

# International Association of Hydrogeologists

**Philip E. LaMoreaux**

**Editor-in-Chief**

**Fakhry A. Assaad**

**Ann McCarley**

**Editors**

## **Annotated Bibliography of Karst Terranes**

**Volume 14  
1993**

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**Volume Five**

**With Three Review Articles**



International Contributions to Hydrogeology  
Series Editorial Board  
G. Castany, E. Groba, E. Romijn











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## FOREWORD

Escalating interest in the hydrology of carbonate terranes by the scientific community and the general public requires access to the published material available on this subject. Responsibility for compiling and publishing a comprehensive list of karst reports was previously accepted by the Work Group on the Hydrology of Carbonate Terranes of the U.S. National Committee for the International Hydrological Decade who worked with the Alabama Geological Survey, USA. As a result of those efforts two reports were published as bulletins: (1) Bulletin 94-A, Geological Survey of Alabama, Hydrology of Limestone Terranes - Annotated Bibliography of Carbonate Rocks, published in 1970; and (2) Bulletin 94-E, Geological Survey of Alabama, Hydrology of Limestone Terranes, Progress of Knowledge About Hydrology of Carbonate Terranes with an Annotated Bibliography of Carbonate Rocks, published in 1975.

The International Association of Hydrogeologists (IAH) is a scientific and educational non-profit international organization established to exchange hydrogeologic information and to advance the science. IAH, which promotes cooperation between scientists who are working on hydrogeologic problems, is affiliated with the International Union of Geological Sciences (IUGS).

The principal activities of IAH are to:

- Promote international interest among scientists in hydrogeologic studies.
  - Sponsor hydrogeologic meetings. IAH has held more than 23 scientific conferences in the past 20 years.
  - Publish hydrogeologic reports. For example: Karst Hydrogeology, 1977; Hydrogeology of Great Sedimentary Basins, 1976; Hydrogeological Map of Europe, and Methods for Evaluation of Ground Water Resources, 1979.
  - Establish commissions to investigate topics of concern to hydrogeologists.
- The work of IAH is accomplished by several special Commissions.

During a meeting of the Karst Commission of the International Association of Hydrogeologists (IAH) in Cambridge, England, on September 8, 1985, the Association voted to issue the third volume of the Annotated Bibliography in the Spring of 1986, and additional volumes of the bibliography every other year. This bulletin represents the third of this new series of IAH bulletins on karst terranes.

The Karst Commission of IAH is comprised of scientists from many different research agencies around the world. Current (1992) members of the Karst Commission of IAH are as follows:

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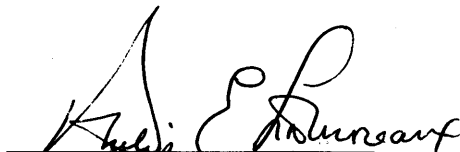
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## INTRODUCTION

Constructive and thorough discussions on karst are carried out by a broad circle of interested scientists and researchers. Various regional symposia and colloquia have been organized worldwide over the past 20 years by IAH, IASH, FAO, and UNESCO within the International Hydrologic Decade (IHD) and International Hydrologic Programme (IHP). The IHD included a Commission for the study of carbonate rocks in Mediterranean countries, and since 1970 a permanent Commission for karst hydrogeology exists within IAH.

The reasons for such an increasing interest in karst include the rapid technologic development of our civilization and its direct and indirect impacts of the surrounding environment; also, problems of water resources and their systematic study, rational utilization, and protection; and management of hydrological and hydrogeological systems. Karst occurs in many parts of the globe (frequently covering a substantial part of the national territory of individual countries), whose water supplies represent the sole or most important natural resource which directly affects their social and economic development. Under such conditions, the problems of study, utilization, and protection of water resources, or using contemporary terminology, management and control of water resource systems obtain an exceptional importance. This has resulted in an increasing effect on the orientation of research.

Limestone areas comprise approximately one-fifth of the earth's surface. These rocks are extremely complex physically, produce a great variety of topographic and geologic conditions, and have been the subject of much research by geologists, geomorphologists, speleologists, geophysicists, and other scientific disciplines. The literature regarding limestone is diverse and the subject has been published in a wide range of articles in newspapers, scientific and technical journals. During the past few years several major reference and textbooks have been published on this subject and are listed as follows:

Back, W., Paloc, H., and Herman, J.S., 1992, Hydrogeology of selected karst regions: Internat. Assoc. of Hydrogeologists, Karst Comm., Verlag Heinz Heise GmbH & Co. KG., Hannover, Germany; Vol. 13, 494 p.

LaMoreaux, P.E., Prohic, E., Zötl, J., Tanner, J.M., and Roche, B.N., 1989, Hydrology of limestone terranes, annotated bibliography of carbonate rocks, Volume Four: Internat. Assoc. of Hydrogeologists, Karst Comm., Verlag Heinz Heise GmbH & Co. KG., Hannover, Germany; Vol. 10, 267 p.

LaMoreaux, P.E., Hughes, T.H. and others, 1989, Hydrogeology assessment: Fiegh Spring, Damascus, Syria: Environmental Geology and Water Science, Springer-Verlag, New York, NY; Vol. 13, No. 2., pp. 72-127.

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- Stoessell, R.K., Ward W.C., and others, 1989, Water Chemistry and  $\text{CaCO}_3$  dissolution in the saline part of an open-flow mixing zone, coastal Yucatan Peninsula, Mexico: *Geological Soc. of America, Bulletin* Vol. 101, pp. 159-169.

Limestone terranes are generally characterized by broad rolling plains; however, in some areas they are characterized by steep bluffs, canyons, and valleys. Owing to the variability in topography and solubility of limestone under diverse climatic conditions, man's development in limestone areas has often been difficult. In some limestone areas there are fertile soils, valued for the production of large quantities of food; in other areas, the surface of the limestone rocks is eroded and barren. In some areas, ground-water supplies are abundant; in others, supplies are sparse and difficult to locate. It is perhaps this diversity of geologic, topographic, and hydrologic conditions that makes the study of carbonate rock terranes so fascinating, complex, and challenging.

During the past 20 years, under the auspices of the Work Group on the Hydrology of Carbonate Terranes of the International Hydrological Decade, and the Working Group on the Hydrology of Limestone Rocks in the Mediterranean Basin of the FAO/IHD, much emphasis has been placed on the study of carbonate rocks. In addition to individual project activities, there have been over 30 field conferences, formal meetings, and congresses, at which results of research on the hydrology of carbonate rocks have been discussed indicating the interest in this subject. A list of these follows:

# Symposia and Conferences on Karst Hydrogeology and Speleology

Location	Title	Sponsor(s)	Date
Karlsruhe (FR Germany)	6th International Symposium on Water Tracing (SWT)	IAH - Karst Commission and National Committee of FR Germany; International Atomic Energy Agency, Vienna; IAHS	Sept., 1992
Italy	International Conference on Environmental Changes in Karst Areas	International Geographical Union Study Group; CNR - Consiglio Nazionale delle Ricerche, Univ. degli Studi di Padova	Sept., 1991
China	IGCP 299 - Geology, Climate, Hydrology, and Karst Formation	IAH, UNESCO, IUGS, The Ministry of Geology and Mineral Resources-People's Republic of China, IGCP National Com.	July, 1991
Dubrovnik-Trebinje, Yugoslavia	Water and Karst International Symposium on Improvement of Karst Water Utilization and Protection	UNESCO, UIS and Academy of Sciences and Arts of Bosnia and Herzegovina	June, 1991
Radford, Virginia USA	Symposium, Karst of the Appalachian Region	Univ. of Radford	Spring, 1991
Houston, Texas USA	Fourth International Symposium on Land Subsidence	IAHS, Commission on Groundwater, and UNESCO	May, 1991
Canary Island, Spain	XXIII International Congress Aquifer Overexploitation	IAH, Spanish Chapter	April, 1991
Antalya, Turkey	International Symposium and Field Seminar on Hydrogeologic Processes in Karst Terranes	IAH, Karst Commission	Oct., 1990
St. Petersburg, Florida USA	3rd Multidisciplinary Conference on Sinkholes and the Engineering and Environmental Impacts of Karst	University of Central Florida, Florida Sinkhole Research Institute	Oct. 1-4, 1989
Guilin City, Guangxi Zhaung Region, China	21st Congress, Karst Hydrogeology and Karst Environmental Protection	Inter. Association of Hydrogeologists	Oct. 10-15, 1988
Melbourne, Australia	4th Inter. Symposium on Interactions Between Sediments and Water	Inter. Association for Sediment Water Science	1987
Vienna, Austria	Inter. Symposium on Isotope Techniques in Water Resources Development	Inter. Atomic Energy Agency	1987



Location	Title	Sponsor(s)	Date
Tomar, Portugal	4th Inter. Meeting of Applied and Environmental Geology, "Karst Systems of the Atlantic Border"	University of Lisbon, Center of Geology and Department of Geology	1987
Orlando, Florida USA	2nd Multidisciplinary Conference on Sinkholes and the Environmental Impacts of Karst	University of Central Florida, Florida Sinkhole Research Institute	1987
Athens, Greece	5th Inter. Symposium on Underground Water Tracing	Institute of Geology and Mineral Exploration and Inter. Working Group on Tracer Methods in Hydrology	1986
Cairo, Egypt	Inter. Symposium, "Water for Mankind in the Year 2000"	Universal Movement for Scientific Responsibility; UNESCO	1986
Spain	Inter. Symposium on the Euskadi's Karst		1986
Beytepe, Ankara, Turkey	Inter. Symposium on Karst Water Resources	Karst Water Resources Research Center, Hacettepe University and UNESCO	1985
Puerto Rico	Friends of the Karst Meeting		1984
Orlando, Florida USA	First Multidisciplinary Conference on Sinkholes	Florida Sinkhole Research Institute	1984
Havana, Cuba	Inter. Workshop on Karst Hydrology of the Caribbean Region	UNESCO Division of Water Sciences	1983
Bucharest, Romania	1st Symposium on Theoretical and Applied Karstology	Institutul de Speologie "Emil Racovita", Enterprise for Geological and Geophysical Prospecting	1983
Havana, Cuba	International Workshop on Karst Hydrology of the Caribbean Region	UNESCO Division of Water Sciences	1982
Bari, Italy	Utilizzazione delle Aree Carsiche - 2 Simposio Internazionale		1982
Neuchatel- Bescancon, France	3eme Colloque d'Hydrologie en Pays Calcaires	Univ. Besancon	1982

<b>Location</b>	<b>Title</b>	<b>Sponsor(s)</b>	<b>Date</b>
Bowling Green, Kentucky USA	8th Inter. Congress of Speleology	International Union of Speleology and National Speleological Society	1981
Besancon, France	1 <sup>er</sup> Colloque National sur la Protection des Eaux Souterraines Karstiques	la CPEPESC	1981
Trieste, Italy	Utilization of Karst Areas -- International Symposium	Union Int. de Speleologie, Societa Speleologica Italiana	1980
	Symposium -- Table Ronde Franco -- Allemande	Assoc. Francaise de Karstologie	1980
Atlanta, Georgia USA	V.T. Stringfield Symposium -- Processes in Karst Hydrology	Geological Society of America	1980
Washington, D.C. USA	Research Needs in Hydrology and Water Resources of Karstified Carbonate Terranes	National Science Foundation	1980
Oymapinar, Turkey	Inter. Symposium on Karst Hydrogeology	State Hydraulic Works, United Nations Development Program	1979
Budapest, Hungary	International Symposium on Karst Hydrology	Hungarian Speleological Society, Hungarian Geological Society, and Hungarian Meteorological Society	1978
Tarbes, France	Le Karst: Son Originalite Physique; son Importance Economique	l'AGSO a Tarbes	1978
Bowling Green, Kentucky USA	Inter. Symposium on Hydrologic Problems in Karst Regions	Western Kentucky University	1976
Budapest, Hungary	Hydrogeology of Great Sedimentary Basins	Hungarian Geological Institute, Inter. Association of Hydrological Sciences, and UNESCO	1976
Besancon - Neuchatel, France	2eme Colloque d'Hydrologie en Pays Calcaires	Univ. Beasancon	1976
Ljubljana, Yugoslavia	3rd Inter. Symposium of Underground Water Resources	Yugoslav Committee for Inter. Hydrological Program	1976
Dubrovnik, Yugoslavia	U.S.--Yugoslavian Symposium on Karst Hydrology and Water Resources	Bilateral U.S.--Yugoslavian Research Project on Karst Hydrology and Water Resources	1975

<u>Location</u>	<u>Title</u>	<u>Sponsor(s)</u>	<u>Date</u>
Huntsville, Alabama USA	12th Inter. Congress, Inter. Association of Hydrogeol- ogists--Karst Hydrogeology	Inter. Association of Hydrogeologists	1975
Kranj, Yugoslavia	8th Conference, Slovenia Speleologists and Karst Explorers in Serbo Croatia		1974
Hannover, Germany	Sinkholes and Subsidence-- Proceedings of a Symposium	Inter. Association of Engineering Geology	1973
Olomouc, Czechoslovakia	6th Inter. Congress of Speleology	Inter. Union of Speleology	1973
Besancon, France	1 er Colloque d'Hydrologie en Pays Calcaires	Univ. Besancon	1971

## **ORGANIZATION, COMPOSITION, AND AVAILABILITY OF ANNOTATIONS AND INDEXES**

Annotated bibliographic citations are listed alphabetically by principal author and numerically by document number.

The annotated citations are followed by secondary author, location, and subject indexes. The subject index is preceded by a key to level terms used. The location index is by country, and secondarily by individual state. Each index lists the pertinent citations by document number.

The bibliography primarily represents citations for the past two years (1988 through 1989) from the following data sources: a computer controlled search of the American Geological Institute (AGI) GEOREF database, which contains the AGI publications; Bibliography and Index of North American Geology (1961-1970); Bibliography of Theses in Geology (1965-1966); Geophysical Abstracts (1966-1971); Bibliography and Index of Geology Exclusive of North America (1967-1968); and Bibliography and Index of Geology (1969 to the present). Manual searches of the Index to Scientific and Technical Proceedings, and U.S.G.S. Water Resources Abstracts were also conducted. In addition, numerous manual searches of the published literature were made.

To assume that any bibliography on the subject of karst hydrology is comprehensive would be a mistake. However, a concerted effort has been made to compile as many works on the subject matter as possible from 1987 to 1991 for this issue. The omissions of published literature discovered during future work on this project will be included in the next issue to be published in 1994.

A multidisciplined staff of geologists, hydrologists, geophysicists, and geochemists were assigned to the project. The project also benefited from the cooperation of many individual scientists and numerous organizations throughout the world. As a result, this bibliography is primarily composed of references to geology, hydrology, geochemistry, and geophysics of carbonate rocks.

The bibliographical material is stored on diskettes of an IBM computer at P.E. LaMoreaux & Associates, Post Office Box 2310, Tuscaloosa, Alabama, 35403, USA. This stored information is available in whole or in part and may be obtained in printout form.

## ABBREVIATIONS USED IN THIS TEXT

AAPG	-	American Association of Petroleum Geologists
Amer.	-	American
Assoc.	-	Association
BCRA	-	British Cave Research Association
Bull.	-	Bulletin
Bur.	-	Bureau
Comm.	-	Committee
concn.	-	concentration
Conf.	-	Conference
Congr.	-	Congress
eds.	-	editors
environ.	-	environment
FAO	-	Food and Agricultural Organization
Figs.	-	Figures
F.R.	-	Federal Republic
Geol.	-	Geological
Geophys.	-	Geophysical
Hydrol.	-	Hydrology
IAH	-	International Association of Hydrogeologists
IASH	-	International Association of Scientific Hydrology
IHD	-	International Hydrologic Decade
IHP	-	International Hydrologic Program
Inst.	-	Institute
Intern.	-	International
Jour.	-	Journal
Nat.	-	Natural
No.	-	Number
NSS	-	National Speleological Society
p.	-	page
Sci.	-	Science
Soc.	-	Society
Spel.	-	Speleological
Symp.	-	Symposium
Trans.	-	Translator
UK	-	United Kingdom
UNESCO	-	United Nations Educational, Scientific and Cultural Organization
Univ.	-	University
U.S.	-	United States
USA	-	United States of America
USSR	-	Union of the Soviet Socialist Republics
Vol.	-	Volume
Z.	-	Zeitschrift



# **REVIEW AND SELECTED BIBLIOGRAPHY ON MINERAL DEPOSITS OF ECONOMIC IMPORTANCE IN CARBONATE ROCKS**

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## **INTRODUCTION**

Mineral deposits are an important part of carbonate rock phenomena. The economic importance of some carbonate-hosted mineral deposits in carbonate terrains can appreciably influence hydrologic and hydrogeologic patterns by changing the general permeability of host rocks. In addition, mineral deposits in carbonate terrains and associated mining greatly influence the quality of the ecosystem by introducing new chemicals into the system and changing its primary environmental parameters. Ore-forming fluids and solids create corrosive activity in the form of very aggressive fluids.

### ***The Classification of Carbonate-hosted Mineral Deposits***

The ability of carbonate rocks to accumulate natural resources has long been known. Moreover, scientists have become increasingly aware that carbonate rocks, which trap certain metals and non-metals can yield vast mineral deposits. The diversity of opinions among ore genesis scientists, however, enables us to make an acceptable classification scheme for carbonate-hosted mineral deposits. Tourtelot and Vine (1976), who made a distinction between copper deposits in sedimentary and volcanic rocks, although proposed a useful scheme in determining the space and time-scale relationships between ore materials and host rocks, studies of particular metal or nonmetal accumulations in carbonate rocks reveal that even in the same deposit more than one type of deposits can be found. This scheme, thus, does not seem to be acceptable for simple reviewing purposes.

A scheme based on general characteristics of carbonate (karst) deposits was proposed by Zuffardi (1976) and accordingly, economic carbonate (karst) deposits were classified after Quinlan (1972) to a new scheme which is useful because it

gives an impression of amounts of elements and minerals which can be accumulated in carbonate rocks. For review purposes, however, most of the mentioned species can be joined in various groups according to their occurrences, genesis and/or geochemical behavior in the carbonate rocks environment. Others have not classified mineral deposits in carbonate rocks according to that scheme because some of the used parameters, particularly genesis, are not clearly defined. In order to assist the review of carbonate-hosted mineral deposits, the following classification scheme is proposed:

- (a) Ore minerals of calcite isomorphic chain - this includes carbonate minerals with cations other than calcium and/or magnesium (e.g. Fe and Mn-carbonates); their weathering products; and ores originated from impurities in carbonate rocks, (i.e. phosphate minerals).
- (b) Carbonated-hosted mineral deposits originated either from host rocks or from remote sources. This broad group includes various metals and non-metals which, depending on the anion present, can be classified as follows:
  - (i) Oxides - Al-oxides - bauxites (Fe, Mn-oxides),
  - (ii) Sulfides - Pb, Zn, Cu, Ag, Co, Sb, Hg, W-sulfides and pyrite,
  - (iii) Sulfates - Ba-sulfate - barite (Sr-sulfate),
  - (iv) Halogenides - Ca-halogenides - fluorite.
- (c) Calcrete-type of mineral deposits - although calcretes (calcareous soil) are not "carbonate rocks", they are included because they precipitate by the same mechanisms as carbonate rocks, and because of the importance of uranium and vanadium minerals which can be accumulated in that soil.
- (d) Non-metallic deposits which are a part of the carbonate rocks complex itself and include the quarries of limestones or dolomites, chalks, marls, travertine (calctufa), quartz sands, coals, clays, pyroclastic rocks, etc.

### ***The Role of Carbonate Rocks in Accumulating Ore-forming Minerals***

Most papers on carbonate-hosted mineral deposits include a discussion of the role of host rocks in accumulating particular ore-forming mineral(s). The opinions are diverse, but some general conclusions can be determined. Carbonate rocks are observed as a simple trap and filter for surface mineralized water and vertically- or horizontally-derived, ore-forming fluids. Decrease in turbulence and changes in Eh-pH parameters yield to accumulation of ore-minerals. This effect is closely connected with the general high permeability of carbonate rocks, progress of karstification processes and tectonic disturbances which provide numerous available spaces for transferring and depositing ore-forming minerals. At the mature stage of a well-



developed karst system, depositional possibilities are manifold (Zuffardi, 1976). In many fossil karst systems the depositional possibilities can even increase by karst rejuvenation mostly under influences of thermal solutions.

Another general conclusion is that carbonate rocks are a source for ore-minerals deposited within the complex. According to Zuffardi (1976), karstification can yield local residual concentrations in ore-bearing complexes with partial to complete ore oxidation. Zuffardi (1976) presented a calculation based upon average calcite solubilities and rainfall in a carbonate catchment area of 100 km<sup>2</sup>; the quantity of limestone dissolved during a thousand years is 4.2 million tons. Assuming a Clarke value of 100 ppm (combined metals), 420 tons of metals should be released in 1000 years, or 10 million tons in 24 million years, which is a relatively brief geological time period. Several attempts have been made by scientists dealing with bauxite deposits to calculate amounts of limestone dissolved for existing karst bauxite deposits (Bardossy, 1982). These calculations lead to establishing the "autochthonous" genesis of karst bauxites (the "terra rossa theory").

Regardless of the specific role of carbonate rocks in accumulating ore-forming minerals, widespread occurrence of ores in carbonate rocks necessitates reexamination of the role of host rocks in ore-forming processes.

### ***The Review of Particular Carbonate-hosted Mineral Deposits***

**Group I - Ore Minerals of Calcite Isomorphic Chain:** Group I includes the minerals which can be simply treated as replacement of limestones, or carbonate minerals other than calcite or dolomite and which can be deposited together or instead of them under favorable conditions, i.e. FeCO<sub>3</sub> (siderite) and MnCO<sub>3</sub> (rodochrosite).

#### ***Iron Ores in Carbonate Rocks:***

- (a) **Geochemical Behavior:** Geochemical behavior of an element in the environment is governed by its crystal chemistry as far as by the environmental parameters of Eh, pH and bacterial activity. Eh-pH diagrams are very common and instructive ways of expressing the speciation of a particular element among various mineral phases and illustrating the stability field and boundaries among different mineral species.

Iron has been mined from a variety of deposits, but production is now almost entirely from two types: banded iron formations and oolitic ironstones. Banded iron formations are mostly of Precambrian age and can be subdivided into the following two varieties: Algoma deposits with a volcanic association, and Lake Superior-type deposits which have a shallow-shelf, orthoquartzite-carbonate association. The latter type occurs almost exclusively in clastic sequences (although they can comprise a siderite or ankerite in its mineral paragenesis), so they will not be treated in this chapter.

Siderite is the most common carbonate mineral in iron formations, followed by ankerite (Maynard, 1983). The sedimentary iron formations of Precambrian age in the Lake Superior region, can be divided, according to James (1954, from Garrels and Christ, 1965), in four principal facies: sulfide, carbonate, oxide and silicate. According to Berner (1971) and Maynard (1983), Eh-pH relations among pyrite, siderite, and hematite indicate that pyrite is the only stable  $\text{Fe}^{2+}$  mineral at the sulfur level of modern seawater. Thus, siderite in ancient rocks suggests low-sulfur waters, such as fresh-water lakes and swamps. Siderite is, in fact, common in fresh-water environments of modern deltas and in coal measure shales. On the other hand, siderite is commonly found in both shales and ironstones of marine origin. Curtis (1977) and Maynard (1983) proposed the model in which slow sedimentation permits complete conversion of reactive iron to pyrite, whereas more rapid rates shut off the sediment from contact with the sulfur in seawater before all of the iron is converted to pyrite, thus allowing siderite to form. Berner (1981) has proposed another approach in which sedimentary environments is classified according to presence or absence of oxygen and the presence or absence of dissolved sulfide, instead of using Eh and pH as variables. In this scheme, siderite is found in two diagenetic environments as follows: (1) decomposition of organic matter has led to the depletion of oxygen in the sediment, but has not proceeded to the point of sulfate reduction; siderite forms in post-oxic environments; (2) if so much organic matter is present that all of the available sulfate is consumed without using up the organic matter, methane fermentation will begin, and siderite will again be stable because so little dissolved sulfide is left. The other mineral competing with siderite is calcite. Maynard (1983) calculated that in the reaction:



siderite should be stable relative to calcite at  $\text{Fe}^{2+}/\text{Ca}^{2+}$  ratios higher than 0.0055. This ratio given by other authors can be 0.073 (Murray and others, 1978) or even 0.05 (Berner, 1971; and Maynard, 1983) respectively, but for all these ratios it can be assumed to exist in natural environment if additional supply of iron is considered. However, Berner's model is likely to be applied for iron sedimentary ores in which siderite is the primary ore-forming mineral.

