation of surface waters and the water supply from barrages connected with it. For this reason, further investigations should concentrate on monitoring developments in the chemistry of soil- and groundwater resources and relevant soil-chemical parameters in potentially endangered catchment areas.

REFERENCES

- Drever, J. I. (1982) *The Geochemistry of Natural Waters*. Prentice-Hall.
- Jacks, G. *et al.* (1984) Effect of acid rain on soil and groundwater in Sweden. In: *Ecological Studies* (ed. by B. Yaron *et al.*), vol. 47, Springer-Verlag.
- Kokotov, Ju. A. (1986) Some aspects of the thermodynamical description of soils as sophisticated ion exchangers (in Russian). *Pochvovedenie* 11, 15-25.
- Krieter, M. & Haberer, K. (1985) Gefährdung des Grundwassers durch saure Niederschläge. *Vom Wasser* 218-242.
- Luckner, L. & Sestakov, V. M. (1986) *Migrationsprozesse im Boden- und Grundwasserbereich*. Dtsch. Verl. für Grundstoffind, Leipzig.
- Materialien* (1984) Gewässerversauerung in der Bundesrepublik Deutschland. Umweltbundesamt Berlin (West).
- Nordberg, L. (ed.) (1985) *Effects of Sulphur Compounds and Other Air Pollutants on Soil and Groundwater*. National Swedish Env. Prot. Board. Report 3002.
- Puhe, J. & Ulrich, B. (1985) Chemischer Zustand von Quellen im Jaufunger Wald. *Arch. Hydrobiol.* 102, 331-342.
- Reuss, J. O. (1983) Implications of the calcium-aluminium exchange system for the effect of acid precipitation on soils. *J. Environ. Qual.* 12, 591-595.
- Steinberg, Ch. & Lenhart, B. (1986) Diskussionsbeiträge zur Geochemie der Gewässerversauerung. *Dtsch. Gewässerkundl. Mitt.* 30, 1-9.
- Stumm, W. & Morgan, J. J. (1970) *Aquatic Chemistry – an Introduction Emphasizing Chemical Equilibria in Natural Waters*. John Wiley.
- Stumm, W., Morgan, J. J. & Schnoor, J. L. (1983) Saurer Regen, eine Folge der Störung hydrogeochemischer Kreisläufe. *Naturwissenschaften*, 70, 216-223.
- Ulrich, B. (1981) Ökologische Gruppierung von Böden nach ihrem chemischen Bodenzustand. *Z. Pflanzenern. Bodenkunde* 144, 289-305.