- (b) The Origin of Iron-Sedimentary Ores of Lake Superior-Type: The main problem concerning the origin of iron-sedimentary ores is the source of iron required. There are at least three theories in which sources of iron are either rivers, volcanic emanations, or ocean water. There is no general agreement among ore scientists of iron sources in Lake Superior-type deposits, and for each theory there are serious objections.

Another interesting approach to the origin of Lake Superior-type deposits was presented by Mendelshon (1976) and Trudinger and Mendelsohn (1976) in their research of mineralization associated with stromatolites. Another approach was

advanced by Cloud (1968, 1975; and Trudinger and Mendelsohn, 1976) who equated the deposition of banded iron formations prior to 2 - 10<sup>3</sup> years B.P. With the development of blue-green algae, pH, Eh and CO<sub>2</sub> concentration brought about by algae and bacteria may have been important factors in the genesis of Precambrian iron formations. Moreover, on the basis of fossil evidence, it has been suggested that microorganisms were possibly instrumental in precipitating the original constituents of iron formations (Trudinger and Mendelsohn, 1976).

More recently, a new, very interesting, genetic model for the North African metasomatic siderite deposits, was proposed by Pohl, et al. (1986).

#### *Manganese Ores in Carbonate Rocks:*

- (a) **Geochemical Behavior:** Manganese, one of the most abundant elements in the crust. Twelfth in abundance, Manganese deposits are accordingly common. Geochemically, manganese behavior is controlled by the oxidation state of the environment. A number of Mn oxidation occurrences are known from laboratory experiments, but only two, Mn<sup>2+</sup> and Mn<sup>4+</sup> are common in nature. The geochemical properties of manganese are similar to those of iron so that its segregation into economic deposits is largely a problem of separating it from iron (Maynard, 1983). However, ferrous ion is more easily oxidized than manganous ion under any naturally occurring pH-Eh conditions. Thus, inorganic processes should always lead to precipitation of iron before manganese from a solution containing both metals unless the Mn/Fe ratio is very high (Garrels and Christ, 1965). Eh-pH relations show a relatively large field of stability for dissolved Mn<sup>2+</sup>. At the pH of seawater (pH = 8) or of freshwaters (pH = 5-7) Mn should be soluble except under strongly oxidizing conditions. The addition of sulfur to the system does not change this situation appreciably because of the small stability field for MnS, but the addition of carbonates creates a large region in which solid Mn species are stable under reducing conditions. Thus, Mn behavior at low Eh is controlled by carbonate minerals, in contrast to Fe, which is controlled more by sulfides. For fresh water, the pH is normally too low for rhodochrosite (MnCO<sub>3</sub>) precipitation, but for seawater a slight increase in the amount of CO<sub>3</sub><sup>2-</sup> should lead to rhodochrosite formation if a supply of Mn is available (Maynard, 1983).

According to Maynard (1983) carbonate rocks have the highest Mn/Fe ratio although the absolute amount of Mn they contain is not especially high. In addition, many deposits contain Mn carbonates, usually described as rhodochrosite, but analyses show the presence of considerable Ca, which leads to the conclusion of probable existence of the mineral kutnahorite (50 mol percent of Mn) or calcian rhodochrosite (80 mol percent of Mn).

- (b) **Origin of Manganese-ores in Carbonate Rocks:** There are a variety of types of manganese deposits from syngenetic deposits in clastic or carbonate sequences and volcanic-sedimentary accumulations to supergene deposits in which the original type of accumulations is obscured by surficial oxidation.

Subdivision type of the bedded manganese deposits in carbonate rocks is known as Moroccan deposits. In addition to Morocco, deposits of this type are found in Lower Cambrian carbonates of the Southern Appalachians (near Sevierville), in Precambrian rocks of India, and in radiolarian marls in a limestone sequences of Hungary (Maynard, 1983). For the manganese deposits in Morocco, Maynard (1983) suggested Mn deriving from weathering of older deposits although this source does not seem likely to apply to all carbonate-hosted Mn. Further, the mechanism of precipitation is obscure.

Thus, it is difficult to generalize about the origins of Mn deposits. Much more research must be conducted on ore geology and geochemistry including stable isotope studies of particular carbonate-hosted manganese deposits.

*Phosphate Deposits in Carbonate Rocks:*

- (a) Regional Setting: There are three types of phosphate rock, namely, (1) sedimentary phosphorites of marine origin, (2) apatite-bearing alkaline igneous complexes, and (3) phosphorites of guano origin. Of these sedimentary phosphorites deposits are the most productive. Belts of deposits extend throughout western Africa through north Africa and the Middle East; the Sinian of Yunnan, China; Christmas, Nauru and Ocean Islands, South Pacific; Palabora, South Africa; Las Kay, Vietnam; and Udaipur, India. In fact, three deposits are dominant: deposits in Florida, U.S.A., Khibiny, Kola Peninsula, U.S.S.R., and Morocco (Howard, 1979). Sedimentary phosphorites are located below the 40° latitude, while the northern deposits are regarded as apatite-bearing alkaline igneous complexes.

The stratigraphic position of phosphorite deposits occurs primarily in two main stages: Paleozoic (Permian and Cambrian) and Tertiary (Neogene-Miocene). The Neogene deposits are of greater economic importance and their occurrence is dominant over the Paleozoic ones. According to Riggs (1984), known Neogene (Miocene) phosphorites have the following general distribution: (1) East Atlantic continental margin, (2) West Atlantic continental margin, (3) East Pacific continental margin, (4) East Australian shelf and Chatham Rise east of New Zealand.

- (b) Origin of Sedimentary Phosphorite: Rapidly increasing worldwide demand for phosphatic rock as raw material for fertilizer warrants a thorough re-evaluation of the international phosphate potential.

With regards to the origin of another type of phosphate deposits, residual type occurs in the Canadian carbonatite province (Erdosh 1979). The rock complex contains a unique, very high grade, residual, phosphate deposit associated with a well-developed karst topography now buried under glacial-lake clays. During karst development, carbonates were dissolved from carbonatite, and residual minerals, primarily apatite, were concentrated in sinkholes and troughs. Sorting and reworking of apatite-rich residuum by surface and subsurface water formed concentrations of nearly pure

apatite sand, with unusual concentration of rare-earth mineral and of vermiculite on the top of residuum.

It is of interest to know that marine phosphorites also contain anomalously high concentrations of numerous trace elements, namely uranium, rare earths, yttrium, scandium, vanadium and many others (Kolodny and Kaplan, 1970). These anomalous enrichments which result from organic activity (Riggs, 1979), are actually the by-product resources of phosphate mining.

**Group II - Carbonate-hosted Mineral Deposits:** This very broad group includes a rather different type of mineral deposits, and the best known carbonate-hosted mineral deposits, i.e. bauxite and Pb-Zn carbonate ores.

***Aluminum Ores in Carbonate Rocks - Bauxites:***

- (a) **Geochemical Behavior:** With a content of 8.1%, Al is the third most common element in the lithosphere, after oxygen (47.5%) and silicon (28.8%). Aluminum displays a marked affinity for oxygen, and it is not found in the lithosphere in a native state. Its ionic radius (0.51 Å for sixfold coordination) is small compared to that of the other metallic elements, and is almost as small as the Si radius (0.42 Å). It is present in minerals either in a tetrahedral form or in an octahedral form (LeLong et al., 1976)

The solubility of aluminum minerals is, however, strongly dependent on pH. The minimum solubility of aluminum minerals is in the pH range 5 to 9, and maximum solubility ranging between a low (pH < 4) and high pH (pH > 10). Consequently, aluminum is only slightly mobile under common surface weathering conditions, contrary to other elements which are generally more soluble under these conditions. (Maynard, 1983). Aluminum tends to accumulate in secondary aluminosilicate minerals (clay minerals) or in purely aluminous ones (gibbsite, boehmite and probable diaspore). An additional parameter can be concentrations of carbonate ion which, according to Bardossy and White, (1979) can inhibit the crystallization of  $\text{Al}(\text{OH})_3$ , the inhibition being stronger for gibbsite than for boehmite.

- (b) **Aluminum-ore Deposits - the Bauxites - Classification, Geographic and Stratigraphic Distribution:** Subdivisions of bauxite deposits are determined according to (1) main ore minerals (gibbsitic, boehmitic, diasporic or various mixed types of bauxite), (2) stratigraphic position (i.e. Triassic, Jurassic, Cretaceous, Paleogene, etc.), (3) bedrock (karst bauxite, laterite or bauxite overlying igneous rocks), (4) relationship with bedrock (autochthonous, parautochthonous, allochthonous, etc.), (5) geographic distribution (Mediterranean, Jamaican, etc.), and (6) shape of deposits (stratiform, blanket, sinkhole, etc.). For our purposes, however, the most acceptable general subdivisions are presented by Bardossy, (1982) in which he classified bauxite deposits as follows:

- (i) **Bauxite deposits overlying aluminosilicate rocks;**

(ii) **Bauxite deposits overlying carbonate rocks.**

In keeping with common usage, the deposits of the second group have been called "karst bauxites" regardless of whether the bedrock surface is strongly or gently karstified; these bauxites will be under the scope of this review.

According to Bardossy (1982), karst bauxites comprise 14% of currently-known bauxite deposits. The great majority of karst bauxites are found in the northern hemisphere between the 10th and 70th parallels. The present author has divided geographic distribution of karst bauxites into the following bauxite belts: (1) Mediterranean, (2) Irano-Himalayan, (3) Pacific (the only belt in the southern hemisphere), (4) Asian, (5) Caribbean, and (6) American. The most productive belt is the Mediterranean belt, however, the largest deposits are in the Jamaican region.

Stratigraphic distribution varies depending on the belt concerned. For example, in the Mediterranean belt, the oldest karst bauxite is Permian, the youngest one is Miocene or probably Quaternary (Susnjara, personal communication), but the largest quantity of bauxite is formed during the Upper Cretaceous. The bauxites of the Pacific islands, however, are post-Quaternary (Bardossy, 1982). In general, the oldest karst bauxites currently known date from Cambrian or from the late Proterozoic according to some authors. According to age distribution of international karst bauxite tonnage (Bardossy, 1982), the majority of tonnage is divided between the Miocene-Pliocene and Upper Cretaceous bauxite deposits, followed by the Carboniferous and Paleocene-Eocene ones.

- (c) **Classification of Karst Bauxite Deposits:** Karst bauxites can be subdivided into several groups according to main features. Although there are several different classifications that are pertinent, the classification by Bardossy (1982) is adopted. In this study, Bardossy (1982) subdivided karst bauxites into the following six group types according to their constitution and depositological features including the rate of karstification of underlying rocks:
- (i) Mediterranean-type deposits;
  - (ii) Timan-type deposits;
  - (iii) Kazakhstan-type deposits;
  - (iv) Ariege-type deposits;
  - (v) Salento-type deposits; and
  - (vi) Tulska-type deposits.
- (d) **The Origin of Karst Bauxite Deposits:** The general conditions under which bauxites form are: those of a humid tropical climate with sufficient drainage

for Na, K, Ca, and Mg to be removed (Maynard, 1983). Specific factors such as parent material, mode of transport and bauxitization, and place and environment of deposition, however, cannot be as readily established. These uncertainties have led to numerous bauxite origins being proposed. According to Bardossy (1982), the following theories on the origin of bauxite can be grouped according to role, importance, and characteristics that they attribute to each of the factors affecting origin:

- (i) Lateritogenic theories propose that karst bauxite derive from pre-existing laterites as erosion products which have been deposited in their present position by various modes of transport. Some bauxite deposits in France, U.S.S.R., Central Greece, and Hungary are explained by this approach.
- (ii) The Terra Rossa theory proposes that bauxite is the product of terra rossa, the weathering residue of carbonate rocks older than the bauxite. It was formed in situ or underwent a very limited transport. With this theory, the origin of some French, Yugoslav and Caribbean bauxites is explained. Some investigators have tried to extend this approach to explain all the origins for bauxite deposits. This theory, however, is not as popular as it was previously.
- (iii) Chemogenic theories propose that aluminum, iron and titanium, dissolved from the rocks by course of weathering, were entrained in solution in lakes and seas where they can precipitate and accumulate. A variation of the chemogenic theory is the "sulphuric-acid theory", which identifies sulphuric acid as the prime dissolving agent. Tusk-type bauxites have been explained by some Russian authors by pyrite decomposition.
- (iv) Hydrothermal theories imply that bauxite could precipitate out of solutions discharged by hydrothermal springs. Some French, Yugoslav and U.S.S.R. bauxites have been explained accordingly.
- (v) Volcanogenic theories suggest bauxite to have formed from the lateritic in situ weathering of volcanic ash which has fallen onto carbonate rocks. The Jamaican, Pacific and some Yugoslav Miocene deposits are explained according to this theory.
- (vi) The Phytogenic theory explains a phenomenon that is not widespread; only one attempt to explain Devonian bauxite deposits in U.S.S.R. is known. According to this theory, bauxite is formed as a result of the life processes of swamp vegetation.

Different authors have suggested that karst bauxite is autochthonous (to be bauxitized in place), allochthonous (transported and deposited as a fully developed bauxite) or

parauchthonous (fully developed bauxite that underwent a rather limited, local redeposition only). According to Bardossy (1982) none of these transport mechanisms can be regarded as exclusively correct.

Some other factors can contribute to the development of bauxite deposits, and, thus, complicate the origin. Other factors, for example include: site and facies of deposition, role of plant cover, geomorphological factors, hydrogeological factors, geochemical and physico-chemical factors, time factor, mode of progress of bauxitization, etc. (Bardossy, 1982).

However, probably the most important aspect of karst bauxite deposits, at least for this review, is the role of karst in bauxite formation. As stated in Bardossy (1982) possible roles are as follows:

- (a) Karst depressions serve as traps collecting the parent material which undergo bauxite accumulations, regardless of whether they are reworked or not.
- (b) Karst depressions provide a fair drainage.
- (c) The weakly alkaline medium favorable to bauxitization is provided by the carbonate bedrock.
- (d) The depression of karst relief protects bauxite deposits from subsequent erosion.

Another very important aspect in the study of karst bauxites is geochemistry of ore deposits together with accessory heavy minerals assemblages. The study of trace elements and heavy minerals distributions in bauxite deposits can be useful in solving many of the problems of bauxite origin and parent rock evaluations (Scavnicar and Scavnicar, et al., or Maksimovic and Maksimovic, et al., in the annotated bibliography). According to Valetton (1972), several trace elements can be enriched in the karst bauxites included Cr, Ni, Be and B, together with known enrichments of Ti, Ga and V which are connected with the main mineral phases in bauxite deposits. Recently Maksimovic (1980) and Maksimovic and Panto (1983) investigated the rare-earth element distributions in karst bauxite and were able to discover some new or rare authigenic minerals (Maksimovic and Panto, 1981, 1985a, 1985b). The enrichment of particular trace elements can be so pronounced, i.e. nickel, that bauxite becomes characterized by this element or it can be a by-product of bauxite mining. The genetical relationship between karstic bauxites and karstic nickel deposits is established for the deposits in the Balkan Peninsula and Greece by Maksimovic (1978, 1979).

By discussing numerous parameter which can be involved in the formation of karst bauxite deposits, the importance of the interdisciplinary approach to the investigations of carbonate-hosted ores is emphasized.



***Metal Sulfides Ores in Carbonate Rocks (Pb, Zn, Cu, Ag, Co, Sb, Hg, and W):*** In this broad group are included all metal sulfides presently known to occur as ores in carbonate rocks. The first two, i.e. lead and zinc mineralization are ubiquitous, with respect to carbonate-hosted sulfide deposits. The next three, copper, silver, cobalt and probably some other heavy metals, occur in these deposits from traces to mineable amounts, respectively, and they are usually treated as by-products in lead-zinc mining. In some deposits, copper, silver or cobalt carbonate-hosted ores are, respectively abundant. However, most if not all ores parameters including genesis, are similar to those of the most abundant Pb-Zn deposits. These Pb-Zn ore deposits in carbonate rocks are discussed in an earlier chapter.

Antimony, mercury and tungsten sulfide ores in carbonate rocks were excluded from the discussion of the above mentioned metal sulfides for three main reasons: (1) they are usually not associated with the Pb-Zn (-Cu-Ag-Co) mineralization, even as traces, (2) they form their own mineral provinces, and (3) they rarely occur as ores in carbonate rocks. In this text a chapter is devoted to these rare but very important mineral deposits with emphasis on increasing demand for the usage of these particular elements.

***Problems on Origin of Carbonate-hosted - (Pb, Zn, Cu, Ag, Co) Deposits:*** According to Amstutz and Fontbote (1983) the genetic discussion may be summarized under two opposite concepts, as follows:

- (a) Migration of basinal brines is the most important "mineralizing factor". The brines would migrate from a source rock towards a favorable lithology able to "trap" the metal content. This hypothesis observe the migration of ore-bearing fluids across several lithologic units, over considerable distance, after the complete lithofication of the sediment. The most important features of this theory is that ore-forming process is not related with the depositional environment at the present site of ore accumulation.
- (b) The ore-forming process takes place mainly during sedimentation and the first stages of diagenesis, and is directly related to the depositional environment. It was pointed out by authors that, this second concept includes all the processes relating to the depositional environment, i.e. also early diagenetic processes such as evaporate pumping, seepage reflux etc. that can produce a migration of connate water.

These two hypotheses have been schematically summarized as follows: in the former theory, source rock is other than reservoir rock (including migration stage between them), while in the later theory the source rocks are identical to ore deposit.

If we observe the relationship among karstic cavities and ore-solution, both in time and space, three hypotheses about the genesis can be proposed (Zuffardi, 1976, Bernard, 1976):

- (a) Hydrothermal ore-bearing solutions opened the cavities and deposited the mineralized filling at the same time. The deposits of this type are often classified as "telethermal" or "cryptothermal" depending on evident or non-evident correlations with deep-seated igneous sources.
- (b) Cavities are of karstic origin, but their filling was attributed to later, igneous-hydrothermal solution. These deposits, likewise, can be "telethermal" or "cryptothermal".
- (c) Karstification (by supergene and/or by artesian waters) is responsible both for the opening and widening of cavities and for deposition of material in them.

The first two theories of this statement correspond to the first genetic model proposed by Amstutz and Fontbote (1983), while the third one is the same as the second model type, respectively.

This is only a general approach to genetic models of carbonate-hosted lead-zinc ores, because more than three models have been proposed for the same deposits by different authors. For example, as cited by Klau and Mostler (1983), as many as six different genetic models have been developed for the Triassic Pb-Zn deposits of the Alps, and more than six models have been proposed for ore genesis in the English Pennines, all of which have been reviewed by Dunham (1983). Usually more than one alternative of genesis is presented in an individual paper dealing with the particular deposits. There are at least three different genetic parameters which have been observed for one genetic model to be established:

- (a) Source rock.
- (b) Physico-chemical characteristics of ore solution - modes of transport and deposition.
- (c) Timing of mineralization.

The differences in approaches and solutions of each of the three genetic parameters have led to various genetic models being established. It is necessary to review some of the ideas concerning the parameters in question.

- (a) Physico-chemical Characteristics of Ore Solution Models of Transport and Deposition: According to Anderson (1983), all hydrothermal ores have three aspects in common - the ores had a source, were transported, and were deposited. Although the author refers to hydrothermal ores, this simple scheme could be applied to the non-hydrothermal genetic models, as well. The main differences in opinions exist regarding source rock(s), distances of transport, and timing of mineralization, the latter being the most pronounced difference. Transport is basically a problem of mineral solubility which is controlled by a few simple factors, i.e., temperature, pressure, pH, and  $H_2S$

concentration (Anderson, 1983). For deposition to occur, some of the main environmental parameters must be changed. Besides the factors mentioned, the salinity control of the solution seems to be an additionally important factor. Three critical stages in ore genesis are (1) remobilization of metals from source rock, (2) modes of transport, and (3) modes of deposition. The problem of source rock is one of geology, geotectonism and/or paleogeography once the metal is in the solution, however, its behavior is explained in geochemical laws.

The problem of remobilization of metal from source rocks is too complicated and complex to be reviewed here in detail. To summarize briefly concerning the problem of remobilization, the return of metallic ions to solution can occur only if conditions change, i.e., main environmental parameters, such as temperature, pressure, salinity of leaching solutions, pH-Eh conditions, etc., or if some mineral rearrangement of transformation occurs. The problem is somewhat simplified if we assume that concentrated ore solutions originate from an environment of evaporitic conditions where the pre-concentration is simply explained by the diminishing of water content due to evaporation processes. Closely related to the remobilization processes is geochemical balance, i.e., the amount of rocks need to be dissolved for the particular ore accumulations. Several attempts have been made by proponents of both general genetic models (Zuffardi, 1976; Bernard, 1976).

An important factor in ore genesis is the transport of material, when both hydrodynamics as well as chemical thermodynamics must be considered. The latter consideration leads us to the conclusion that in most, if not all, cases we are dealing with hot solution (usually more than 100°C and less than 200°C), and high salinity (chloride content). The temperature of ore solution alone, as stated by Boni (1986) and temperature range is not necessarily exclusive to either a purely supergene or hydrothermal origin. In view of the high salinity of an ore solution, most authors (especially proponents of "supergene-enrichment ores") suggest the influence of evaporitic sediments or brines from evaporitic environments. Other investigators propose an influx of highly saline magmatic liquid or involvement of membrane filtration processes (Ohle, 1980). None of these ideas are universally accepted, thus the problem of ore-solution salinity is still a subject of controversy.

Proponents of the "intrakarstic genetic model" refer to Cvijic's model (Cvijic, 1918) of mature karst systems and water circulation in the karst, to explain both transport and deposition of metals in karstic cavities. The existence of three different zones (percolation, permanent circulation, and general inhibition zone) with different dynamic and chemical properties enables explanation of transport and deposition of metals contemporary with karstification processes (Zuffardi, 1976; Bernard, 1976).

Those who suggested that ore material derived from adjacent evaporite beds or evaporitic environment or evaporitic-like environments, mechanism suggest seepage reflux (Geldsetzer, 1976) or evaporite pumping as possible transport mechanisms, (Hsu, 1984).

A simple approach to the problem of deposition of metals from ore-bearing solutions is that it happens when changes in solubility of particular species occur. Deposition can occur when environmental parameters change (temperature, pressure, salinity etc.), or parameters of solution change (pH, Eh, salinity), and/or if new ions are introduced. In the latter case, the most crucial ion to be introduced is sulfide anion because the deposition of most metals is very fast in the presence of sulfide anion.

- (b) **Timing and Mineralization:** The timing or age of mineralization is probably the most critical parameter in ore genesis. When the exact time or time span of mineralization is determined, development of the genetic model is only one final step. Or, as stated by Amstutz and Fontbote (1983), "the sequence of questioning in modern ore genesis is reversed compared to twenty or thirty years ago.

*Barite and Fluorite Deposits in Carbonate Rocks:* Although barite and fluorite ore occurrences in carbonate rocks need not be genetically related, they are herein discussed together because they occur almost exclusively with sulfides, i.e., lead and zinc, in more or less transition forms from "pure" Pb-Zn deposits with or without traces of barite and fluorite, to deposits in which each of them is the main ore mineral, with Pb and/or Zn sulfides as mine by-product.

Source rock(s) is remote from the basin of ore accumulation ("basinal brine" theory), and is considered to be the rock from the same sedimentary basin ("supergene-enrichment or intra-karstic" theory). For both genetic models the source rock(s) for barium can be the same rock as for the lead and zinc and other chalcophile metals, while the origin of fluor in some other rocks has to be considered. This is because carbonate and other sedimentary rocks in general, rarely contain appreciable amounts of fluor enough to be considered as a source rock for the ore accumulations.

Fortunately, the transport and deposition of both barium and fluor is less vague than the source rock, although there is no unique solution of the problem. However, it is known that  $Ba^{2+}$  can be transported only in the solution of very low activity of sulfate anion, because of the low solubility of  $BaSO_4$ . From this point of view, both "single-solution theory" (Barnes, 1983) or "mixed-solution theory" (Anderson, 1983) is suitable for transport mechanism, because none of these presume the sulfate-rich transporting media. The deposition of barite occurs when the initial ore solution is mixed with sulfate-rich solutions ("mixed-solution theory") or sulfate is producing in the initial solution by oxidation of its own  $H_2S$ , HS, thiols, or other sulfide containing species. Because barite is a typical mineral of oxidizing environments contrary to metal sulfides, its dual associations require certain zonation which is the observed feature in most, if not all, barite deposits. Proponents of the "intrakarstic theory" determined that this zonation can be due to the oscillations of the water table, because barite is a typical mineral of the most upper "percolation zone" (Bernardi, 1976; Zuffardi, 1976). Although the concentration of  $SO_4^{2-}$  is the critical factor, one must not forget that the solubility of barium sulfate increases with temperature and

ionic strength of the solution (chloride salinity); with cooling, a certain amount of barite will precipitate from barite-bearing solution (Bernard, 1976).

For the fluorite to deposit, it is necessary for the solution to be supersaturated both with respect to the fluor and calcium. The presence of fluor is deduced from the fluor-bearing rocks (or solution) while supersaturation with respect to calcium is presumed, because of a carbonate environment. However, there is no restriction for fluorine to be transported together with chalcophile elements, very probably in fluoro-complexes. According to Moller (1980), fluorine is transported together with magnesium as a complex ion  $MgF^+$  which is destroyed due to the loss of magnesium in dolomitization processes. The  $F^-$ , which is liberated combines with  $Ca^{2+}$  to form an early diagenetic  $CaF_2$ . This is a very elegant solution which comprises both the transport and precipitation mechanism for fluorite.

*Group III - Calcrete-Type Mineral Deposit - General Classifications and Modes of Formation:* The calcretes (calcareous soils) are not "carbonate rocks" and they can be treated as "soft" equivalent of "hard" carbonate rocks, or rocks form close to recent carbonate sediments, as well. However, U-V-bearing calcretes differ from "pedogenic" calcrete in certain characteristics which will be outlined later.

In the Glossary of Geology (Bates and Jackson, 1980) calcrete is defined as: "a term suggested by Lamplugh (1902) for a conglomerate consisting of surficial sand and gravel cemented into a hard mass by calcium carbonate precipitated from solution and redeposited through the agency of infiltrating waters, or deposited by the escape of carbon dioxide from vadose water; or as a calcareous duricrust."

Mechanisms of precipitation of calcretes include all possible mechanisms for calcium carbonate precipitation both in fossil and recent carbonate rocks. However, because of today's climate conditions in the area of calcrete formations, it is likely that evaporation together with transpiration are the most important mechanisms for the precipitation of calcrete-forming pedodiagenetic calcrete. The source of calcium carbonate can be the rain water, or some plants which can accumulate carbonate within their tissue, and/or atmospheric dust and marine aerosols (Klappa, 1983). As it is pointed out, calcretes occur within any host material given an adequate source of  $CaCO_3$ .

*Uranium - Vanadium Ore-Bearing Calcretes:* In the arid regions of Western Australia, Namibia and South Africa, some ore-bearing calcretes occur which differ from pedogenic calcrete *sensu stricto*. According to Carlisle (1983), Ba, Mg,  $CO_3$ , U, and V undergo lateral transport rather than vertical redistribution (which is one of the main soil formation features).

In the ground water of a carbonate aquifer, uranium is transported as extremely soluble uranyl di- or tricarboxylate complex ions. For carbonatite,  $K_2(UO_2)_2V_2O_8$ , which is a ubiquitous ore mineral in calcrete-type ores, few requirements must be satisfied for precipitation from U-V-bearing solution. The most critical factor for carnotite

precipitation is low activity of  $\text{CO}_3^{2-}$ . Consequently, precipitation of carbonate results in lowered  $\text{CO}_3^{2-}$  with consequent destabilization of uranyl carbonate complexes and eventual precipitation of carnotite along with the carbonate (Carlisle, 1983). Additionally, four-valent vanadium in ground water must be oxidized to the five-valent form required for carnotite. According to Briot (1983; Fuchs, 1984) two different types of water occur in the channel-calcrete: upper water with pH of about 7 and only a minor quantity of elements in solution, and a lower water with slightly alkaline pH between 7.5 - 8, with a lower redox potential and a higher metal content (U, F, Zn, Sr, Si). A geochemical barrier between different waters leads to oxidation of  $\text{V}^{4+}$  to  $\text{V}^{5+}$ , and carnotite can precipitate. Briot has shown that dolomitization has induced both a lower activity of the  $\text{CO}_3^{2-}$  ion and the decomposition of uranyl complexes that are additional requirements for carnotite precipitation. Another mechanism contributing to the carnotite precipitation is, as stated by Carlisle (1983), reaction of U-V bearing ground water with  $\text{K}^+$  enriched hypersaline waters in salt lakes or elsewhere. In every case, uranium remains in the oxidized or hexavalent state, and reduction plays no role in its deposition. Furthermore, according to Carlisle (1983), near-simultaneous precipitation of calcrete and carnotite may not in itself yield ore, but ore grades may result from the dissolution and reconcentration of carnotite. Carlisle (1983) suggested that the most significant factor in separating the pedogenic (non ore-bearing) and non-pedogenic (ore-bearing) calcretes is the seasonal distribution of rainfall and consequent retention of water in the soil moisture zone, because more severe arid conditions favor formation of ore-bearing calcrete.

Concerning the uranium and vanadium ore occurrences in carbonate rocks, calcrete-type deposits are probably not the only type of carbonate-hosted U-V ores. Routhier (1963; Zuffardi, 1976) considered their deposits of Tyuya Mayun, Fergana, U.S.S.R., to be karstic, but the source of metals is unknown. It has been suggested that U and V originated from overlying graphitic shales, which were later supplied through remobilization.

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## **REVIEW AND SELECTED BIBLIOGRAPHY ON MOVEMENT OF CONTAMINANTS IN KARSTIFIED CARBONATE ROCKS**

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### **INTRODUCTION**

The Project Summary of the Environmental Protection Agency (EPA) Ground water Research Programs (Lobel, 1986), states that in the United States approximately 56 quadrillion liters of water are stored within 0.8 kilometer of the land surface. Twenty-five percent of all fresh water used is ground water; 50 percent of the population obtains all or part of its drinking water from ground water; and 95 percent of rural households depend totally upon it. In other parts of the world, there is an even higher usage of water stored in the subsurface. It is very difficult or almost impossible to quantify the part of this water withdrawn from carbonate rock aquifers. Although less emphasized in the past, investigations of potable water stored in carbonate rocks is today, and will be in the future, one of the main goals of hydrogeologists. The chemical character of ground water in carbonate rock is commonly more mineralized, and the investigation required for development and water-supply design expenses are several times greater in comparison to those for water stored in clastic rocks. However, limited amounts of water in granular clastic aquifers, together with the uncontrollable population growth in settlements in carbonate terrains (especially in coastal regions), will force scientists to intensify the search for potable water in carbonate aquifers.

We must be aware, however, that ground water, regardless of the type of aquifer in which it occurs, serves not only as a widely distributed source of water but as a host and a transporting medium for contaminants, derived from point or non-point sources. The fact that the carbonate rock aquifer is more vulnerable to pollution, and the clean up and restoration of the contaminated aquifer requires relatively more sophisticated and costly technical efforts and methodology than clastic aquifer, gives to this problem a new dimension. Moreover, most of the contaminant-transport models in

ground water are exclusively made for flow in porous clastic rocks, only a few of them deal with contaminant transport in fractured and fissured rocks, especially if we are concerned with the quantification of these processes. Regions of intensive karstification are special cases of the later and make the problem even more complicated.

## **GENERAL APPROACH TO THE MOVEMENT OF CONTAMINANTS IN GROUND WATERS AND VARIOUS MODELS**

Ground-water flow and solute transport models describing the movement of contaminants through the discontinuous karst media can be classified into two main groups: physical and mathematical-statistical models, respectively (Komatina, 1984).

Physical models are based upon the physical connections in the system, assuming knowledge of conditions and processes for the particular hydrogeological system. The validity of this type of model depends upon the information available. The hydrogeological characteristics of the karst environment, as a rule, are very complex. The representative parameters commonly are unknown, which excludes the use of models that take the measured characteristics as a base for observing the entire ground-water flow as a dynamic system. It is for this reason the mathematical-statistical models are considered which treat the hydrogeological environment as a "black box", which means that it is not necessary to have prejudice of the processes that occur within the system. The advantage of the latter models is that the assumptions in the physical models are difficult to estimate, and its convergence is difficult to prove. Obviously, as for other numerical models, the validity of the mathematical-statistical models for contaminant transport in ground water depends mostly on the reliability of input data, particularly hydrogeological parameters. The differences in hydrogeological properties of aquifers may be very large. Basically one can distinguish three hydrogeological systems:

- (a) Porous, permeable, normally unconsolidated aquifers where flow is laminar (Darcy flow).
- (b) Fractured, consolidated rocks where ground-water flow mainly takes place through fractures, and may be laminar or turbulent.
- (c) Karstic aquifers where the flow takes place mainly through the solution channels, which are irregular in dimension and direction. The flow can be laminar, turbulent, and/or have characteristics of the flow in the pipe open channel.

The first type of aquifer is ideal for mathematical estimation of flow regimes; for the second there are fewer possibilities for a mathematical approach; for the third one, in general, there are no possibilities for mathematical approaches. However, taking into account some assumptions, dynamic flow systems and the contaminant transport in



karstic aquifers can be mathematically expressed by the basic equations evaluated primarily for the flow in porous, highly permeable aquifers. A summary of some of the main equations follows; however, for the detailed study, readers are referred to particular articles cited in the reference list.

## **BASIC EQUATIONS FOR THE TRANSPORT OF CONTAMINANTS THROUGH PERMEABLE ROCKS**

According to Freeze and Cherry (1979), the common starting point in the development of differential equations to describe the transport of solutes in porous materials is to consider the flux of solute into and out of a fixed elemental volume within the flow domain. A conservation of mass statement for the elemental volume is:

$$R = \text{Flx (out)} - \text{Flx (in)} \pm m$$

where

R	=	Net rate of change of mass of solute within the element;
Flx (out)	=	Flux of solute out of the element;
Flx (in)	=	Flux of solute into the element; and
m	=	Loss or gain of solute mass due to reactions.

As one can see, the main scope of the contaminant transport in ground water is to establish the "attenuation", which is defined as any physical, chemical, or biological reaction or transformation occurring in saturated or unsaturated zones that brings about a temporary or permanent decrease in the maximum concentration or in the total quantity of an applied chemical or biological constituent in a fixed time or distance traveled. From this definition, it follows that the attenuation mechanisms can be categorized as physical, chemical, or biological. The physical processes control the flux into and out of the elemental volume in the above equation, while the loss or gain of solute mass in the elemental volume can occur as a result of chemical or biological reactions, respectively.

Three main physical processes can affect the spreading of contaminants in ground-water: advection, hydrodynamic dispersion, and dilution.

Advection is the component of contaminant movement attributed to transport by flowing ground water. Owing to advection, non-reactive solutes are carried at an average rate equal to the average linear velocity,  $v$ , of the water, where  $v = v/n$ ,  $v$  being the specific discharge and  $n$  the porosity (Freeze and Cherry, 1979).

Hydrodynamic dispersion can be observed on both microscopic and macroscopic scales. The former can be further divided, depending on which part of the system is considered to move host fluid or contaminant particles, into mechanical dispersion (or hydraulic dispersion) and mechanical diffusion, respectively.

**Mechanical dispersion on a microscopic scale is a result of deviations of velocity on a microscale from the average ground-water velocity (Anderson, 1984). It can be caused by three mechanisms:**

- (a) In individual pore channels molecules travel at different points across the channel due to the drag exerted on the fluid by the roughness of the pore surfaces (for example: water in the center of a pore space travels faster than water near the wall).**
- (b) Because of differences in surface area and roughness relative to the volume of water in individual pore channels, different pore channels have different bulk fluid velocities.**
- (c) Tortuosity, branching, and interfingering of pore channels cause spreading of the contaminant in the direction of bulk flow, known as longitudinal dispersion, or perpendicular to the flow, called lateral dispersion. In porous, permeable media, longitudinal dispersion is usually much stronger than lateral dispersion, which causes the contaminant to spread out in the direction of flow and a decline in concentration (Freeze and Cherry, 1979). This basic phenomenon suggests a geometrical aspect of dispersion: the first one in the direction of the mean velocity, due to differences between the velocity components along this direction (longitudinal dispersion); the second one in the plane orthogonal to the main direction, due to differences between the velocity components in that plane. These effects are fundamental in the application of the theory of dispersion to pollution problems (Fried, 1975).**

**Molecular diffusion affects the spreading of contaminants due to motion of the molecules at the interface with the receiving fluid. This motion is random in character, and the molecules of contaminants are constantly colliding with those of the receiving body of water. Because of these collisions, the molecules of contaminants sometimes move toward a region of higher concentration and sometimes toward that of a lower concentration. In general, the net transport of the molecules of contaminants is assumed to be from the region of high concentration to that of lower concentration (Whitehead and Lack, 1982). With respect to turbulent flows, its effects are negligible in comparison to other processes.**

**Some of the contaminant-spreading phenomenon can be explained as a result of macroscopic dispersion. According to Anderson (1984), on a macroscopic scale dispersion is caused by the presence of large-scale heterogeneities within the subsurface. Some of these heterogeneities are expressed as differences in the various parts of the general aquifer. It can be considered within the "model of dual porosity", which will be discussed later.**

**The third general physical process that can provide effective attenuation of a given contaminant on a large scale is simple dilution by soil moisture and ground water.**

In the last 10 - 15 years there has been much effort and progress in quantifying contaminant transport in porous and permeable media. The equations are derived mostly from the statement of the law of conservation of mass, originally introduced in classical papers by Ogata (1970) and Bear (1972). The aquifer is considered to be a saturated, porous, isotropic, and homogenous medium; the flow is steady-state; and Darcy's law applies (Freeze and Cherry, 1979). The main governing equation is known as the advection-dispersion equation. This basic equation is, with certain limitations and assumptions, applicable to fractured and karstic aquifers, so it needs to be mentioned briefly here. Reference is made herewith to the simplified approach given by Anderson (1984). For detailed study of the mathematical solution of the advection-dispersion process, the reader is referred to Anderson (1984) and Freeze and Cherry (1979).

## ADVECTION-DISPERSION EQUATION

Contaminant transport is generally viewed as the net effect of two processes, advection and dispersion.

Advective transport is attributed to the transport of contaminants at the same speed as the average linear velocity of ground water ( $v$ ):

$$v = K l/n \quad (1)$$

where

K	=	hydraulic conductivity,
l	=	the head gradient, and
n	=	effective porosity.

The average linear velocity defined macroscopically at the point in the porous medium is the microscopic solution velocity averaged over the "representative elementary volume" (REV) about the point (Gillham and Cherry, 1982). Thus, K, l, and n from the above equation are assumed to represent an average of K, l, and n within the REV. Likewise, spatial averaging is obtained by deriving the advection-dispersion equation.

Dispersion can also be represented by an expression analogous to Fick's second law of diffusion:

$$\text{Mass flux due to dispersion} = \frac{\partial}{\partial x_i} \left( D_{ij}^* \frac{\partial c}{\partial x_j} \right) \quad (2)$$

where

c	=	concentration,
$D_{ij}^*$	=	the coefficient of dispersion, and
i and j indices	=	Cartesian coordinates.

The coefficient of dispersion is:

$$D_{ij}^* = D_{ij} + D_d \quad (3)$$

where

$$\begin{aligned} D_{ij} &= \text{the coefficient of mechanical dispersion, and} \\ D_d &= \text{the coefficient of molecular diffusion.} \end{aligned}$$

For the moderate and high water velocity (in other words, velocity in karst aquifers) the  $D_{ij}$  is one or more orders of magnitude larger than  $D_d$ , so the latter in practice can be neglected. The coefficient of mechanical dispersion ( $D_{ij}$ ) is considered to be the product of the magnitude of the velocity vector times a parameter known as dispersivity, which is commonly referred to as a characteristic mixing length.

According to Anderson (1984), the advection-dispersion equation in its most general form is written:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij}^* \frac{\partial c}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (c v_i) - \frac{c'w}{h} + \sum_{k=1}^s R_k \quad (4)$$

where

$$\begin{aligned} c' &= \text{the concentration of solute in a source or sink fluid,} \\ v &= \text{ground-water velocity} \\ n &= \text{porosity} \\ W &= \text{the volume flow rate of the sink or source fluid per unit volume of porous material,} \\ R_k &= \text{the rate of production of the solute in reaction } k \text{ of } s \text{ different reactions.} \end{aligned}$$

This is a one-dimensional form of the advection-dispersion equation. In most mathematical models this basic equation is extended to the two- and/or three-dimensional form.

One can see that the right side of equation 4 consists of four main terms, each of which represents contributions from the particular process. The first term is the "dispersion term" and the second is the "advection term". The last two terms are effective in the presence of a "non-conservative substance", in other words, the reactive substances that undergo changes of concentrations along the flow due to chemical or biochemical reactions or radioactive decay. The third term is the "sink/source term", while the fourth term is the "chemical-reaction term". These terms can vary greatly depending on the characteristics of the aquifers and the rate of the contact between dissolved species and solid rocks.

## MOVEMENTS OF CONTAMINANTS AND GROUND-WATER FLOW THROUGH FRACTURED MEDIA

Mathematical analysis of mechanical dispersion in granular media, as indicated above, assumes the media to be isotropic with respect to dispersivity. Fractured geological materials and karstified carbonate rocks, being the extreme case of the former, are highly anisotropic with respect to the orientation and frequency of fractures. Because of that, one can expect that contaminant transport through fractured consolidated rocks cannot be explained by the advection-dispersion equation evaluated for granular, non-consolidated rocks. In the case of fractured rocks, "representative elementary volume" (REV), for which average hydrogeological and physico-chemical parameters of the system are known, is assumed to be a single fracture or a channel. A single fracture as a starting point in fractured hydrogeology is commonly used, while the concept of channel as the elementary volume is a new concept recently introduced by Tsang and Tsang (1987), following the earlier study by Neretnieks (1985).

Fracture-based flow models can be broadly grouped into two approaches. In the first approach fractured rocks are visualized as a system of individual and possibly interconnected fractures in a permeable or impermeable host rock, in other words, fractured medium is treated as an equivalent porous medium. For the "continuous fracture flow models" the critical input parameters are equivalent permeability tensor for fluid flow and dispersivity, for which the analogy with the porous medium flow is considered to be constant along the path flow. The constancy of dispersivity in the heterogeneous medium has been reviewed critically by several authors (Neretnieks, 1985). The second approach considers the system with less connectivity of the fractures, representing the system as a discontinuous fracture network. The critical point of discrete representation of the fractures is to measure the directional permeability of the networks and determine whether or not an equivalent permeability tensor could be used to predict flux through the network. Although these approaches treat the problem in different ways, they all start with the common assumptions that the single fracture is the basic unit and that each fracture can be represented by a pair of parallel plates with a constant aperture (Tsang and Tsang, 1987). It is assumed that fluid flow in a fracture is governed by Darcy's law, where the hydraulic conductivity term is derived by idealizing the fracture as a parallel plate opening. A number of authors have derived equations describing the flow between parallel plates (for references see Gale, 1982) in which velocity in fractures can be represented by a so-called cubic law, which is formed from Darcy's law in which the equivalent hydraulic conductivity of the fracture,  $K_f$ , is

$$K_f = \left( \frac{\delta g}{12\mu} \right) b^2 \quad (5)$$

where

- |          |   |                              |
|----------|---|------------------------------|
| b        | = | the aperture of the fracture |
| g        | = | acceleration of gravity      |
| $\delta$ | = | the density of water         |
| $\mu$    | = | dynamic viscosity            |

The cubic law for the volumetric flow rate through the fracture is:

$$Q = \left( \frac{\delta g}{12\mu} \right) Wb^3 \quad (6)$$

where

- $l$  = the head gradient across the length of the fracture segment  
 $W$  = the width of the fracture segment (Anderson, 1984)

From equations 5 and 6 it follows that the statistical models for fracture network based on cubic law include the data for the fracture aperture, fracture length, fracture spacing, and fracture orientation. As the fractures are highly stress-dependent, additional parameters for stress variations must be included.

For fractured rocks where effects of rock matrix diffusion cannot be neglected, numeral models such as double porosity models were developed. The concept of a double-porosity medium as representative of the behavior of a fractured aquifer was first introduced by hydrologists from the Soviet Union (Barenblatt and others, 1960), and commonly used by petroleum engineers. Their model assumed the existence of two regions of different porosities and permeabilities within the formation, fractures, and blocks, respectively. In this model, the "primary" porosity in the rock matrix and the "secondary" porosity in the fractures are each treated as a continuum. The global flow in the medium occurs only through the fracture continuum, while matrix and fractures interact locally by means of "interporosity" flow. The matrix fed liquid to the fissures and acted as a uniformly distributed source. From the contaminant-transport point of view, it is important to emphasize that the chemical processes mostly occur in the rock matrix and not in the fracture, because of the higher reactive surface area of the rock matrix and relatively low flow velocity, which allowed equilibrium to be attained. Furthermore, it has been proven by many authors that diffusion of contaminants from fractures to the rock matrix can serve as a significant retardation mechanism, which cannot be ignored in the contaminant transport study, especially with the increase of the traveling distance of the contaminants (Neretnieks, 1985).

Recently, after applying the parallel-plate description of each single fracture to the specific field situations, it was determined that this model does not fit reality completely. It was Neretnieks (1985) who showed that flow in the fracture has characteristics of channeling flow rather than fracture flow. Tsang and Tsang (1987) mathematically expressed this idea, assuming that the fluid flow and contaminant transport through a tight rock medium is by means of a limited number of tortuous and intersecting channels. These channels have variable apertures along their lengths. The authors used as characteristic parameters: 1) aperture density distribution, 2) effective channel length and width, and 3) aperture spatial correlation length. From the aperture distribution and a spatial correlation length, systems of channels are generated using geostatistical methods.

In summarizing flow through fractured rocks, both fracture-based or channel-based flow and solute transport need to be confirmed by field studies in various types of consolidated fractured rocks.

## **MOVEMENT OF CONTAMINANTS IN GROUND WATER - CHEMICAL PROCESSES**

In the general advection-dispersion equation (equation 4), the last two terms refer to the influence of chemical processes upon the spreading of contaminants in the subsurface aqueous system. Contaminant concentration in the plume at a certain point from the place of injection into the ground water can be either decreased or increased due to the chemical processes in the water and/or at the rock/water interface. Chemical rates of changes and exchanges are difficult to predict and quantification is even more sophisticated than in the physical processes. For simplification, some of the mathematical models for the contaminant movement in ground water take into account only the physical processes, assuming that the system is conservative with regard to the chemical species in the water. For some particular chemical species in water having certain characteristics, this approximation is valid; however, if we consider the contaminant transport as a dynamic process, the contaminant plume as a mixture of different chemical species, and the water vulnerable to the physico-chemical changes along its path, which is closer to reality, then the contribution of chemical processes cannot be neglected.

In cases involving non-conservative systems (reacting chemical species), transport fluxes may depend on thermodynamic relations as well as on the rate and extent of chemical reactions. The governing equations of solute transport must then include terms accounting for transfer across phase boundaries and for transformations of dissolved species by homogenous reactions. According to Bahr and Rubin (1987), if the rates of reaction are fast relative to the rate of advection transport, then one can approximate the macroscopic scale that local chemical equilibrium attains throughout the flow system. This permits simulation of transport of non-conservative chemical species using equilibrium relations that can be expressed as algebraic equations. The data on geochemical equilibrium generally are numerous in the literature and are easy to obtain experimentally for a particular system. This is with regard to simulation of transport involving kinetically limited reactions that require knowledge of rate laws and rate constants, data which are not so abundant in the literature and which are difficult to obtain experimentally. Generally, the kinetics-based models must be used where the rate of advective transport is faster relative to the rate of reactions and/or where the dispersion coefficient is significantly larger than the diffusion coefficient (James and Rubin, 1979). Flow in fractured rocks, especially in carbonate fractured rocks, generally satisfied these requirements. The description of the kinetics-based model, called "separation of the kinetically influenced term" (SKIT), method is given by Bahr and Rubin (1987) and will not be considered here.

Computer programs that calculate chemical equilibrium in natural water or similar aqueous systems have appeared in literature since 1965. The applicability of these

models is considered here in view of the possibility of each program to calculate "mass transfer" and/or "mass transport" calculations. Mass transfer is defined here as "the transfer of mass between two or more phases, such as precipitation or dissolution", which is commonly included in most of the referred models, while mass transport is "solute movement during fluid flow". Combining mass transport with chemical equilibrium models is a very new subject in which only a limited amount of work has been done. An additional degree of complexity can be induced by considering reactions progress wherein states of partial equilibrium are attained during the path toward complete equilibrium, which can be important in the solute movement in fractured rocks. In addition, a model taking into account the redox balance seems to be more promising. Both of the requirements mentioned are achieved in the computer model PHREEQE (Parkhurst and others, 1980), which has been developed for the interpretation of ground-water chemistry, and, when used together with its accompanying program, BALANCE (Parkhurst and others, 1982), provides a valuable tool in the understanding of geochemical processes in ground-water systems (Plummer and others, 1983).

Based on the previous discussion on chemical models, there are several chemical processes that must be considered in the chemical part of the contaminant-transport mechanism, namely: adsorption-desorption processes, solubility-precipitation control, hydrolysis, complexation and chemical speciation, oxidation-reduction processes, and mineral dissolution and acid consumption.

According to Cherry and others (1984), there are two main approaches that are commonly used to predict the behavior of most chemically reactive inorganic contaminants in groundwaters. The first approach involves the incorporation of a simple chemical mass-transfer term representing only adsorption in the advection-dispersion equation. This predicts the advance rate and the shape of the front of a contaminant zone emanating from a continuous or temporary source. The second approach predicts the contaminant concentration in the zone of contamination after chemical mass transfer has resulted in equilibrium concentration that has been achieved by precipitation, dissolution, oxidation, or reduction. No one approach is completely correct because all these processes usually occur simultaneously in zones of contaminated ground water.

Adsorption is usually incorporated into the basic advection-dispersion equation with the assumption that the concentration of the contaminant in the solution phase (C) is a function of the concentration in solid phase (c) under equilibrium conditions existing between the solution-phase and solid-phase concentration.

$$C = fc \quad (7)$$

This relation is normally determined in the laboratory by means of batch tests in which a known mass of the geologic medium is immersed in a solution representing the leachate or ground water. When this test is repeated using different concentrations of the contaminant in solution, the  $C = fc$  relation, which is known



as the adsorption isotherm, is obtained. Isotherms from batch tests usually fit closely to a functional relation known as the Freundlich isotherm,

$$C = kc^a \quad (8)$$

where  $a$  and  $k$  are empirical coefficients (Cherry and others, 1984). Another possible description may be the Langmuir isotherm, which is possibly the better mathematical definition,

$$C = \frac{Kbc}{1 + Kc} \quad (9)$$

where

$K$  = a constant relating to the bonding energy  
 $b$  = the adsorption maximum when the adsorbent is completely saturated (Matthess and others, 1985).

The primary mechanism of adsorption is commonly ion exchange, which for univalent species can be represented as:



where

$X^+$  = the cationic contaminant in solution,  
 $XS$  = the contaminant in the adsorbed states on the exchange medium designated as  $S$   
 $A^+$  = the resident cation initially on the exchange medium ( $X^+$  and  $A^+$  are considered to be competitive cations for exchange positions in solid phase).

Application of the law of mass action provides:

$$K_{ex} = \frac{[A^+][XS]}{[X^+][AS]} \quad (11)$$

where

$K_{ex}$  = the equilibrium coefficient for the exchange reaction (Cherry and others, 1984), also known as a selectivity quotient (Matthess and others, 1985).

The equilibrium coefficient for the exchange reaction,  $K_{ex}$ , or selectivity quotient, is related to the distribution coefficient,  $K_d$ , if the cation exchange capacity,  $Q$ , (referred to as the amount of exchangeable ions in meq/100g solids at pH F), of the exchange medium,  $S$ , and the total competing cation concentration in solution  $C$  are known and the system under consideration is at equilibrium (Jackson and Inch, 1980):

$$K_{ex} = K_d \frac{[C - X^+]}{[Q - XS]} \quad (12)$$

If the contaminant  $X^+$  is present in amounts much less than  $A^+$ , which is commonly the case, assuming major cations like  $Na^+$ ,  $K^+$ ,  $Ca^{++}$ ,  $Mg^{++}$ , to compete with  $X^+$ , the relationship can be simplified as:

$$K_d = \frac{K_{ex} \cdot Q}{C} \quad (13)$$

Therefore the distribution coefficient is directly proportional to the cation exchange capacity and the equilibrium coefficient for the exchange reaction, and is inversely proportional to the total competing cation concentration. More complex cases including monovalent-divalent exchange may be developed using a similar approach (Matthess and others, 1985).

The empirical distribution coefficient,  $K_d$ , is a useful measure for the affinity of a specific geological material for a certain contaminant defined as the ratio of the adsorbed substance in meg/100g solid to the concentration of the same substance in solution in meg/l. In dilute suspension,  $K_d$  is equal to the coefficient of the Freundlich isotherm (Matthess and others, 1985).

The other useful parameter in contaminant transport is a retardation factor,  $R_d$ , expressed as a quotient of the mean ground-water velocity  $v$  to the mean transport velocity of the contaminant ( $v_c$ ) and can be calculated from the equation known as the one-dimensional retardation equation:

$$K_d = \frac{v}{v_c} = 1 + \frac{\delta b}{n} \cdot K_d \quad (14)$$

where  $\delta b$  is the bulk density of the aquifer material. The calculation of the transport velocity of contaminants with the help of  $K_d$  and  $R_d$  values is valid only when the reversible, kinetically-fast adsorption process is present (Jackson, 1980). Additionally, certain geological materials show a selective tendency toward the adsorption of particular cations and, consequently, desorption can occur if the cation of stronger selectivity toward the particular exchange site is present in the solution. This complicates the relationships as well as the complexing of cations by inorganic or organic ligands, which usually change their adsorption properties. Furthermore, use of the isotherm approach rests on the premise that isotherms can be determined in the laboratory on samples that are representative of the geological materials as they exist in the field. However, deviations of field data vs laboratory data are reported in the literature (Cherry and others, 1984). This deviation can be minimized if field tracer data are used instead of laboratory data. Apart from all these difficulties, Cherry and others (1984) have given us examples of transport models based on incorporation of the adsorption term into a general advection-dispersion equation.

The behavior of many contaminants in ground water is influenced by their solubility and/or precipitation in the aqueous system. The equilibrium relation for a contaminant species controlled by precipitation or dissolution is specified as:

$$xX + bB = yY + cC + dD \quad (15)$$

where X is the inorganic contaminant in the solution; Y is a mineral or solid amorphous compound in which the contaminant species is incorporated by precipitation or from which it is released by dissolution; B, C and D are other elements or compounds in solution; and x, b, y, c, and d are stoichiometric mole numbers. From the law of mass action, the equilibrium expression is obtained:

$$X = \frac{[C] \cdot [D]}{K_{eq} \cdot [B]} \quad (16)$$

where  $K_{eq}$  is the equilibrium constant and the quantities within the brackets are chemical activities. If X is initially above the equilibrium concentration when it enters the ground-water system, adjustment toward equilibrium will occur by precipitation of mineral or amorphous solids. If X is below the equilibrium concentration, minerals or amorphous solids that contains X as a part of the chemical structure will dissolve when such solids are present in the system (Cherry and others, 1984). The later case is more common. Apart from difficulties rising mostly from not knowing the reaction-rate control in contaminated ground water, it must be mentioned that only a few computer programs are available for calculations in aquatic equilibrium systems, for example, WATEQF (Plummer and others, 1976) and GEOCHEM (Sposito and Mattigod, 1980). The activities and quantities of the species present in the solution are calculated.

Hydrolysis complexation and chemical speciation are the processes occurring in the aqueous system that change the form of the contaminant in the ground water. These forms, or species, can have different valences and, therefore, different mobilities in ground water owing to different affinities for adsorption and different solubility control. Knowledge of the distribution of species in solution is therefore necessary for consideration of the behavior of most inorganic contaminants in ground water. Several papers dealing with the complexation of trace metals in natural water, together with the analytical techniques for measuring the speciation, are contained in the book edited by Kramer and Duinker (1984), and will not be repeated here.

The mobility of many inorganic contaminants is strongly dependent on oxidation and reduction processes involved in ground-water systems. According to Cherry and others (1984), of the 16 inorganic constituents that have recommended or mandatory concentration limits in drinking water supply, nine have more than one possible oxidation state in ground water. These are arsenic (As), chromium (Cr), iron (Fe), mercury (Hg), manganese (Mn), selenium (Se), uranium (U), nitrogen (N), and sulfur (S). Of the remaining elements listed in the drinking water standards, four can be strongly influenced by redox processes (silver (Ag), copper (Cu), cadmium (Cd), and zinc (Zn)), even though they have only one valence state in aqueous systems. The only elements on the list that are relatively insensitive to the redox (oxidation-reduction, Eh) conditions are chloride (Cl), fluoride (F), barium (Ba), and radium (Ra) although the last two can be affected, if present in reactions with sulfate ( $SO_4^{2-}$ ) and

iron (Fe), which are redox dependent. Numerous pH-Eh diagrams published in classical papers by Garrels and Christ (1965) and Hem (1970) can be used as a conceptual guide to some of the possibilities of element behavior in ground water. Computer models, such as PHREEQE described by Parkhurst and others (1980), can provide predictions of pH and Eh if the mineral and amorphous solids that comprise the system are specified (Cherry and others, 1984).

The last chemical processes that influence contaminant movement in ground water discussed here are mineral dissolution and acid consumption. In some situations mineral dissolution may cause contaminant concentrations to increase if the contaminants of interest are released from the minerals, or to decrease if the contaminant is removed from the solution. Basically, processes are the same as previously described if the conditions in the aquatic system change. They can be influenced by lowering the pH because most of the leachate is or can be very acidic (up to pH 1). Neutralization, or acid consumption of the leachate, is an important process in calculating the retardation factor, more specifically defined here as the acid-front retardation factor, particularly in the systems with high buffer capacity, as in the case of carbonate ground waters.

Biological reactions that may be the most important mechanism for transformation of organic contaminants are not considered to be important in the case of inorganic contaminants, at least not to the extent of chemical reactions. As the main scope of this article is inorganic contaminant movement in ground waters, biological reactions will not be discussed. The same applies to the movement of immiscible organic fluids entering into the ground as a result of leaking storage tanks, or when accidentally spilled. The inorganic contaminants considered here are assumed to be soluble in the water, taking into account certain solubility constraints mentioned previously.

## **TRANSPORT OF CONTAMINANTS THROUGH CARBONATE AQUIFERS**

Although several authors share the opinion that there has been significant progress in delineating and quantifying the extent of contaminant transport in isotropic porous media in the last ten years, much work has yet to be done. This is especially true for transport over small times or small distances from the source, where the standard form of the advection-dispersion equation does not apply, because of the difficulties in expressing the dispersivity in terms of statistical properties of the hydraulic conductivity distribution (Anderson, 1984). Furthermore, study of contaminant transport in fractured rocks is in its infancy, although in the last five years several mathematical transport models have been published. These models generally lack appropriate verification by field experiments because of the difficulties involved in characterizing the geometry of a fractured-rock system in the field. The lack of verification complicates testing of the theory. If we consider carbonate fractured rocks as a special case of fractured consolidated rocks, one can see that all the models in the hydrogeology of fractured rocks are dealing with and are based on transport modeling through non-carbonate fractured rocks such as metamorphic and

igneous and non-carbonate sedimentary rocks. Much effort has been made in defining the transport of contaminants through these rocks as a site evaluation for low- and high-level radioactive waste disposal. It is uncertain how the predictive flow in this type of rock can be transferred to the carbonate aquifers with intensive karstification. Water quality models already completed for some carbonate aquifers have already been discussed by Plummer (1977), and by Schwartz and Domenico (1973). These models are useful in estimating the minimum time required for a contaminant to arrive at a certain discharge location in a flow system such as a well or stream, or in determining the probable path of migration of a contaminant. However, to predict the concentration of a contaminant at a point within the flow system or to predict the average concentration of the contaminant in the system, a flow model must be coupled to a water quality model. As for any other system, contaminant transport in carbonate rocks is a summary effect of both physical and chemical processes involving the aqueous systems containing certain contaminants. Furthermore, ground-water velocity in karstified carbonate rocks of more than 1 km/day has been recorded. At this velocity flow conditions are turbulent and Darcy's law is no longer valid. The laminar flow through non-carbonate fractured rocks is the basic assumption. Although it follows from the equation for transition conditions of laminar-turbulent flow (see for example, Thrailkill, 1968) that the turbulent flow occurs in a fracture opening more than 1.5 to 2 mm in diameter, it was also established that in karst solutional channels of even smaller diameter Darcy's law is applicable only for small flow velocities and low hydraulic gradients. Another difficulty for simple transfer of the non-carbonate fractured-rock model to carbonate rock lies in the persistivity of fracture geometry during contaminant flow. The fractures in non-carbonate rocks are considered to be pressure dependent, but if we assume the constant pressure, which can be assumed for the shallow aquifers, the fracture geometry is assumed to be unchanged during contaminant flow through it. Because of the higher solubility of the carbonate rocks this need not be the case in carbonate aquifers. For instance, suppose an aquifer is contaminated by acidic leachate (pH 1.5 - 4), which can occur where a source of pollution is base-metal mines where acid-leachate milling occurs or where tailings become acidic because of the oxidation of pyrite. Neutralization of acidic leachate can occur as an effect of dissolution of calcite or dolomite, which can cause widening of the initial karst channel. The opposite process, filling of the existing fracture or channel by the authigenic chemical minerals and/or weathering products and narrowing the fractures, was discussed by Neretnieks (1985) for non-carbonate fractured rocks.

Higher ground-water velocity in most carbonate aquifers can lead to the conclusion that for contaminant transport the advection part of the advection-dispersion equation is physically responsible. Undoubtedly the advection process is more important than dispersion, but it would be wrong and misleading to completely ignore dispersion in carbonate aquifers, especially in the shorter distance from pollution point source.

According to Komatina (1984), the porosity distribution in the karstified carbonate rocks can be, as a first approximation, expressed by means of "double porosity models", and flow either by continuous or discontinuous models for the fractured

rocks. Fractures in karstified carbonate rocks are mostly influenced by tectonics, at least at the initial stage, and enlarged by karstification processes, and it is assumed, follow preferential directions at least at the smaller scale. This will favor the model of continuous fractures for which Darcy's law applies, as was shown before. Either this or discrete fracture models must be based on known fracture arrangement in the field. Structural geological maps with a defined structural unit as already made for part of the Dinaric karst area in Yugoslavia, can be a very useful base for field checking the applications of the models mentioned above (Komatina, 1984).

If we consider the chemical processes involved in carbonate rocks, we must be aware of certain facts. First, because of the usually high velocity relative to the rate of the chemical processes, the local equilibrium between the artificially introduced solutes and the transport medium will hardly be attained, thus limiting the application of certain models based on equilibrium approach. Second, adsorption, which is the main chemical process involved in some models, is not the process that is considered to be important in a carbonate environment. Models based on dissolution-precipitation processes with or without oxidation-reduction processes seem to be more realistic. Unfortunately, most of the models are based on data obtained for the "pure phases", mostly calcite. The competitive ions other than alkaline-earths, which can influence the calcite solubility, are usually not considered. The same applies for the imperfections of the crystals and/or magnesium (Mg) incorporation in the calcite lattice either by the substitution for calcium (Ca), or solid crystals in the calcium carbonate-magnesium carbonate ( $\text{CaCO}_3\text{MgCO}_3$ ) chain, or the presence of aragonite as a main calcium carbonate ( $\text{CaCO}_3$ ) phase, which is the common case in some carbonate aquifers.

It can be concluded that contaminant transport through karstified carbonate rocks can be treated as a special case of transport in non-carbonate fractured rocks with certain limitations. However, much laboratory and especially field investigation must be done to establish a reliable and realistic mathematical model for contaminant transport in carbonate rocks. Continued research can reduce the uncertainties associated with predicting the fate of contaminants and quantification of flow in carbonate aquifers.

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# **REVIEW AND SELECTED BIBLIOGRAPHY ON QUANTITATIVE DEFINITION OF KARST HYDROGEOLOGICAL SYSTEMS**

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## **INTRODUCTION**

Karst water resources have been playing in many countries one of the most important roles, not only in public or industrial water supply, but also in energy production and irrigation. However, the intense usage of these resources in many cases has not been followed by proper research efforts in their quantifying. In addition, the growing industrialization and population, particularly since the middle of this century, brought to light all derived consequences such as the rapidly increasing demand for drinking water and environmental pollution. Comparing to any other porous medium containing groundwater, karst aquifers are probably the most nonpredictable in at least two senses - their possibility to provide additional quantities of water to those discharging naturally, and their response to different kinds of pollution.

The aim of this reviewing paper is to present a short history of development of various quantitative methods being applied in karst hydrogeology, as well as to introduce the recent trends in this challenging research field.

### ***Karst Hydrogeological System - Definition***

System approach is widely present as a basic research concept in various scientific fields dealing both with laws of nature and society. The term "system" is usually understood as a complex collection of more or less interdependent particles acting as one whole. Reliable defining of such whole is a task not necessarily connected with defining of each of its particles, which is also usually impossible. A bigger number of evaluated (or defined, or explained) constituents of a system should result in its better understanding. However, when physical laws within a system are not well known, the number of elements studied may sometimes mislead the researcher from his main objective - a solution acceptable from the engineering point of view.

A typical example of a complex whole with various possible types of interconnections between its constituents is karst hydrogeological system (KHS). It is exposed to different external influences (such as infiltration of precipitation, inflow of surface streams, air temperature etc.), and it has a constantly changing structure.

Though for those reasons hard to define, one may accept the following short explanation of the term: KHS is a whole, having a karst aquifer for its basic unit, that may be consisted or under the influence of more aquifers and surface streams. Since karst aquifers have high transmission capabilities they often act as a base of discharge for surrounding fissured or intergranular aquifers, so that the later ones present in a fact the parts of a large system. A good example are extensive interconnections between phreatic aquifers in karst poljes' deposits and underlying karst aquifers. The regime of surface streams sinking at contacts between non-karstified and karstified rocks also influence hydrogeological characteristics of karst aquifers; such streams should be considered as parts of the system as well.

Karst hydrogeological system is characterized by the following major elements:

- (a) System's structure;
- (b) System's boundaries;
- (c) System's boundary conditions.

**System's structure** is generally connected with the type and degree of aquifer porosity. Primary porosity of the rocks susceptible to the process of karstification (i.e. porosity formed during the lithogenesis) is usually much smaller than secondary porosity which is the result of endogenous (tectonic) and exogenous (atmospheric) forces. Karst aquifers are probably the most famous for their unique "mixed" porosity - one can find porosity of homogeneous rock blocks, then porosity of small-to-large fissures, then porosity of karstified large faults (i.e. channels), porosity of karst caverns or cavities in general, and finally porosity of clastic deposits in all the above mentioned discontinuities. Aquifer porosity, together with the characteristics of present fluid, determine hydrodynamic laws of groundwater (fluid) flow in the system studied. Defining of these laws is probably the most difficult task in karst hydrogeology having in mind all possible types of porosity usually present in a karst aquifer.

**System's boundaries** are divided in two types: inner boundary discontinuities such as low permeable fault zones, lithological (mineral) difference between strata or stratigraphic units etc., and outer boundary discontinuities such as contacts of karst aquifer with other low-to-impermeable geological formations. The outer boundaries are also usually considered as the so-called "zero flux boundaries". However, when two karst hydrogeological systems, or two karst aquifers, are in contact, this definition may not be appropriate from the physical point of view, but it is necessary for the modeler.

**System's boundary conditions** are defined by hydraulic and hydrologic characteristics along its boundaries. These are usually named as inputs (infiltration of precipitation, sinking of surface streams, seepage from other aquifers, artificial recharge etc.) and outputs (evapotranspiration, discharge into surface streams or other aquifers, spring discharge, tapping-artificial discharge etc.) or flux when considered together.

The final consequence of system's structure, boundaries and flux is shape and behavior of karst groundwater table, i.e. piezometric surface.

It is obvious from this short introduction how complex and complicated is the process of quantitative defining of karst hydrogeological system, especially when the majority of listed system elements are included. In fact, development of karst hydrogeology is based on the constantly increasing number of quantitatively studied system constituents.

## DIFFERENT APPROACHES

Pioneer work in quantitative karst hydrogeology was processing of water tracing data. Methodology of dye tracing is probably the most studied and published among other topics present in karst research. In the beginning primarily used for determining of groundwater flow directions and delineation of drainage areas, then for simple calculation of fictive groundwater flow velocities, tracing has been recently a very important part in establishing of sophisticated numeric models.

Analysis of recession hydrograph, i.e. discharge during the period without significant precipitation or aquifer recharge, was especially popular among karst hydrogeologists during the sixties. Introduced at the beginning of this century by Boussinesq and Maillet as a method of separation of the so-called base flow of surface streams, it was applied in karst hydrogeology with the similar idea. Namely, steep falling limb of hydrograph is considered to present discharge from large karst channels and fissures, while its mild ending part is a consequence of slow draining of small fissures and clastic material within the aquifer. The surface equivalents would be flow in stream due to rapid runoff in the first case, and flow mostly due to aquifer drainage in the second case.

Two other methods widely applied in classic surface hydrology were also used in karst studies since the middle of this century - defining of catchment water balance (budget), and regression analysis. The first one is based on exact measuring and derived calculation of major parameters of water balance, such as (effective) precipitation, moisture content in unsaturated part of the aquifer, surface runoff, evapotranspiration, concentrated or diffuse discharge of groundwater etc. Regression analysis defines mathematical connection between (usually) one dependent variable, such as spring discharge or piezometric level, and more independent variables which are known to have a significant influence on the first one. These are precipitation, air temperature, moisture, flow rates of sinking surface streams, etc.

Regression, together with the unit hydrograph as a traditional method used in rainfall-runoff hydrology, represent actually the link between two conceptually opposite approaches to quantitative karst hydrology - parameter and stochastic. Though based on numerous criteria and limitations (e.g. unchanged channel conditions, areas which do not have appreciable storage etc.), the unit hydrograph method showed to be practical approach to karst aquifers since the response of springflow to storms is similar to that of surface runoff. This response is mostly studied as controlled by linear physical mechanisms and is described by linear unit-response functions - kernels, similarly to the instantaneous unit hydrographs in surface runoff. Various functions of unit response have been applied in system analyses to karst aquifers and implemented in classical stochastic modelling of time series as well.

Neglecting the physical laws of transformation of system inputs to system outputs, and in the same time providing of considerably reliable predictions of system behavior, stochastic methods have been increasingly applied in karst hydrogeology. The exploding development of computer techniques and a chance (sometimes maybe too pragmatic) for a karstologist to avoid difficult and long-lasting studies of system's physical structure, gave a powerful background to stochastic system approach. System inputs, outputs, their basic elements, and their interconnections are explained by a large variety of terms such as autocorrelation, cross-correlation, moving average, autoregression, periodicity, harmonics, convolution, system memory, etc.

Another fundamentally statistical procedure extensively developed in the last three decades, the so-called geostatistics, has been recently introduced to hydrogeology. It is the theory of regional variable, founded on the analysis of variogramme and basically applied in mineral resources research and mining industry. Importance, or weight, of each field point information is statistically determined comparing to neighboring data. Derived maps of areal distribution of a particular element (e.g. piezometric level) show more objectively the present inhomogeneity in the region studied than conventional methods of isoline construction. This procedure, called Kriging (after Krige) has a very favorable and logical field of application in karst aquifer studies for its distinct mixed porosity, i.e. inhomogeneity.

The majority of the above mentioned methods of quantitative karst hydrogeology were primarily established and evaluated in surface hydrology. Another large group of methods is based on physical defining of karst aquifer properties such as its saturated depth and hydraulic conductivity, jointly known as transmissibility, then effective porosity or storage coefficient, and also its physical and chemical response to different kinds of transferred fluids (pollutants), e.g. hydrodynamic dispersion, molecular diffusion, absorption/desorption, ionic exchange, dilution, precipitation etc.

All the methods based on physical laws of groundwater flow are a part of the so-called hydrogeological approach to KHS.

As it was already pointed out, karst aquifers are completely inadequate porous media for the application of standard equations of groundwater flow used so far in

hydrogeology - Darcy's law, Dupuit's, Laplace's, Bousinesq's, Theis's equations etc. However, in absence of a better tool, the equations derived on strict assumptions about intergranular and homogeneous nature of porous media are, with various modifications, still used. In general, these modifications firstly represented replacing intergranular by fissured media having uniform or heterogeneous sets of fissures with corresponding hydraulic conductivity (the term is conductivity tensor). Soon, this fissure approach was supplemented by the concept of double porosity. Namely, the aquifer porosity was understood as consisted of two parts - porosity of homogeneous rock blocks ("matrix porosity") and porosity of fissures.

The solutions of derived equations of groundwater flow are obtained in two major manners - analytic and numeric. In the first case usual bases of calculation are radial flow towards one or several wells, and planar flow towards linear drains. In the second case entire flow domain is under the calculation by deterministic models which are classified according to division of the studied area. Three main types are finite difference models, finite element models and boundary element models. The method of characteristics, though present in hydrogeology, has not yet been evaluated in karst studies.

The major limitation for the application of both groups of solutions is the question how representative are the field data used for the identification of hydrogeological parameters of a karst aquifer. In other words, the so-called effect of scale in karst hydrogeological system research incapacitates generalization of the results obtained in a portion of aquifer. A good example is monitoring of head drop in several observation wells during the pumping test - one observation well may be located entirely in homogeneous rock block, the other one in highly permeable karst channel, the third one in "dead-end" cavity etc. In such cases obtained data are practically useless. Similar problems appear in processing of water permeability test data. Established by Lugeon in 1933, and primarily designed for fissured non-karstified rocks at dam sites, the test has been improved by various authors and is still irreplaceable during dam construction both in karstified and fissured media. However, various empiric transforms of the Lugeon unit (Lu) into the coefficient of permeability, which are more or less satisfactory in fissured rocks, showed to be inadequate when applied to highly karstified aquifers. In such cases, the results of water permeability tests may serve for relative comparison of particular portions of an aquifer.

After this short review of the methods applied in the process of quantitative defining of karst aquifer systems, the following general classification may be introduced:

- (a) Hydrologic methods:
  - (i) Water tracing
  - (ii) Recession hydrograph
  - (iii) Hydrograph component separation
  - (iv) Water balance (budget)
  - (v) Unit hydrograph

- (b) Statistical and stochastic methods:
  - (i) Probability distribution
  - (ii) Regression
  - (iii) Kernel functions (Convolution)
  - (iv) Variogramme and Kriging
  - (v) Stochastic models (AR, MA, PAR, AR(I)MA(X) etc.)
- (c) Hydrogeological methods (homogeneous, fissure and double-porosity approach):
  - (i) Analytic solutions
    - a. Pumping test
    - b. Slug test
    - c. Water permeability (Lugeon) test
  - (ii) Numeric solutions
    - a. Finite-difference method
    - b. Finite-element method
    - c. Boundary-element method
- (d) Other
  - (i) Mixing cell models
  - (ii) Combined models (deterministic + stochastic)

Some of the methods most often applied in quantitative karst hydrogeology will be presented more closely in the following paragraphs.

## **WATER TRACING**

An exceptional review of "karstwater tracing techniques", presented by J.G. Zoetl (1989) in Volume Four of Annotated Bibliography, provide numerous data and references on the topic. It includes both the history of water tracing in karst and comments on the achieved results, i.e. applicability of particular methods in different conditions. Isotope hydrology in karst, or what is often called "tracing with environmental isotopes", is also presented in the paper.

Interpretation of tracing in karst could be conditionally divided into qualitative and quantitative. In the first case it is a simple registration if and where the introduced tracer has occurred indicating the general direction of flow. In the second case both a rigorous study of tracer's characteristics such as detection limits (i.e. quantity of dye for injection) or possible interaction with karst porous media, and quantitative processing of collected samples should be performed (Atkinson and Smart, 1981; Thrailkill, 1983; Smart et al., 1986).

The traditional and the simplest quantity obtained by tracing in karst is fictive velocity of groundwater flow. As a consequence of great variety of karst aquifers and their mixed porosity, these velocities have values within a wide range. Classification of

numerous dye-tests performed in classical Dinaric Karst indicate the most common fictive velocity of 1-2 cm/s (Milanovic, 1978; Fig. 1).

Study of tracer breakthrough and recovery curves gives a very important indirect information on aquifer's structure and hydraulic conditions controlling groundwater flow. Smart et al. (1986) list the following "shortcomings of non-quantitative tests compared with full network definitions by means of quantitative dye mass balance; Non-quantitative tests may not:

1. Pinpoint the locations of tributary and distributary links in the system.
2. Indicate whether distributaries are independent or common to several sinks.
3. Show that springs share a common feeder.
4. Permit downstream additions of dye to be detected in system with multiple or unknown springs".

C.C. Smart (1988) stresses the importance of continuous sampling for determining of bimodal and polymodal breakthrough curves, and further explanation of these anomalies by a proper structural model of karst aquifer (Fig. 2). More precise conclusions about hydraulic conductivity of portions of karst aquifer may be based on tracing and corresponding measurements in boreholes. These include recording of tracer dilution at different depths in the same borehole or sampling in pairs of close boreholes (Atkinson and Smart, 1981), then geophysical logging during simultaneous injection of tracer (Morin et al., 1989) etc.

An extensive study of quantitative application of dye-tracing techniques and derived predicting of contaminant transport is presented by Mull et al. (1988).

Environmental isotopes play increasingly important role in hydrogeological research of karst terrains. "The naturally occurring isotopes of oxygen and hydrogen ( $^{18}\text{O}$ , Deuterium and Tritium) which are the isotopic species of the water molecule are the ideal tracers commonly employed" for tracing water movement (Yurtsever and Payne, 1985). Various mathematical models describing tracer input/output relationship have been developed in the last two decades, bringing answers on resident time of discharged water, presence and degree of mixing of newly infiltrated water, groundwater flow velocities etc. (Dancer, 1985; Yurtsever and Payne, 1985; Zoetl, 1989). Beside the above mentioned "environmental tracing" with natural isotopes having short half life (e.g. 10.26 years in the case of Tritium) and thus applied in open karst hydrogeological systems, "Carbon-14 measurements from deep ground waters stored in the Paleokarst provide invaluable data for estimating storage capacity and the balance of deep ground waters". A good example is work of Hanshaw and Back (1974) on determining of regional hydraulic conductivity of Central Florida's artesian karst aquifer.

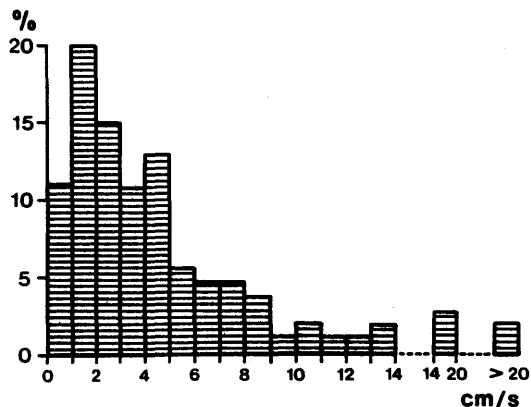


Figure 1. Percents of the most common groundwater flow velocities in Dinaric karst (after Milanovic, 1979).

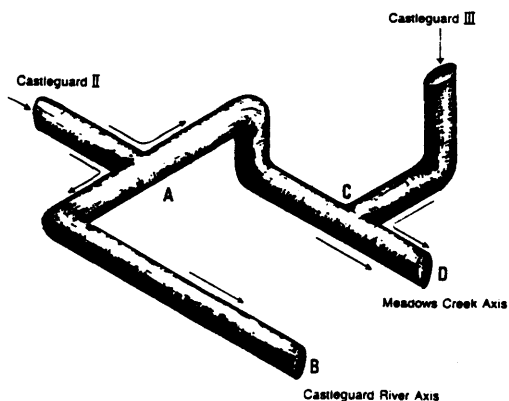
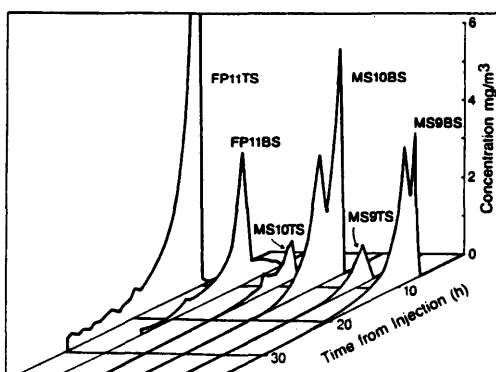


Figure 2. A - Pairs of tracer breakthrough at Big Spring (BS) and Tangle Spring (TS); B - The "hydraulic semiconductors", a structure providing a possible explanation of the anomalies in figure 2A (after Smart, 1988).



## RECESSION HYDROGRAPH ANALYSIS AND HYDROGRAPH COMPONENT SEPARATION

As shown in Fig. 3, outflow from karst aquifer is a combination of several responses to recharge (input). Determination of these responses through the analysis of spring discharge hydrograph has been for a long time an obligatory procedure in karst studies. Since the main hydrogeological parameters of a karst aquifer, such as coefficients of transmissivity and storage, are practically impossible to define correctly by classical methods (pumping test, water permeability test etc.), continuous monitoring of spring discharge (system output) is sometimes the only basis for quantitative identification.

For the mathematical expression of groundwater discharge through springs or surface streams during dry period, i.e. period with zero or negligible precipitation commonly called "recession period", Maillet (1905) and Boussinesq (1903-1904) proposed two functions (1 and 2 respectively):

$$Q_t = Q_0 e^{-\alpha t} \quad (1)$$

$$Q_t = Q_0 / (1 + \alpha t)^2 \quad (2)$$

These equations, of which the Maillet's is more known, define the spring discharge at time  $t$  ( $Q_t$ ) as the function of spring discharge at the beginning of recession period ( $Q_0$ ). The coefficient  $\alpha$ , called coefficient of recession ("coefficient de tarissement"), characterizes both aquifer's transmissivity and storage coefficient. Though without theoretical expression this relationship must be of the following form (Karanjac, 1978):

$$\alpha = f(T)/f(S, X) \quad (9)$$

Where  $T$  and  $S$  are transmissivity and storage respectively.

When a karst aquifer is not with uniform structure, the consequence may be discharge consisted of several subregimes indicating predominant types of porosity being drained (Fig. 4). After the works of Boussinesq and Maillet numerous equations have been proposed by different authors, of which the majority has practically the same exponential or hyperbolic basis (Schoeller, 1948, 1967; Forkasiewicz and Paloc, 1967; Drogue, 1967, 1972; Mijatovic, 1968). On the basis of 100 discharges studied in France, Drogue (1972) proposed application of hyperbolic function of Boussinesq type with power coefficients having values 1/2, 3/2 and 2 (Fig. 5).

Presented functions enable defining of volume of water that was stored or has been discharged from the beginning of recession period, by a simple integrating of  $Q_0$  within the corresponding time interval (Castany, 1967).

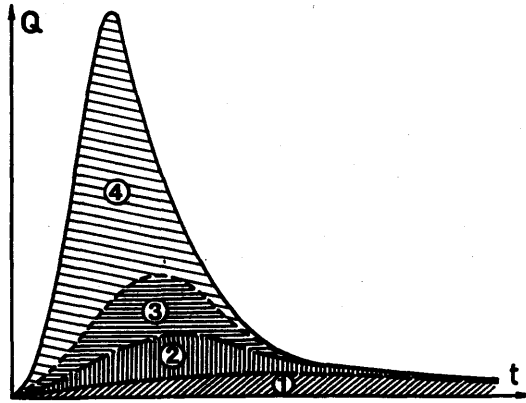


Figure 3. Schematic decomposition of unit hydrograph response of a karst aquifer or a system of underground channels and rock fissures. (1) Very slow response of finest fissures and clay-silt deposits; (2) Slow response of silt and sand deposits and medium sized fissures; (3) Medium, rapid-to-slow response of sand-to-gravel deposits and medium sized fissures; (4) Rapid response of large channels and enlargements (Yevdjovich, 1976).

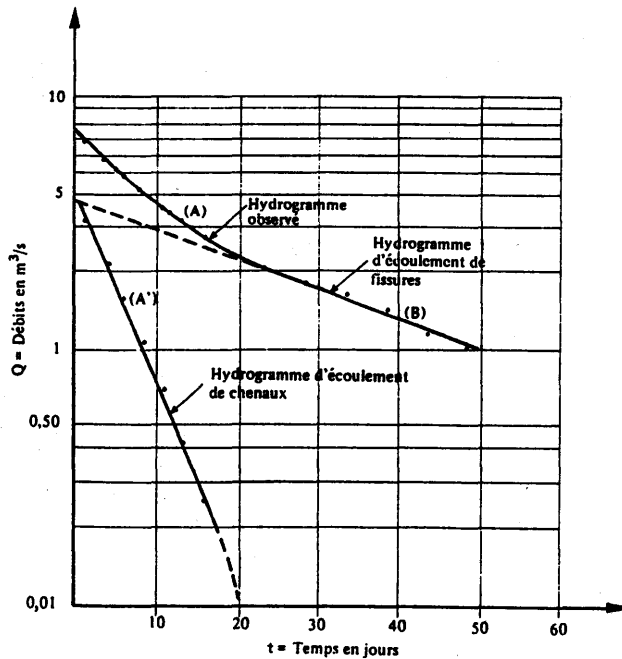


Figure 4. Components of hydrograph of a karst spring (Source of Lez, November 1962; Droque, 1967).

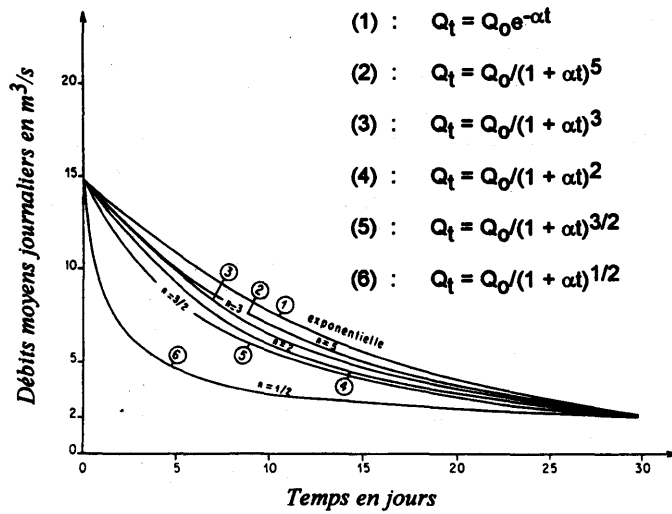


Figure 5. Graphic representation of patterns of decreases studied (Droque, 1972).

Limitations of application of recession discharge formulas for three types of karst systems (divergent, monoclinic and convergent) were studied by Berkaloﬀ (1967).

**Separation of hydrograph** to its components is the method often applied in surface hydrology. Since the response of karst aquifers to rapid infiltration is similar to that of surface streams to storms, certain analogy in hydrograph separation may be applied. Thus, one may consider the so-called base flow of surface streams, which is a consequence of groundwater discharge, as discharge from small joints and clastic deposits in the case of groundwater hydrology. Various methods of hydrograph separation are based mostly on determining of base flow at the ending part of recession hydrograph and its extension back under the observed hydrograph (Gray, 1973; Linsley et al., 1975). The residual after the separation of base flow is considered to be surface runoff + interflow. However, in the case of karst aquifer discharge it is impossible to determine whether and which part of discharge hydrograph is consisted of newly infiltrated water after the storm event. Namely, this water may cause the effect of rapidly transmitted pressure through conduits and discharging of long-resident groundwater. Thus, separation of hydrograph components on the basis of water resident time is equally important for the evaluation and management of karst groundwater quality and quantity. On the basis of frequent monitoring of Ca and Mg concentrations in discharge of a karst spring before, during and after major storm events, Dreiss (1989a) concluded, among other things, that:

- "A cation balance for the discharge of one spring indicates that about 25 % of the total spring flow is storm derived water", and
- "The observed chemical fluctuations and hydrograph components differ from those observed in streamflow where the time of the maximum dilution usually coincides with the time of peak discharge".

Hooper and Shoemaker (1986) compared results of chemical and isotopic hydrograph separation at an instrumented watershed in New Hampshire. The conclusion was that similar results were obtained from naturally deuterated water and dissolved silica, both being the conservative tracers. Another comparative study of two basically different methods of hydrograph separation - filter-separation autoregressive method and environmental isotope tracers, showed their considerable applicability (Hino and Hasebe, 1986).

## **WATER BALANCE**

The method of water balance (budget) is traditional in the so-called parameter hydrology and its reliability is directly dependent on number of elements (parameters) of hydrological cycle that can be instrumentally measured. It is seldom, however, that the all major hydrologic parameters are correctly recorded and balanced in a catchment studied. The whole complexity of water balance approach may be seen

from the example presented by Dublyanskii et al. (1984). Namely, calculation of water balance of Southwestern Upland Crimea is performed by a model having the following independently determined elements: vertical precipitation ( $X_v$ ), horizontal precipitation ( $X_h$ ), evapotranspiration ( $Z$ ), condensation ( $K$ ), surface runoff ( $Y_{sr}$ ) and deep karst water discharge ( $Y_d$ ) that includes discharge to other karst aquifers and sea. These variables are connected through the following equation:

$$X_v + X_h + K_{csr} + K_{cfk} = Z + Y_{sr} + Y_{srs} + Y_d \quad (4)$$

where  $K_{csr}$  is condensation in soil and rock,  $K_{cfk}$  is condensation in fissured karst storages and  $Y_{srs}$  is surface runoff from large springs.

Castany (1967) and Boni and Bono (1984) presented methodology of calculation of hydrogeological balance for several karstic catchments in Tunisia and Central Italy, respectively.

Model BEMER (Bezes, 1976) widely applied in France, that simulates karst system output, is mostly based on determining of elements of catchment water balance which are afterwards interconnected through the several reservoir levels. The applicability of the model is verified on the example of four karst systems in central France.

## PROBABILITY DISTRIBUTION

Common statistical procedure in various scientific fields is determining of the best fitting theoretical probability distribution for a certain set of data. In hydrological research usual objects of such statistical calculation are different time series - characteristic discharge (minimum, maximum, average), groundwater level fluctuation, daily-to-yearly precipitation, etc. Which probability distribution would describe best certain set of measured hydrologic data is controlled by numerous factors varying from place to place. However, particular functions showed to be appropriate for some characteristic hydrologic values (Jovanovic, 1981): the Poisson distribution for describing of rare occurrences such as long-lasting dry or wet periods; the geometric distribution for the analysis of drought or rain episodes; the Gumbell distribution for the analysis of extreme discharges or very short precipitation; Log-Pearson distribution for the probability analysis of maximum discharges etc. After the study of minimum discharges of numerous karstic springs in Serbia (Yugoslavia), Kresic and Kukuric (1987), Kresic (1989) and Kresic et al. (1990a,b) concluded that the best fitting probability distribution for the absolute minimum discharges during summer months is Log-Pearson type 3.

The basic requirement for the correct statistic analysis is the sufficient number of data (i.e. at least 30) and testing of the obtained empirical probability function by several tests - commonly chi-square, Student's (t-test) and F test.

## REGRESSION ANALYSIS

Connecting of measured hydrologic data of different time series that represent behavior of a certain karst hydrogeological system by linear or nonlinear regression is common in karst research.

Though nonlinearity of karst aquifer processes is evident, linear regression is more often applied for its relatively simple calculation. Moreover, when nonlinear approach is chosen, the establishing of corresponding equation is usually performed through the linearization of its predictor variables (e.g. by logarithmic transforms) thus having the same calculation procedure (Draper and Smith, 1966). The general equation of multiple linear regression has the following form:

$$y_t = b_0 + b_1X_{1t} + \dots + b_kX_{kt} + \epsilon \quad (5)$$

where  $y_t$  is the dependent variable (e.g. spring discharge or groundwater level) on a set of  $K$  independent variables called predictors (e.g. precipitation, air temperature etc.) at time  $t$ , while  $\epsilon$  is random variable. Coefficients  $b_0$ - $b_k$  are evaluated by means of least squares.

Simulating the water table response in the Vryburg area (S. Africa), Hodgson (1978) proposed introduction of the autocorrelation coefficient  $\lambda$  into equation (5) which would approve the usage of regression in defining of a stochastic process:

$$y_t = b_0 + b_1X_{1t} + b_kX_{kt} + \lambda y_{t-1} + \epsilon \quad (6)$$

With the same idea of overcoming the limitations caused by using of physical measurable-only parameters in defining of stochastic process, such as outflow of the enclosed karst polje ( $Q_0$ ), Zibret and Simunic (1976) introduced two non-physical predictors - index of previous precipitation ( $I_{pp}$ ) and seasonal parameter  $M$  (i.e. disordered number of month);  $H$  is level of polje retention:

$$Q_0 = A_0 + A_1H + A_2M + A_3I_{pp} \quad (7)$$

Among other statistical methods, Kovalevsky (1977) and Zaltsberg (1984) presented the application of regression analysis in forecasting of karstic water regime. Multiple regression model based on wide autocorrelation and cross correlation analysis of used variables, served to Houston (1983) for simulating of water level fluctuations of the well field developed in dolomitic limestone aquifer (Kabwe, Zambia), as well as for forecasting of Broken Hill mine discharge rates.

The possible procedures for selecting the best regression equation, i.e. the proper predictors, are: (1) All possible regressions, (2) Backward elimination, (3) Forward selection, (4) Stepwise regression, (5) Two variations on the four previous methods,

and (6) Stagewise regression (Draper and Smith, 1966). Highly crosscorrelated independent variables should be avoided.

## KERNELS (CONVOLUTION)

Precipitation, as the primary source of system recharge, is transferred to groundwater level and system recharge in a damped form as a consequence of passing through many subsystems (i.e. surface retention, snow pack, infiltration, soil-moisture storage etc.). Some of the factors that influence system input-output processes are shown on Fig. 6 (Adamowski and Hamory, 1983). The theory of unit hydrograph, established by Sherman (1932, 1949) has been widely applied and improved by surface hydrologists (see Dooge, 1959, 1973). Primarily with an analytic hydrologic approach, the theory has soon served as a basis for the so-called input-output or black-box approach to system analysis, which mathematically describes system input-output processes without considering their physical background (Canceill, 1974).

Assuming karst hydrogeological system as linear and time-invariant (stationary), its behavior may be described by the following convolution integral:

$$y(t') = \int_0^t h(t-t') x(t') dt' \quad (8)$$

where  $y(t')$  is the continuous system response,  $x(t')$  is the input series, and  $h(t-t')$  is the kernel function or the linear unit-response function (Dooge, 1973; Canceil, 1974; Fig. 7 (Dreiss, 1989). However, since the absence of linearity and time-invariance of a karst system is evident (e.g. doubled precipitation intensity would not automatically cause doubled discharge, and the effect of rain is not the same during a year), the optimum kernel function is identified in various ways such as parametric smoothing, defining of effective precipitation for the system input etc. (Neuman and Marsily, 1976; Marsily, 1978; Dreiss, 1982).

To avoid an obvious consequence of convolution, i.e. that in the case of long-lasting dry period which has the base wider than that of unit response, the calculated discharge becomes zero, Canceill (1974) suggested the following equation modified according to (8):

$$Q_t = \int_{-\infty}^t h(t-t') x(t') dt' + C_k e^{-\infty(t-t_k)} \quad (9)$$

where the second member represents the limit with decreasing power,  $t_k$  being the last date with precipitation of non-zero efficiency.

By including in convolution integral index  $p$  that has time fluctuations following the characteristics of the system stage evolution, Poittrinal (1974) improved the model for simulating Vaucluse karstic spring discharge (Fig. 8).

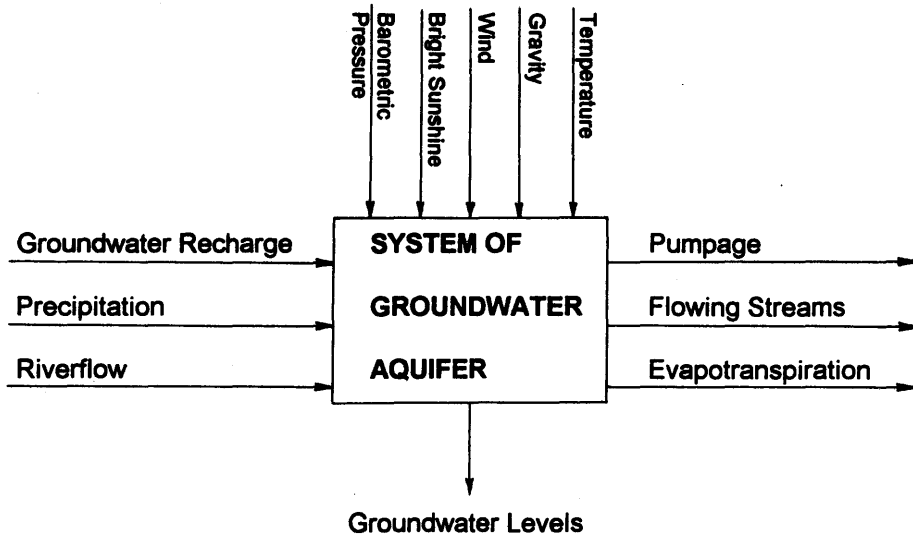


Figure 6. Input-output view of groundwater hydrology (Adamowski and Hamory, 1983).



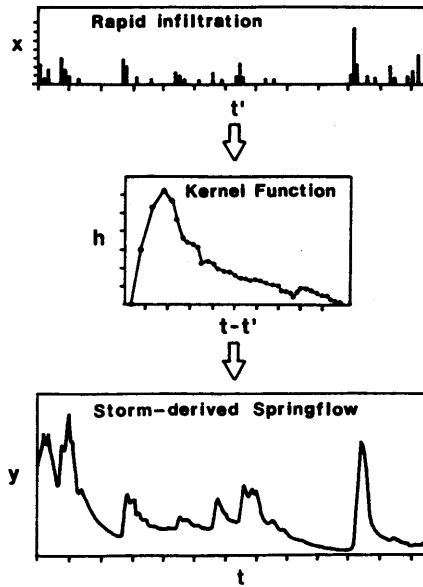


Figure 7. Schematic diagram of linear systems analysis of karst-type spring flow (Dreiss, 1989).

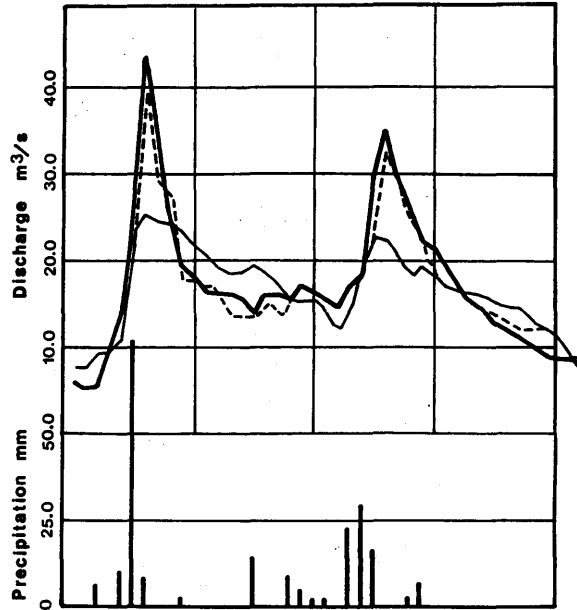


Figure 8. Fontaine de Vaucluse karstic spring - Example of adjustment obtained for the period used for the calculation of impulse response. Bold line: measured discharge; Fine line: first adjustment; Dashed line: adjustment obtained by using into consideration the direction of flow evolution. Time interval is 5 days (Poitrinal, 1974).

## STOCHASTIC MODELS OF TIME SERIES

Time series approach to quantitative karst hydrology has been increasingly applied, while it is already the most widely used in mathematical modelling of surface rainfall-runoff hydrology. Stages in the analysis of time-series models have been developed by Box and Jenkins (1976, 1970 first ed., after Houston, 1983) and are:

- (a) Hypothesis of system structure
- (b) System identification
- (c) Parameter estimation
- (d) Checks of model fit

It is usually assumed that the process (system) studied is linear and stationary, with the transformation of rainfall (input) to runoff (output) controlled by certain attenuation and delay, and influenced by a stochastic random component or noise.

The stage of system identification necessarily involves estimating the order of the autoregressive and moving average components, as well as obtaining approximate initial estimates of the parameter values (Weeks and Boughton, 1987). Namely, autoregressive character of the time series is presented by the fact that fluctuations in groundwater level or spring discharge are dependent upon antecedent corresponding values. This dependence upon prior conditions is studied by autocorrelation, and if autoregressive terms are dominant, the stochastic model may be built solely of these elements (Houston, 1983). Such model is called **Auto-Regressive (AR)** with the order defined by testing the significance of autocorrelation function (Box and Jenkins, 1976; Graupe et al., 1976). **Moving Average models (MA)** describe the delayed response of the system (e.g. karst aquifer) to inputs (e.g. rainfall). Their significance is studied by cross correlation between inputs and outputs. Combination of AR and MA models gives **ARMA models (Auto-Regressive Moving Average)** which are used in many different hydrologic analyses. A detail study of ARMA models is of great importance in karst hydrogeological system research. The general form of ARMA model is (Weeks and Boughton, 1987):

$$y_k = a_1 y_{k-1} + a_2 y_{k-2} + \dots + a_r y_{k-r} + b_0 u_{k-1} + \dots + b_s u_{k-s} + v_k \quad (10)$$

where

- $y_k$  = output (discharge) at time  $k$
- $u_k$  = input (rainfall) at time  $k$
- $a_i$  = auto-regressive parameters (total of  $r$ )
- $b_i$  = moving average parameters (total of  $s + 1$ )

ARMA models, as well as AR and MA models, are based on the assumption that the system modeled is linear and stationary.

However, most hydrologic processes, including rainfall-runoff, have certain periodicity or trend and such seasonal time series have to be deseasonalized before nonseasonal ARMA model is fitted to the data. Analysis by Fourier series and various other identifications of periodicity (harmonics) in time series have been applied so far; see e.g. Fig. 9 (Knisel, 1972; Adamowski and Hamory, 1983). The most common, however, are (1), subtraction of the seasonal mean, and (2), subtraction of the seasonal mean and division by the seasonal standard deviation (Thompstone et al., 1987). Effects of incorrectly removed periodicity in parameters on stochastic dependence have been studied in detail by Yevjevich and Obeysekera (1985).

A good example of the application of ARMA model for predicting of runoff from karstified catchments was presented by Graupe et al. (1976). The authors also described the use of Kalman filtering (see Kalman, 1960) for improving the stochastic model.

After comparing the reliability of ARMA and PAR (Periodic Auto-Regressive) models fitted to three monthly hydrological series, Thompstone et al. (1987) stressed the advantage of the former one. Namely, PAR models attempt to preserve seasonally-varying autocorrelation structure by fitting a separate and different autoregressive (AR) model to each of the season of the year.

Stochastic models, when properly fitted, are a very good tool for forecasting natural behavior of time series. They are also invaluable for generating the system output (e.g. spring discharge) on the basis of measured inputs (e.g. rainfall) and further probability analysis of simulated characteristic data, e.g. minimum spring discharge (see Kresic et al., 1990a).

## HYDROGEOLOGICAL METHODS

### *Pumping Test*

Pumping tests were the first and are certainly the most used methods for determining major quantitative characteristics of an aquifer such as hydraulic conductivity (permeability), transmissivity and storage coefficient. Their methodology was developed basically on assumptions about homogeneity, i.e. intergranular nature of aquifer porosity, and it should be well known to all groundwater specialists (e.g. see reference books: Wenzel, 1942; Todd, 1959; Bear, 1979; Rushton and Redshaw, 1979).

The first attempts to apply pumping tests in karst hydrogeology were made on the basis of modifications developed in study of flow in fissured media, mainly for petroleum industry purposes. Such fissure approach was roughly divided in two directions: (1) presentation of aquifer by systems of discrete fractures (Fig. 10), which requires detailed information on fracture apertures, density, orientation and connectivity, and (2) double porosity approach where fractured medium and the

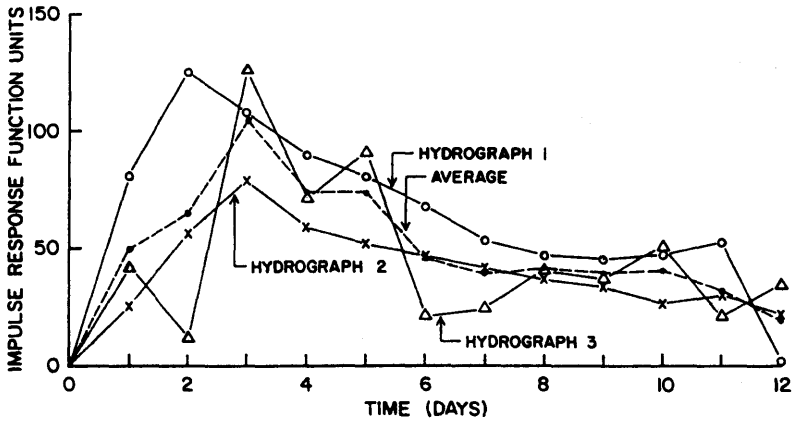


Figure 9. Impulse response function ordinates from autocorrelation and cross-correlation functions. Goodenough Springs near Comstock, Texas (Knisel, 1972).

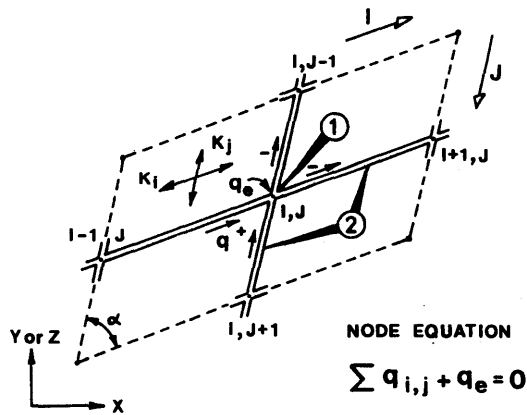


Figure 10. Basic element for the simulation of 2D flow in fissured media. (1) I,J intersection node; (2) Real or fictive fractures with the hydraulic conductivities  $K_i$ ,  $K_j$  (Louis, 1974).

porous matrix blocks are studied as two separate overlapping continua, each with its own flow equation (Sauter, 1990).

Though karst aquifer by no means should be considered as discrete fracture model, certain interest for the background theories may arise during recent and future combined approaches to modelling groundwater flow in karst (e.g. see Snow, 1966; Louis, 1974). The major objection to fissure approach is that assumption on linear (non-turbulent) flow in discrete fractures can easily be rejected in the case of karst aquifers - what to do with large karst channels, i.e. caves (see e.g. Fig. 11). However, in certain cases, when karstification is not so intense, an equivalent study based on anisotropic porous medium model may lead to satisfactory results (Papadopoulos, 1967). Considerable improvement in fissure approach may arise from stochastic and geostatistic study of aquifer inhomogeneities (Sagar and Runchal, 1982; Razack, 1984; Long and Witherspoon, 1985; Neuman, 1987; Anderson and Dverstorp, 1987).

Double porosity model has been much more applied both in fissured and karstified porous media. Proposed by Barenblatt et al. (1960) the concept has been constantly improved by numerous authors (Rofail, 1967; Streltsova, 1976; Duguid, 1977; Moench, 1984; Binsariti, 1985). In Streltsova's approach the drawdown in the system caused by radial flow toward pumped well is the function of the drawdown in the fracture, drawdown in the adjacent rock block, time and the radius of the well. Binsariti (1985) extends the theory for unsteady radial flow to a pumped well in a fissured confined aquifer by combining the effects of elastic deformation of the porous blocks with the elastic deformation which takes place in the associated fissure space.

A situation often present in karst, i.e. when homogeneous aquifer is bisected by a fracture having the permeability sufficiently large so that its ratio to the aquifer permeability approaches infinity, is studied by Jenkins and Prentice (1982) and Zekai (1986). Under such condition flow in the aquifer is linear toward the fracture which, thus, may be considered as an extended well. From the data of at least two observation wells location of a concealed fracture and hydraulic diffusivity of the linear karst aquifer system may be determined (Jenkins and Prentice, 1982).

### ***Water Permeability Test (WPT)***

Similarly to the problems occurring with the application of pumping test, WPT limitations are evident in the case of karst aquifers. The effect of scale on uncertainty of the obtained parameters is here the most obvious, since the methodology developed in fissured media completely fails when water is injected into e.g. karst channel with practically infinite permeability. However, the application of water permeability test in karst regions is sometimes invaluable for defining of relative permeability relations between portions of an aquifer. Moreover, during the studies of dam sites and artificial reservoirs in karst WPT is the obligatory procedure for the

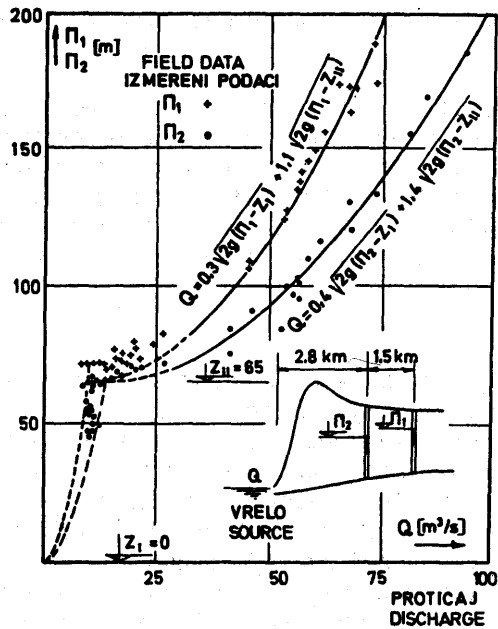


Figure 11. One example of the square law of resistance (flow) in karstic environment. Ombla Spring near Dubrovnik (Hajdin and Ivetic, 1976).

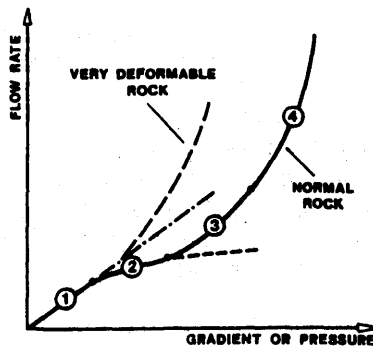


Figure 12. Typical results of field water test. (1) Laminar flow; (2) Turbulence effect; (3) Turbulence offset by fissure expansion; (4) Predominance of fissure expansion effects (Louis, 1970).

quantitative defining of possible water losses, economic design of watertight curtains etc. (Borelli and Pavlin, 1967).

Established by Lugeon in 1933, and thus often called Lugeon test, it has been widely applied particularly by geological engineers for the various construction purposes. Fig. 12 illustrates the possible responses of the fissured porous media to WPT. Detail presentation of WPT background and interpretation of the obtained results may be found in the works of Louis and Maini (1970), Louis (1974), Attewell and Farmer (1976), Houlsby (1976), Pearson and Money (1977) and Castany (1984).

### ***Numeric Models***

Though karst hydrogeological systems are widely spread throughout the World with the rapidly increasing man-made changes in karst environment, numeric models which provide powerful tool for groundwater management, still have not been applied in karst studies with a satisfactory extension. One of the main reasons are difficulties occurring during the preparation stage of a model: above all uncertainties on aquifer characteristics (transmissivity, storage, piezometric level) which, even when correctly recorded, may not be generalized throughout the modelled area for its inhomogeneity. On the other hand, the stage of model calibration allows the modeler to correct numerous previously made assumptions and gives the important backward information on aquifer's characteristics.

As in "classical" field of numeric model application, i.e. intergranular homogeneous aquifers, two methods are the most widely used: 1) **finite-difference model (FDM)**, and 2) **finite-element model (FEM)**. The advantages of the latter one are flexible geometry (Fig. 13), which is important in karst studies because of the effect of scale, and high accuracy easily included, while disadvantages are the complicated programming and data input. FDM allows the modeler to use its intuition on karst nature freely and it has easy data input (because of regular grid) and the calculation procedure. The main disadvantage is, however, its often low accuracy.

Detail presentation of the stages and theoretical requirements in modelling karst groundwater systems is given by Kovacs (1986) and Sauter (1990).

Various attempts to overcome modelling limitations in karst caused by its inhomogeneous porosity have been introduced. Kiraly (1984, 1988) presented joint modelling of regional high transmissivity fault zones within the continuum (the examples are from Swiss karst). The obtained results made reasonable to "model the regional faults or karstic networks by 2-D or 1-D discrete zones, whereas the volumes between them (which contain only lower order fractures or channels) might be modelled by a 3-D equivalent continuum" (Fig. 14).

Cooley et al. (1986) presented a nonlinear regression model based on a Galerkin finite-element discretization which was applied in study of Madison karst aquifer flow (U.S.). Regression parameters estimated include intrinsic permeabilities of the main



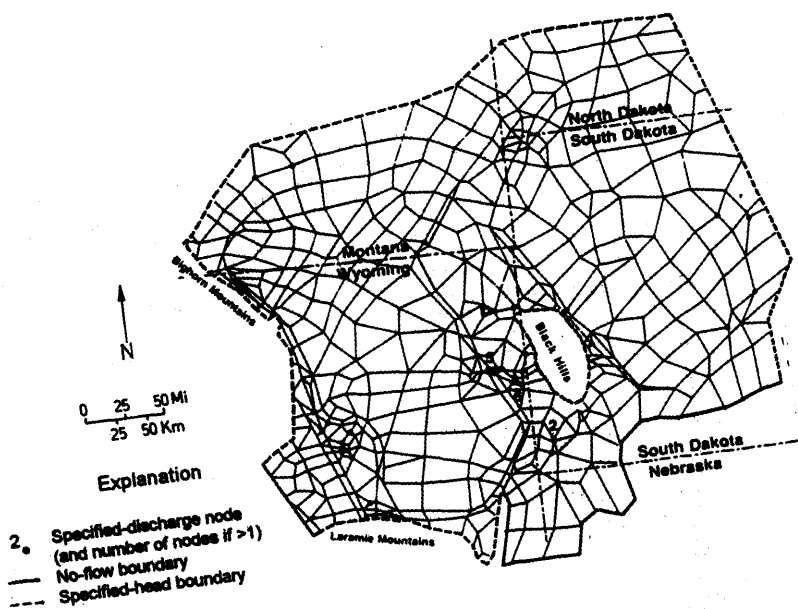


Figure 13. Finite-element grid showing boundary conditions and locations of specified-discharge points (Cooley et al., 1986).

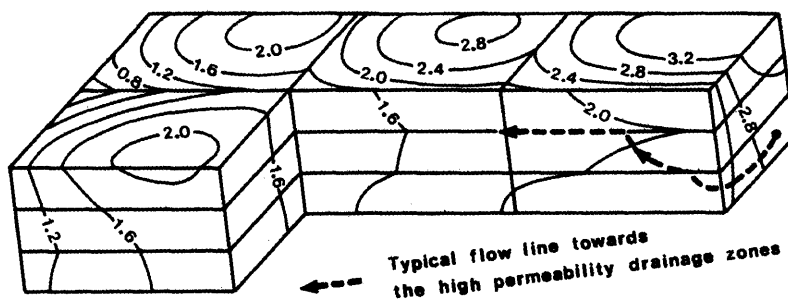


Figure 14. Calculated head distribution for a fractured block model (Király, 1988).

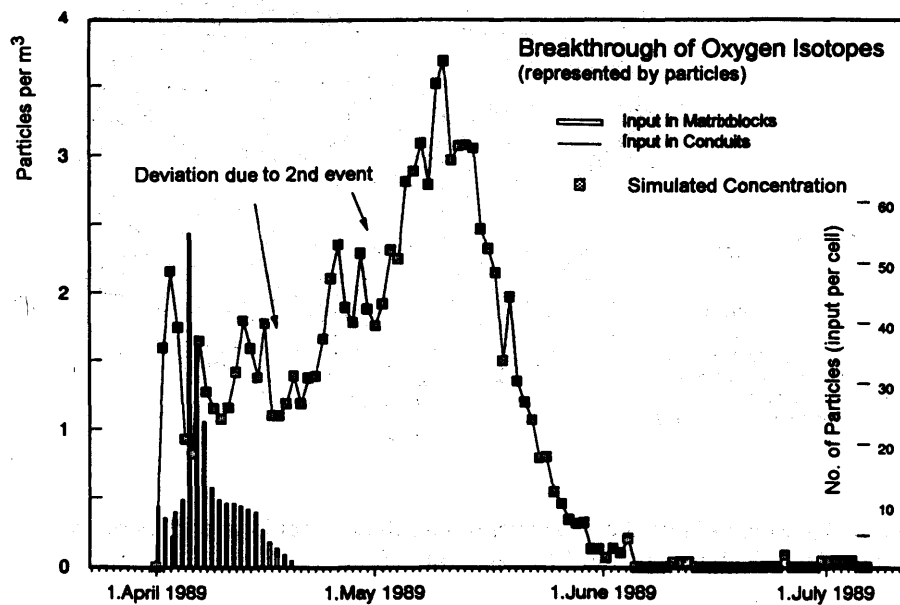


Figure 15. Simulated breakthrough of a regional tracer (Sauter, 1990).

aquifer and separate lineament zones, discharges from eight major springs and specified heads of the model boundaries, while aquifer thickness and temperature variations were included as specified functions.

Sauter (1990) introduced the complex "Double Continuum Ground Water Modelling approach in karstified limestone areas". Its model, applied in a karst aquifer in the Southwestern Germany, included time series analysis of rainfall events utilizing well hydrographs, spring discharge,  $^{18}\text{O}/^{16}\text{O}$  ratios, temperature, electrical conductivity and turbidity of the water. Quantitative distinction between the fast and the slow component of the storm derived water (i.e. inputs in matrixes and blocks - see Fig. 15) was made on the basis of  $^{18}\text{O}/^{16}\text{O}$  ratio, while further transport parameters were provided by tracer tests.

As a conclusion to this presentation of quantitative methods in karst hydrogeology, one may say that all should be applied according to current needs and not antagonized. This is particularly true in the case of stochastic and numeric models - they should be combined whenever possible providing the combined model in which the deterministic part will use stochastic approach to transform "gross inputs" into "effective" ones (which are often unmeasurable) and then serve as a powerful tool in management of groundwater quantity and quality.

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Surface geochemical exploration for microseeping hydrocarbons using biogeochemistry is described as indirect, low cost, and a first step in petroleum exploration. The method is based on the assumption that low molecular weight hydrocarbons seep to the surface and near-surface soil layers through faults and fractures. Their oxidation results in a reducing environment which can affect the solubility and mobility of redox sensitive trace elements and the alkaline earth elements in soil solutions. This process will result in the precipitation of the alkaline earth elements as carbonates, hence depleting the soil solution in these elements. Transition elements, on the other hand, will be adsorbed by the soil solution in the reduced form and taken up by plants. The study area is the Cave Canyon oil field located at the Paradox Basin, southeastern Utah. The plant species *Juniperus monosperma* (Utah juniper) and *Artemesia tridentata* (Big sagebrush) were analyzed for Zn, Fe, Mn, Cu, Al, Ni, Mo, Cd, Ti, Cr, Sr, B, Pb, V, P, K, Ca, Mg, and Na using inductively coupled plasma atomic emission spectrometry (ICP-AES). Statistical techniques were used to establish relationships among the different variables. These techniques include correlation analysis, analysis of variance, and factor analysis.

The elemental concentrations were contoured to investigate any relationship to petroleum production at Cave Canyon. Generally, the maps did not show a clear relationship to oil production. The pH of the soils along with the lack of any known major faults in the area were considered the two possible reasons for the absence of a relationship between biogeochemistry and oil production.

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Sinkhole density maps were constructed for the Forest City Quadrangle, Central Florida, and used for terrane evaluation. Earlier investigations showed that the study area has the highest frequency of new sinkhole collapses in the Orlando area. New sinkholes and old sinkholes were treated as subpopulations of the total sinkhole population in the area. The terrane evaluation is part of the geomorphological quantitative analysis of karst relief. A lack of correlation of old and new sinkhole densities eliminate it's application to sinkhole hazard predictions in thickly covered karst. This method could expand the data base for sinkhole-risk models and may be applicable to sinkhole risk assessment in thinly to moderately covered karst where old and new sinkhole densities do correlate, as well as in other land use and population distribution terrain evaluations.

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San Salvador Island is located on the eastern edge of the Bahamian Archipelago and is one of 29 inhabited islands which are part of the island nation of the Bahamas. The physical isolation of the island, inland saline lakes, karst topography, and vertical and lateral variations in bedrock permeability make it difficult to characterize the groundwater environment. Previous investigations have shown that the freshwater lens is partitioned by coastline irregularities, inland lakes, and eolian dunes into a number of distinct aquifers. Lens volume, chemistry, and shape are highly variable. The present study is an assessment of water quality and

distribution on San Salvador. Water samples were collected from wells and catchments, and a base line study was conducted to establish various physical and microbial parameters. Measurements were made of conductivity, pH, dissolved oxygen, and temperature. Microbial analyses were made of total coliform, fecal coliform, and fecal streptococci. Karst processes may be allowing the rapid subsurface dispersal of bacterial contaminants in what would otherwise be a fine-grained porous aquifer. In a few locations higher total coliform indicates occasional aquifer contamination by human waste.

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In 1988, a road was closed near Pont-Rouge due to a nearby collapse of the roof of an inlet tunnel leading to the McDougall hydroelectric powerhouse owned and operated by Domtar Inc. The almost uneconomical plant had to be closed down because of a massive influx of sediments, the presence

of trees in the tunnel and debris railings. This new sinkhole has given us insights in what geologic, geomorphologic and hydraulic factors were favorable to the initiation and development of such a phenomenon over the original karstic conduit (meander cut-off), partially excavated and protected during the 1927s powerhouse construction works. Topographic surveys of 1927, 1952 and 1988 have given us information on how and how fast the underlying dome has formed before the final collapse in May, 1989. In this part of the gallery, the top and roof of the wall are made up of very compact till, ice-pushed and folded limestone slabs, and blocks on a length of 40 meters. Because of the till's high compaction, no remedial work was suggested; rather a surveillance program was proposed and a geotechnical investigation was put forward to decide how the closed road should be moved.

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Karstic erosion of the land surface is controlled by processes occurring in the epikarstic zone--the upper portion of the limestone which is most intensely dissolved. Sinkholes developing today are generally the effects of downward movement of mantling sediment into the major karren shafts which drain the epikarstic zone deeper into the true karstic aquifer. Dissolution of the limestone itself does not cause significant changes in man's time frame. The downward erosion of mantling sediment is termed ravelling. Only in uniform sediment will an arched cavity occur. In unconsolidated sediment which is stratified, lateral tunnelling may even occur. Only the major karren can transmit sediment downward, the majority are ineffective. In mantled karst the location of surficial depressions and photo-linears does not necessarily correlate to areas of new collapse. The irregular and highly dissolved character of the epikarstic zone complicates foundation engineering. Downward drainage through this zone may be limited and cause flooding. An understanding of processes in the epikarstic zone is essential in developing on karst.

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The Middle Ebro Basin is characterized by strong evaporitic profiles from the Miocene period, and in which gypsum formations are predominant. These groups of easy solubility produce in many areas typically karstic landforms, although there are certain features specific to them. The generated landforms appear on the surface as different morphological types of doline, which very often develop on the alluvium deposited by the River Ebro and its affluents. On the agricultural land of the Peñaflo-Vilamayor area the functional character of karst causes collapse dolines to appear after heavy storms, and these are constantly filled in by farmers. Motorways and roads that cross these areas, as also the industrial estates existing on the outskirts of Zaragoza, are affected by dissolution processes that bring about continual collapses. The infiltration of water from unlined canals causes the generation of numerous dolines along canal banks.

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Agricultural activities have been identified as major nonpoint sources of pollution of water resources. Karst topography and drainage can present special concerns to farmers and other rural ground water consumers. Cropping and livestock operations can cause direct pollutant entry through sinkholes, or diffuse entry by leaching of nutrients, pesticides, bacteria, and other contaminants into shallow carbonate-rock aquifers, which are vulnerable to NPS contamination. Best Management Practices for cropland NPS control include conservation tillage, crop rotation, management of fertilizers and manure, and infiltration, however, may be detrimental in karst areas. For livestock and poultry operations, planned grazing, livestock exclusion, and hygienic management of waste from confinement facilities are beneficial. Land-use changes by urbanization of existing farmland presents a special challenge for those concerned for karst ground water quality.

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This study compares the sensitivity and resolution of seven geophysical methods in mapping a known ground-water contaminant plume. The seven geophysical methods are line current electrode (LCE), mise-a-la-masse (MAM), spontaneous potential (SP), ground-penetrating radar (GPR), horizontal electrical profiling (HEP), very low frequency (VLF), and loop-



loop electromagnetic conductivity (LLEM). Four alternative methods not commonly used in ground-water surveys (LCE, MAM, SP, and GPR) are compared to the three commonly used techniques (HEP, VLF, and LLEM). The aquifer at the test site consists of 1-3 meters of fine sand overlying silty-clayey sand and clay. Specific conductance data from twenty monitor wells outline a conductive plume created by injecting a saline solution into the aquifer. Highest fluid conductivities measured were 40,000 micromhos/cm. The seven geophysical methods are evaluated by comparing their ability to detect the conductive ground-water plume, an anomalous near-surface clay layer, and karst features. Geophysical data were collected on a 100x70 meter grid using a 10-meter grid spacing. Potential gradient anomalies from the LCE and MAM methods delineate the 500 micromhos/cm boundary of the conductive plume. Negative SP anomalies; up to -70 millivolts, occur over a sinkhole and a doline, apparently caused by the vertical movement of water. Sinkholes, depressions, depth to clay, and shallow stratigraphy were successfully mapped with the GPR method. Apparent resistivity anomalies from the HEP and VLF data occur over the area of near-surface clay. Terrain conductivity anomalies from the LLEM data detect the near-surface clay and part of the conductive plume. Finite difference modeling results indicate that the LCE method can detect an anomaly when a conductive plume overlies conductive clay only when the plume is more conductive than the clay. LCE field data indicate that the contaminant plume is more conductive than the underlying clay layer. The alternative methods were successful in mapping the conductive plume and sinkholes. LCE and MAM can be used to outline the edges of conductive plumes. SP and GPR can be used to map sinkholes. The commonly used methods mapped the near-surface clay.

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A survey of radon concentrations in 59 basements and crawl spaces within houses built on karst in the Highland Rim and Central Basin provinces of central Tennessee had a measurement range of 0.1 to 37.6 pCi/L with twenty-two percent of the measurements exceeding EPA's 4 pCi/L recommended maximum. Excepting the highest measurement, the population had an arithmetic mean of 2.6, a median of 2.2 and a standard deviation of 1.95. Although the Chattanooga Shale and lower rocks were poorly

represented within the survey compared to Fort Payne and Warsaw strata, the ranking of the means according to rock type was as follows: Bigby-Cannon (4.4 pCi/L), Fort Payne (3.4 pCi/L), Chattanooga (3.3 pCi/L), and Warsaw (1.6 pCi/L). The similarities between the means suggests that no single lithology other than perhaps the Warsaw was found to have a significantly different radon occurrence potential.

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Karst terrane is generally regarded as a fragile and vulnerable environment. Its underground drainage system can aggravate both drought and flood problems; the lack of filtration in an underground conduit makes waste disposal more difficult; and the lack of soil cover in bare karst land can enhance deforestation. Moreover, karst terranes are quite often haunted by a series of engineering problems, such as water gushing into mines or transportation tunnels; leakage from reservoirs; and failure of building foundations. In China, there are more than 200 cases of karst collapses, which include many thousands of individual collapse points. Some of these are paleo and natural collapses, but most of them are modern collapses induced by human activities and they have caused serious damage:

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A subsurface mapping project has been undertaken by the Hong Kong Geological Survey to study buried karst problems associated with an area of intense building activity in the New Territories of Hong Kong. The project has led to the identification of a volcanic breccia composed largely of marble clasts, which has unique weathering and karst characteristics. Steeply dipping breccia layers subcrop beneath Quaternary superficial deposits in a northeast-trending valley, which extends through northwest Hong Kong and into the Guangdong Province of China. Other rocks underlying the valley include Carboniferous marble, which is presumably the source of the clasts in the breccia. The breccia unit comprises the newly named Tin Shui Wai Member of the Upper Jurassic Tuen Mun Formation.

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St. Petersburg Beach, FL, Oct. 2-4, 1989: Netherlands; A. A. Balkema, Rotterdam, p. 107-113.

The karst developed in the Ordovician carbonates of southwestern Wisconsin contains several hundred sinkholes, in response to which landowners have adopted landuse strategies to minimize personal inconvenience and risk. Of 263 field-documented sinkholes, 75 percent are formed in the Oneonta Formation dolostones of the Prairie du Chien Group, and the remaining 25 percent are in the Platteville and Galena dolostones of the Sinnipee Group. Sinkhole densities are generally low, but often individuals are clustered on the tops and sides of interfluvial ridges between dry valleys. Although contemporary dissolution rates are low, sinkholes are currently forming at a rate of 5 to 10 per year. Most sinkholes are small, but locally they are a significant hazard to livestock and farm machinery. Contemporary landowner response includes avoidance, fencing and infilling. During the nineteenth century some sinkholes, particularly on the Platteville and Galena dolostones, were mined in search of lead ores.

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There is no doubt that the present level of productivity exhibited by the agricultural community cannot be sustained without the use of pesticides. The level of knowledge and concern toward pesticides occurrence in groundwater is only in its initial stages. The urgency to increase this awareness is being reflected in present legislation by the U.S. Government to assess the occurrences of pesticides in groundwater by the early 1990's. Mature karst areas, such as the Sinking Valley region of Pulaski County, Kentucky, are especially susceptible to non-point source contamination from pesticides. The open conduits and increased solutional permeability within the vadose zone create excellent avenues for leached chemicals to travel through. The karst swallet acts like a large drain

within this intricate plumbing system, and acts as a point of convergence for both surface and subsurface water. The swallet should be the most likely location to begin a study in a mature karst region. Shipp Swallet and its adjacent conduit system act as an upper level overflow for the main phreatic valley conduit. Precipitation falling on crops in the valley bottoms passes through the soil profile, into the subcutaneous zone, then into fractured bedrock and finally emerges as seeps or flow into the conduit system. The insecticide Methoxychlor was applied to the crops overlying the conduit system and was then monitored for its occurrence in the seeps and conduit water below. The seeps were monitored for at least a month prior to application and then for 21 weeks after application. Samples were analyzed using an electron-capture gas chromatograph for Methoxychlor, and an atomic absorption spectrophotometer for calcium-magnesium ion concentration. Standard water quality parameters were also determined on the sampled waters. The water quality results and ion concentrations were subjected to statistical manipulation which included lag transformations and cross-correlation. Estimated flow-through times for precipitation events were calculated and compared to Methoxychlor analyses results.

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Karst subsidence is a big problem in the Lehigh Valley, the portion of the Great Valley of the Appalachians that cuts diagonally from northeast to southwest across Pennsylvania. More than \$1,000,000 damage occurs each year with several single episodes exceeding \$500,000. In addition, groundwater pollution has endangered the productive aquifers

of the area. This paper is based on the premise that the best way to keep subsidence and groundwater problems from occurring is to stop them before they occur by placing karst concepts and safeguards in local zoning ordinances, comprehensive plans, and subdivision ordinances. Since few municipalities have zoning ordinances with karst precautions, a model ordinance was created for Lower Macungie Township in the Lehigh Valley in order to serve as a guide for other municipalities. The Lower Valley in order to serve as a guide for other municipalities. The Lower Macungie Township Zoning Ordinance of 1989 is an example of what can be done under Act 247, the Pennsylvania Municipalities Planning Code, in protecting an area from unwise building practices on karst features. The ordinance defines certain karst features, delineates major karst features on an official map, and sets up zones where construction may not occur unless geotechnical expertise can show that there will be no ill-effect. The onus of legality is thus moved from the government body to the developer. This ordinance can be used as a model for new and/or improved ordinances in other municipalities in Pennsylvania and other states.

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A dramatic sinkhole collapse measuring some 100 feet in diameter by 41 feet deep occurred suddenly in the Borough of Macungie on June 23, 1986. The sinkhole collapse resulted in a major disruption of traffic, utility services, as well as a major health and safety hazard. Continual growth of the sinkhole could have resulted in almost certain damage or loss to more than 17 residences adjacent to the sinkhole collapse. Stabilization and repair costs totaled some \$450,000 and

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A detailed investigation into the groundwater hydrology of the catchment of the Fergus River Springs, the largest subterranean catchment in the karst plateau of the Burren, Co. Clare, Ireland. The numerous water tracings undertaken

in the area reviewed and evidence to suggest that the extent of the basin is being extended via capture of cave streams.

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A national survey of natural underground cavities in Great Britain has been commissioned by the Department of Environment. A large natural cavity database (in excess of 10,000 records) is being collected and entered into a database held on a PC-based computer system which is linked to a CAD package to enable the information to be presented in plan format. The natural cavity types include not only those developed on soluble carbonate and non-carbonate rocks but also certain non-soluble rocks, as produced by the processes of dissolution, piping, erosion and cambering. Particular attention has been paid to cavities occurring in urban areas and those affecting infrastructure. The study has revealed general patterns of subsidence incidence, mechanisms, triggers and effects on existing and proposed surface development. The interaction of natural cavities with man-made cavities has also been explored.

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majority of new "difficult" and "household" sites were lined. Lining usually consists of infill by inert material up to the level of the highest water table recorded prior to disposal, followed by 1 m of clay, but variations in practice occur between different regional regulatory authorities. Significant groundwater contamination has only been reported from "difficult" and "household" waste sites. In some cases, rapid and gross contamination of adjacent springs occurred, while in others migration of contaminants appears to be by diffuse flow. In both situations regional geological structure is a strong controlling factor but aquifer heterogeneity is a major problem in prediction of contaminant movement. At present there are no national guidelines or requirements for site monitoring and this has lead to confusion and differences in practice. Boreholes and springs are employed at new high risk sites, but for the majority of sites, regular monitoring has only taken place after a pollution event has occurred. Tracing studies have been few and generally inconclusive.

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The Township of Clinton, New Jersey is underlain by solution-prone Cambro-Ordovician aged carbonate rocks. As the locale has been identified by both State agencies and regional planners as a prime population growth area, the township is the target of development pressures. As a result of the environmental awareness of the Township leadership, a lay, legal, and technical group prepared a geotechnically oriented Ordinance which mandates consideration of the problem of karst in a multi-disciplined, multi-phased investigation. The results of a developer's investigation are reviewed by the Township Planning Board and an experienced geotechnical consultant. To date, the Ordinance appears to function as intended, has been well received by the Township officials and generally accepted by the developers.

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Solution-prone carbonates are found in many Appalachian valleys. Once relatively ignored, their significance in many rapidly developing areas requires a plan of investigation not in accordance with conventional soil mechanics concepts. Preliminary investigations should start well in advance of typical site development planning procedures. Conventional

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A project in the north west New Territories of Hong Kong, undertaken by the Geological Survey of the Hong Kong Government, has provided geological maps at a scale of 1:5,000 of a region known as the Designated Area which is largely earmarked for new-town "high-rise" development. It has proved a complexly faulted area of Carboniferous metasediments associated with Jurassic and Cretaceous granites and volcanic rocks. The rocks have been faulted and metamorphosed and are now buried beneath a superficial cover of late Tertiary and Quaternary superficial deposits to depths of 80 m. Carboniferous limestone has been metamorphosed into marble and at some stage during the Tertiary was exposed to sub-aerial denudation resulting in extensive karstification with an epikarst zone some 10 to 30 m thick. This zone contains all sizes of solution features from widened joints to caverns 20 m high. The cavities contain clays, silts and sands, the dating of which is in progress. The

epikarst surface is highly irregular with a relief of some 60 m showing hollows which are interpreted as dolines. The maximum frequency of dolines coincides with the underlying Ma Tin Member of the Yuen Long Formation - a unit of particularly pure, white massive marble. The largest cavities also occur in this Member in close proximity to major structural lines of weakness often associated with intruded igneous rocks.

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The Far West Rand in the Transvaal Province of South Africa is the location of some of the world's largest gold mines. The area is underlain by dolomite which is sub-divided into a series of separate ground-water compartments by dikes. A policy of dewatering some compartments has therefore been adopted due to economic and safety considerations. The dewatering of the Gemsbokfontein Compartment commenced in 1986. Prior to this a field trial was conducted to assess the potential of grouting as a preventative geotechnical treatment for protecting an important traffic route against the effects of sinkhole development. During the field trial ground movements occurred as a result of the grouting.--Modified journal abstract.

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Throughout the last two years, dye tracing techniques have been used to delineate the subterranean pathways between sinking streams and springs in Putnam County, Tennessee. A portion of Putnam County is located on a sinkhole plain underlain by nearly flat-lying Mississippian carbonates. Over 300 sinkholes have been delineated from topographic maps. An earlier study (Mills et al., 1982) showed that approximately 25 percent of the sinkholes contained solid waste, organic fill, or were receiving sewage. This alarming information prompted the present study aimed at delineating the recharge areas to the springs. The three largest communities in the county (Cookeville, Algood, and Monterey) have experienced growth that has contributed to ground water contamination from a variety of sources such as leaky underground storage tanks, municipal storm water runoff, poorly treated and untreated wastewater, and acid mine drainage. The end product of the research is a map delineating the recharge areas for the springs in the study area. This map can be utilized for planning purposes, contamination remediation, and for emergency response to spills along Interstate 40 and state highways within the county.

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The use of ground modification techniques to treat sinkholes has advanced from remedial grouting after the problem has occurred to also encompass pre-construction site improvement. A range of techniques is available, including dynamic deep compaction, vibro-compaction, vibro-replacement, slurry grouting and compaction grouting. Each has merit for particular applications and has been closely monitored in the field. A description of each technique as applied to sinkhole remediation is presented and their relative advantages and disadvantages evaluated. Case histories covering each technique illustrate the growing awareness of the ability to pre-treat sites and thus greatly reduce the potential for future sinkhole subsidence. The range of options available permits the engineer to select the most appropriate solution for the site in question so that project objectives may be achieved in an efficient and cost-effective manner.

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Natural dissolution of Permian salt beds in the northern Texas Panhandle during late Cenozoic time has resulted interstratal karst, wherein sheet-like dissolution occurs in extensive areas beneath covering layers of nonkarstic rocks. A result of such

interstratal karst is the disturbance of overlying strata as they subside or collapse into dissolution cavities. A study of interstratal karst in the Permian Flowerpot salt in the vicinity of the proposed Palo Duro dam and reservoir was conducted to determine whether karst development is an ongoing process and whether any special construction was needed to accommodate the interstratal karst. The Flowerpot salt is 0-107 m (0-352 ft.) thick; it is at a depth of 180-335 m (600-1,200 ft.), but most of it already has been dissolved from most of the study area. The Flowerpot salt is totally absent from the well just northeast of the dam. Strata beneath the Flowerpot salt are essentially flat-lying and undisturbed, whereas Permian and Tertiary strata overlying the interstratal-karst areas in the Flowerpot salt are chaotic and are structurally low.

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Subsidence and collapse have occurred in surficial mantles of glacial, glaciofluvial, periglacial and alluvial origin that are widespread overlying karstified rocks in Tasmania. Sinkholes have formed in several areas within a few years of forests being cleared for pasture or by the timber industry. These sinkholes have probably resulted from increased water movement through the regolith due to decreased transpiration, coupled with the rotting of tree roots that formerly helped bind the regolith. Other sinkholes have formed at some road margins, particularly where culvert design is poor, and some of these collapses have damaged roads. Sinkholes that are probably the result of groundwater pumping have formed adjacent to a large limestone quarry. Because economic losses associated with individual sinkhole incidents have generally been comparatively minor, and because the incidents have been geographically dispersed, they have attracted little official attention. However, the individuals affected may suffer significant personal loss and the combined cost of karst-related land surface instability in Tasmania is probably significant.

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Induced subsurface ground movements in areas of pre-existing metastable ground conditions associated with natural solution features developed in Cretaceous Chalk bedrock can result in sinkholes at the surface. These ground conditions are potentially hazardous and may not, prior to surface development, be apparent at ground level. Man's activities in creating urban and infrastructure development tends to increase the incidence of subsidence. Unless the ground conditions are carefully investigated and the appropriate foundation solutions adopted severe structural damage and even a threat to public safety can result. The programme of investigatory works requires careful planning and close monitoring to ensure that all necessary data for design is obtained in a cost-effective manner and that the likely scope and nature of the problematic ground conditions are defined

at an early stage. Thereafter the foundation design options have to be explored to provide a safe economic answer and any further investigations tailored to optimize the solution(s). A methodology is proposed in which the use of desk study and hazard mapping assessment is used to provide cost-effective geotechnical data to aid in the development of foundation design options to overcome these problematic ground conditions associated with chalk.

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- This report is part of a state-wide project undertaken to define areas of carbonate bedrock that are susceptible to sinkhole development as well as those areas that have had a history of sinkhole occurrence. The primary use of the report is to serve as a source of background information for land development and foundation design to help avoid subsidence problems related to sinkholes. The nineteen maps are based on careful field and air photo examination to identify subsurface features that have some surface expression.
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The McMonnigal Limestone and Rabbit Hill Limestone of Lochkovian and Pragian (Lower Devonian) age are sediment gravity flows that are intercalated with basinal lime mudstones. Both units were deposited at the outer edge of the continental shelf in a silled basin complex (Matti and McKee, 1977, p. 181). The carbonate beds of the McMonnigal Limestone (Lochkovian) derived their sediment from a localized, geologically short-lived shoal-water environment atop the Toiyabe Ridge to the west. Turbidity currents and grain flows carried sediments down the eastern flanks of the Toiyabe Ridge into a shallow (>50 m), dysaerobic basin. The carbonate beds of the Rabbit Hill Limestone (Pragian age) had their source to the east in the shoal-water carbonate platform environment of the cratonic margin. The two lithostratigraphic units, occurring in adjoining tectonic blocks of the Ikes Canyon Paleozoic window, record a regressive-transgressive cycle in the Lower Devonian of central Nevada. An abundant and varied conodont fauna, ranging from eurekaensis to kindlei zone was recovered from the two units. This faunal succession corroborates the conodont zones established for the Cordilleran region, provides additional data regarding the ranges of the respective conodont zones, and permits biostratigraphic correlation. Ostracodes were also abundant and varied and morphometric analyses were completed for two beyrichiid ostracodes, Alaskabolbina sp. Berdan and Copeland, 1973 and Nevadabolbina obesita (McClellan, 1973). Both species display limited ontogenetic variability, and N. obesita displays limited stratigraphic variability.

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Many of the closed depressions found on, or near, the outcrop of the Chalk formation in England are dolines, or sinkholes, and have a significant impact upon engineering projects and the environment. These features potentially provide direct access of pollutants to a major groundwater aquifer, i.e., the Upper Chalk, and constitute a hazard to buildings and civil engineering works. In recent years, there have been many recorded cases of ground subsidence in Southern England, producing either steep-sided holes, up to 4 metres in diameter and depth, or shallow circular depressions with lower slope angles. These are considered to be associated with dissolution of chalk and the ongoing process of doline formation. Investigation of three sites in West Suxxex, between Chichester and Arundel, has provided an understanding of the subsidence mechanisms. There i strong evidence to suggest that voids exist within the Slindon Sand formation, resulting from the washing of the silty sand into solution pipes and fissures in the underlying chalk.

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Carbonate rocks of early Ordovician (Beekmantown) Age extend into northwestern New Jersey, where caverns and sinkholes occur in a number of areas. Construction of Interstate Highway 78 near Alpha, NJ, encountered problems associated with karst development in and around the Epler Formation, a fine-grained limestone that is not noted elsewhere in the state for cavern or sinkhole development. Engineering problems included gabion collapse, cracked concrete structures, undermined pavements, and tension cracks and collapse features at the surface. Problems were ameliorated by excavating to bedrock, and pouring or pumping grout into the cavities. Geotextiles were used to prevent washing out of fines in the grout. Ground-penetrating radar (GPR) was used to monitor the engineering solutions and to attempt to locate any sinkholes that were missed in the remediation process.

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Dynamic flow systems and transport of contaminants in karstic aquifers result from the actions of physical and chemical processes involving aqueous systems containing certain contaminants. These processes are elaborated, and pertinent mathematical and chemical equations are discussed, herein. Contaminant transport in karstic aquifers can be

mathematically expressed by the basic equations evaluated primarily for the flow in porous, highly permeable aquifers. The effects of advection, hydrodynamic dispersion, and dilution are elaborated as physical processes that effect the movement of contaminants through ground- water in permeable rocks. Physical and chemical mechanisms that govern contaminant movement and groundwater flow through fractured media are proposed as the basis of an approximate scenario of contaminant transport through karstified carbonate rocks.

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The El Cajon Project, completed in 1985, provides the necessary hydroelectric energy to relieve Honduras of the need for importing oil for generating purposes. Construction began in 1980 following nine years of effort that included a final feasibility study, field investigations, design, and procurement of the necessary financing. One of the major aspects of the project was the treatment of the limestone foundation that contained solution features and large caves. Because of the geologic relationship between the limestone and nearby volcanic rocks upstream, the geometry of the grout curtain is unique. The curtain, developed by grouting between adjacent galleries, begins at the dam, enters the abutments and then curves upstream to close against the volcanic rocks.

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The catastrophic flood of February 1986 in the polje of Cetinje, unrecorded in the 500-year long written history of the old Montenegrin capital, was an opportunity to examine some

specific features of the complex hydrogeologic system. Above all, it is the incompatibility of the epikarst and endokarst systems of karst aquifers, collectors-conductors, and groundwater reservoirs that causes a hydrological environmental impact on the polje in extremely wet (autumn-winter) periods of the year. This year's flood has indicated that this epikarst system, generally dry most of the year, has a relatively large water-receiving capacity, and that the deeper endokarst system has all attributes of a karst aquifer, much variable transmissivity and low storage capacity.

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The region of eastern Herzegovina and Dubrovnik coastal belt is one of the hydrogeologically and hydrologically most interesting regions of Yugoslavia karst. The main water course in the region is the Trebisnjica river, the largest sinking river in Europe. All the poljes in the catchment area are temporary flooded, hydrologically separated, and closed karst entities. Enormous quantities of available water are not evenly disturbed neither in the time nor in the space. The Trebisnjica Hydrosystem project uses the basic concept of total water regime organization and its multipurpose utilization. With the construction of seven dams, six artificial reservoirs, six tunnels (with total length, 57 km), and four canals (with total length 74 km) the natural regime of surface and underground waters has been completely changed. As a consequence of water regime disturbance, a lot of changes have been observed in the catchment area: changes in the karst aquifers; local changes of climate conditions; eolic erosion effect; influence on the karst underground and littoral belt; influence on the springs yield; influence on adjacent catchment area; pollution of karst aquifers and influence of storage reservoirs on seismicity--induced seismicity. This article presents influences observed after the first stage of hydrosystem construction.

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For 30 years a wood preserving company treated timber with creosote and pentachlorophenol, disposing waste to a three-acre unlined lagoon in a paleosink basin. This basin has been naturally filled with reworked Hawthorn clays and a thin veneer of sand. The lagoon is dependent on rainfall for its water supply. A thick layer of creosote sludge had accumulated in the deepest part of the lagoon. Recent subsidence occurred along the west shore line of the lagoon. The upland areas are underlain by slightly sandy Hawthorn clays which contain extensive secondary fracturing. The Suwannee Limestone is encountered at variable depths and dips into the basin. The area is semi-artesian with regional groundwater flow to the south and southwest. Monitor wells were installed and geophysical techniques employed to determine the local geologic conditions. The monitor wells and residential wells were samples, no creosote products were found. Analysis of data indicated anomalies in the ground water levels and the stratigraphic column. Subsequently, additional monitor wells were installed. Sampling indicated no water quality problems. Because questions remained about ground water flow direction, sinkhole development and recharge, another level of geologic investigation was initiated. Split spoon samples were taken and the geologic information was mapped and interpreted. Based on the new information additional monitor wells were installed. When sampled, one of the two new wells and one of the old wells was found to have creosote products present.

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A 300 m deep monitoring well was completed to the Detroit River Group in Sarnia, Ontario, to evaluate potential near-surface impacts resulting from previous deep injection of industrial waste. Detailed logging, testing, and sampling were performed to evaluate vertical distribution of industrial waste and to determine hydraulic conductivity and hydraulic head in the disposal horizon and confining formations. Results indicate the hydraulic conductivity of the disposal formation is  $2 \times 10^{-9}$  to  $2 \times 10^{-7}$  m/s and that of most of the confining shale and limestone formations is less  $1 \times 10^{-10}$  m/s. Analyses of groundwater samples and results from other studies show that industrial waste, characterized by elevated phenol concentrations, is present in a 10 m horizon in the Lucas dolomite disposal formation at 192 m depth. Waste is also likely present within 2-3 m thick, high-permeability limestone layers at 74 and 123 m depth in confining units of Hamilton Group. Because of generally low vertical hydraulic conductivity of the confining formations,



waste in the permeable limestone layers was likely introduced via poorly constructed disposal wells, cavern storage wells, or abandoned oil and gas wells. The hydraulic conductivity and hydraulic head data indicate the high pressures from injection into the disposal formation have dissipated. The head within the zone of residual contamination in the disposal formation is now 8 m below the level of the St. Clair River. The hydraulic data and chemical composition of the injected waste show that the discharges of tarry liquids on the bottom of the St. Clair River in 1984 and 1985 were not caused by upward migration or injected waste.--Modified journal abstract.

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Bowling Green, Kentucky is built upon a sinkhole plain and is almost entirely located within the Lost River Karst Groundwater Basin. Recharge of the aquifer predominantly occurs via sinkholes, sinking or losing streams, caves and storm water drainage wells. The existence of contaminants entered the aquifer led to concerns about groundwater contamination in Bowling Green. Fourteen contaminant levels and related parameters were monitored for fourteen months at four sites. Composite and grab samples were collected at (1) the Lost River Rise, the final resurgence of the Lost River which is the master subsurface stream that flows under Bowling Green, (2) By-Pass Cave, a tributary to the Lost River located in a commercial area, (3) The Lost River Blue Hole, located just upstream from the city and (4) Federal Well, located in a rural area three kilometers upstream from the Blue Hole. This investigation revealed that groundwater contamination is a more serious problem in the rural area south of the city near Federal Well end in the urban area near By-Pass Cave. Federal Well had the highest concentrations of cadmium, chromium, nitrates and total dissolved solids. By-Pass Cave had the highest recorded concentrations of silver, copper, lead, and microbiological constituents. All these contaminant levels were substantially lower at the Lost River Rise due to the more contaminated waters mixing with less contaminated waters, thus reducing overall concentrations. Therefore, the Bowling Green area has nonpoint source groundwater contamination problems at some specific locations. However, when the overall picture is viewed, contamination of the Lost River under Bowling Green is not that substantial, primarily because of the dilution of contaminants by water from the entire groundwater basin.

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ridge. Regional and site-specific numerical simulations indicate that leakage from lakes to the Floridan Aquifer occurs under the majority of geologic settings typical of the study area. Regardless of the presence or absence of fractures and other high permeability conduits associated with solution or subsidence features. In particular, leakage through the lake bottom can be expected to occur where: the anisotropy ratio ( $K_h/K_v$ )  $\leq 100$ , the hydraulic gradient  $\leq 0.02$ , or a water table mound is absent on the regional downgradient side of the lake.

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The Bhandar Limestones of the Vindhyan Supergroup (Precambrian), exposed around Rewa in northeastern Madhya Pradesh, Central India, show excellent development of sinkholes (dolines) of various shapes and sizes. They are commonly funnel-, bowl-, trough-, oval-, and irregular-shaped. The diameter of the dolines varies between 0.40 m and 10 m with a depth up to 2.5 m, and the surface area between 0.33 m<sup>2</sup> to 80 m<sup>2</sup>. Density of the dolines varies from 20 d/km<sup>2</sup> to 1550 d/km<sup>2</sup>. Sinkholes in the area are mainly solutional and collapse types. Solutional sinkholes have formed primarily due to pronounced karstification of limestones around some favorable points, generally at the intersections of joints, while collapse sinkholes are the product of cavities lying near the surface. Those areas where sinkholes are well interconnected have been identified, and it is suggested that non-disposal of the industrial and municipal effluents in such areas would prevent groundwater pollution, ensure fresh water supply and maintain aquatic environmental balances in the area.

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Virginia's Valley and Ridge Province consists of 24 counties on the western edge of the Commonwealth. Due to the karst/limestone geology that characterizes the region these counties share a common vulnerability to their ground water resources. Karst aquifers are among the most sensitive to disturbance and are readily contaminated. One of the most

visible and obvious sources of contamination is the dumping of trash and waste into sinkholes. Botetourt and Rockbridge Counties, the areas which were the focus of the research, have thousands of sinkholes within their boundaries. The possibility of contamination to local ground water is great due to the presence of household hazardous waste dumps. A total of 260 illegal dump sites were documented in the study area, with 75% of these existing in karst areas. Approximately 23% of the illegal dumps were in sinkholes. More than 90% of the population of the study area takes their water from wells and springs. The research has concentrated on an effective methodology of locating and assessing potentially dangerous sinkhole dump sites. The project has documented these techniques allowing other counties in karst terrain to obtain similar results. A slide show and video are also being produced to show local schools and citizen organizations the hazards associated with sinkhole dumping. The results of the research underscores the need for local governments to play an active role in the areas of waste disposal, land use, and protection of ground water quality in their critical karst areas.

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The well developed karst commonly causes the limestone terrains lack of surface water and very dry, while the abundant underground water is not adequately used. Recent decades, a lot of subsurface reservoirs and hydropower stations have been built in South China. The underground reservoirs are constructed predominantly in the locations of karst geomorphology: (1) the connecting between fengcong depression and fenglin basin. It is the monoconduit pattern of reservoir and characterized by the small capacity and big regime; (2) on the monoconduit in the block between two basins with the hydraulic connecting as the Wangou reservoir with small regime and high capacity for water storing in the network of karstic fissures and conduits under the basin in the upreaches; (3) at the topwindow of the underground river in fengcong region. The capacity of storage is rather small but with high gradient that is good for generating like Beiyan underground reservoir and hydropower station; and (4) when the emergence of underground river on the limestone cliff, the dam may be built just up the resurgence to form the reservoir generally for irrigation and power station. Usually, the dam of the reservoir is built on the underground river up the knick point of the resurgence.

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The study area is Xichou County of Yunnan Province. The limestone, dolomitic limestone and dolomite with total thickness of 4000 m occupy 72.3% of the total area. Under the function of Yenshan Movement, the carbonate formations have been revolved, folded and fractured. They distribute as the shape of an "ear" striking from NW to NE and EW. The funnels, sinkholes, depressions, stone teeth, fengcong extensively develop in the area. As the clastic rocks distribute besides the carbonate rocks and the surface rivers develop in the southwest and northeast, the middle region of carbonate terrain forms the watershed. The karst geomorphology is characterized by (1) the large depressions distribute in the waterdivid region and the small one in the two ends of the "ear"; (2) the surface rivers deeply cut down about 200-300 m, the depressions by the river valleys are more than 100 m deep in the northeast, but the rivers in the southwest are shallow, the depressions about 50-100 m deep; (3) the long axes of the depressions and fengcong in the central zone of the carbonate terrain coincide with the geological structural line as the shape of the "ear", but in two zones of sides that are vertical to the carbonate terrain boundary; (4) the dimension of depressions in pure thick limestone is larger than that in dolomitic limestone; (5) in the watershed area, the uplifting of earth's crust causes the rejuvenative fengcong-depressions, while the relic fenglin-plain still remains in the watershed area.

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Several aspects of the urban geology of Kuala Lumpur are discussed. The topics of discussions range from problematical soils to foundations in limestone as well as landslides in hilly terrains. Problematical soils comprise mine tailings, municipal wastes and the collapsed soil zone above limestone bedrock. They are characterized by very poor engineering properties and have been responsible for various incidences of ground settlements and failures. Foundation problems in limestone are attributed to the various solution features that are inherent and are especially well developed in tropical karst, namely the pinnacled bedrock profile, cavities, overhangs, thin limestone slabs and boulders. Landslides in hilly terrains can be related to various geologic features such as the nature and orientation of the rock joints, the soil-rock interface, the thin residual soil cover, seepage and the grades of weathering. The influence of grades of weathering on various physical properties of the rocks are also discussed. The various topics of discussions are illustrated with actual examples or case histories.

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Sinkholes can have a significant impact on the ground water flow characteristics of a confined/unconfined aquifer system. This is particularly true in the Floridan Aquifer system in Central Florida. Most of the sinkholes in this area breach the confining unit between the surficial and Floridan Aquifers and thus provide a mechanism for large quantities of water to flow between the two aquifers. From a regional perspective, the sinkholes provide for a major source of ground water recharge to the Floridan aquifer which can increase water levels miles away. Locally, sinkholes cause a depression in the water levels of the surficial aquifer. Therefore, when and how to represent sinkholes is an important consideration when modeling ground water flow in sinkhole terrain.

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The investigation included a karst hydrologic inventory, construction of a potentiometric map of the upper karst aquifer and seventeen dye tracer investigations. Two main subsurface flow routes were identified in the upper part of the drainage basin. These cave streams merge downstream to form the subsurface/surface Overall Creek. A spill or leak of hazardous materials on the site could contaminate the groundwater for as much as 15.5 kilometers (9.7 miles). A groundwater monitoring and emergency containment system was recommended. It included continuous monitoring instrumentation located in the cave stream under the Campus Complex. Groundwater contaminated by a spill would be detected and immediately pumped into a retention basin located on the surface for treatment before being released back into the groundwater system.

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Six springs in the karst region of South-Central Indiana are analyzed for both water chemistry and sulfur isotopes during a water year (June 1986 to April 1987). Trends in chemical parameters are plotted against both time and discharge in an attempt to understand hydrologic controls. Two springs (Pluto 1 and Trinity) have constant chemistry unrelated to discharge. Pluto 2 and White River Fresh vary significantly in chemical concentration and isotopic signature, but not in relationship to discharge. White River Brine and Orangeville Rise have variable chemistry which, can be correlated to discharge. Beds of anhydrite and gypsum in the lower St. Louis Limestone (Mississippian), as well as a regional dip to the west-southwest, are considered to be major controlling factors on flow and water chemistry. A model based on this site-specific information is proposed to explain observed chemical trends. The degree of variation in a spring's flow path, the depth of flow within the St. Louis Limestone and the contributions to flow from variable sources (i.e.--mixing) are proposed as reasons for hydrochemical variations.

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- Before risk assessments for sinkhole damage and indemnification are developed, a database must be created to predict the occurrence and distribution of sinkholes. This database must be evaluated in terms of the following questions: (1) are available records of modern sinkhole development adequate, (2) can the distribution of ancient sinks be used for predictive purposes, and (3) at what areal scale must sinkhole occurrences be evaluated for predictive and risk analysis purposes?
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A one-day discussion by nineteen geologists and engineers involved in assessing the safety of dolomitic terrain for township development, roads and railways on: (a) investigation techniques, (b) engineering geological characteristics of dolomitic areas affected by dewatering by mines as well as areas not being dewatered, (c) classification of terrain according to risk of sinkhole formation/subsidence. (summary J.R. Vegter).

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A new classification system to delineate zones with different degrees of risk of sinkhole formation is proposed for use in dolomitic areas. A dolomite terrain is subdivided by using surface information, drainage history and gravity data. A drilling programme follows from which the information obtained is used to classify the terrain into sinkhole risk zones.

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Precambrian dolomitic strata outcrop over 2900 km<sup>2</sup> in the Transvaal and Northern Cape. Dykes of different ages and trends have compartmentalized the carbonate rocks in more or less separate ground water units. In the Southern and Western Transvaal mainly, karstified dolomite is overlain by extensive patches of residual solution debris and younger sediments. The solution debris and the underlying zone of leached dolomite constitute the aquifer.

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Much of the Maya civilization in the pre-Columbian Meso-America was established on karst terrain that included parts of what are now Belize, Guatemala, northern Honduras and southern Mexico. By definition, little surface water exists in karst, so for the Maya to flourish on that terrain they had to effectively and efficiently utilize all their water resources. Access to groundwater was by means of springs and caves. Maya groundwater retrieval methods were primitive, inefficient, labor intensive, and uninnovative, as compared to their other technologic achievements. Groundwater contamination, from human effluent, could have resulted in widespread disease and contributed to the Maya's downfall.

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A large number of karstic structures and cavernous zones occurring in calcareous formations of lower Cuddapahs and Kurnool of Proterozoic period are reported from the southwestern portion of Cuddapah basin, Andhra Pradesh, India. The most important finding of the geological, (structural, geomorphological) and geophysical (geoelectric resistivity sounding, profiling, total magnetic intensity and shallow seismic refraction) studies is the close correlation of the levels of cavernous zones with planation surfaces. Similar

observations were made in Japan, UK, USA, Canada and Africa. Such correlation appears to be a global phenomenon. It appears that the eustatic movements which occurred during the Quaternary period might have played a significant role in causing karstification of carbonate rocks of this area.

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Cavernous limestone creates engineering difficulties only in isolated cases in Britain, as little of its outcrop is in areas of extensive development. Less cavernous rocks have caused more widespread hazards: failures on the chalk are common but are generally small except for some dramatic collapses

associated with old mines. Major subsidence in the Cheshire saltfield have largely ceased due to the reduction in brining, while sandstone caves in Nottingham have been conserved beneath buildings which bridge them. Research on the Yorkshire limestone karst includes mapping of caves and sinkholes which suggest that studies of their distribution and correlation are of limited value to engineering predictions of failure sites. More applicable are preliminary results from model testing of cave roof stability; the importance of bedding and jointing is demonstrated, but many caves only have a major influence on ground bearing capacity where their width approaches or exceeds their cover thickness.

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The first part of the paper discusses the importance of understanding the local context in which the intervention is being implemented. This includes a thorough understanding of the community's culture, values, and beliefs, as well as the social and economic structures that shape the community's life. The second part of the paper describes the design of the intervention, which was based on a combination of community-based participatory research and evidence-based practice. The third part of the paper presents the results of the intervention, which showed that the intervention was effective in improving the health and well-being of the community. The fourth part of the paper discusses the challenges and lessons learned from the intervention, and the fifth part of the paper provides a conclusion and recommendations for future research and practice.

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1794	1967			
Herzegovina				
1409	1424	1633		
Kvarner Isl.				
1351				

**Yugoslavia, continued**

**Postojna**  
1128

**Sarajevo**  
167

**Serbia**  
378 1130 1133 1422  
1583 1604 1639 1953  
1954 1956

**Slovenia**  
260 516 517 679  
736 737 738 739  
740 741 742 743  
744 745 746 747  
748 749 750 751  
772 773 795 796  
797 798 799 800  
801 802 803 804  
805 806 807 808  
809 810 811 812  
813 814 815 816  
817 819 924 949  
957 958 959 964  
971 1087 1088 1089  
1090 1091 1092 1093  
1123 1124 1125 1126  
1127 1160 1172 1173  
1195 1208 1209 1210  
1335 1394 1395 1398  
1536 1537 1538 1556  
1619 1623 1635 1668  
1669 1786 1787 1788  
1789 1851 1879 1880  
1968 1978 1979 1980  
1982 1983 1984 2049  
2062 2065 2413

**Zagreb**  
197

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2052 392 437 1028 1445  
1559 1731

#### Construction

1318 1409 1410 1426 1444  
1572 1587 1731 2012 2328

#### Engineering Methods

107 220 262 393 481  
521 629 709 710 723  
766 780 839 843 875  
900 938 944 950 956  
981 1128 1197 1244 1321  
1341 1342 1372 1377 1444  
1460 1698 1701 1705 1706  
1707 1709 1710 1713 1716  
1718 1720 1723 1727 1750  
1751 1853 1875 1908 1913  
1918 1932 1934 2046 2064  
2068 2071 2088 2173 2175  
2184 2206 2218 2260 2340  
2346 2389

#### Flooding

751 1163 1374 1401 1438  
1439 1578 1971 2072 2228

#### Land Use/Resource Management

153 412 443 447 448  
450 451 452 453 454  
455 462 465 495 618  
763 794 836 846 947  
970 1032 1077 1103 1220  
1241 1247 1253 1254 1333  
1348 1425 1930 1977 2015  
2016 2063 2299 2396

#### Pollution

13 20 139 288 334  
357 483 602 604 608  
690 715 816 836 841  
964 997 1004 1151 1220  
1378 1411 1425 1489 1665  
1684 1792 1905 1921 1952  
2084 2216 2217 2335

#### Waste Disposal

537 603 690 938  
1645 1887 1960 2254  
2261

### Subsidence (Collapse)

11 142 198 204 206  
271 302 303 307 347  
495 496 498 519 538  
566 567 779 960 973  
981 1013 1014 1033 1043  
1048 1055 1242 1249 1355  
1368 1386 1449 1657 1719  
1907 2017 2018 2201 2204  
2309 2320 2327

### Urban Karst

478 1253 1871 1994

### Water Supply

3 31 135 167 257  
267 324 325 330 386  
387 397 501 502 544  
549 550 553 554 555  
557 558 560 561 562  
583 592 750 774 788  
794 801 833 834 859  
886 908 933 976 978  
1000 1032 1106 1108 1115  
1122 1175 1270 1331 1407  
1458 1481 1489 1598 1659  
1853 1867 1874 1991 2015  
2016 2067 2076 2077 2081  
2084 2096 2154 2194 2197  
2202 2246 2257 2300 2312  
2313 2314 2315 2316 2342  
2357 2358 2359 2385 2393  
2394

### GEOLOGY

1 9 19 23 24  
25 29 48 54 63  
72 74 78 79 86  
87 88 89 91 96  
112 113 116 127 133  
137 138 140 146 149  
152 160 162 172 187  
188 200 204 222 224  
225 226 227 228 229  
234 238 246 252 253  
258 260 270 280 285  
289 291 328 384 388  
408 425 439 445 458  
472 475 497 514 522  
528 533 534 541 567  
576 584 586 587 590  
595 596 597 600 606



**GEOLOGY, continued**

613	614	615	616	617
621	622	647	650	651
655	656	659	660	662
669	675	685	686	699
704	705	707	719	727
730	731	735	752	759
767	768	782	786	791
820	844	863	865	867
869	871	889	904	907
912	916	921	922	923
935	939	941	942	943
965	967	968	969	979
996	1001	1008	1009	1015
1019	1020	1044	1056	1067
1071	1072	1096	1097	1113
1154	1155	1157	1158	1161
1162	1164	1171	1191	1211
1235	1287	1297	1334	1336
1346	1347	1359	1361	1370
1384	1413	1419	1420	1421
1422	1428	1462	1464	1465
1470	1473	1474	1493	1499
1504	1515	1533	1535	1539
1546	1550	1553	1560	1576
1580	1582	1584	1592	1593
1596	1609	1610	1613	1615
1624	1628	1637	1644	1647
1649	1656	1658	1667	1674
1680	1695	1699	1700	1702
1707	1708	1711	1712	1715
1721	1724	1725	1728	1729
1732	1735	1742	1744	1757
1768	1771	1772	1782	1790
1794	1795	1796	1797	1800
1801	1807	1809	1814	1817
1818	1823	1828	1833	1836
1837	1838	1839	1840	1841
1847	1858	1875	1877	1882
1883	1884	1885	1889	1901
1912	1922	1929	1933	1936
1937	1938	1940	1941	1943
1944	1945	1946	1948	1956
1957	1972	1974	1975	1989
1993	2010	2011	2026	2027
2030	2031	2057	2099	2100
2106	2107	2108	2109	2110
2111	2112	2113	2117	2118
2125	2130	2131	2133	2134
2139	2148	2149	2156	2159
2168	2169	2170	2172	2185
2186	2187	2188	2198	2203
2205	2210	2211	2212	2213
2215	2220	2229	2231	2232
2258	2259	2271	2272	2287
2291	2292	2293	2296	2302

2304	2317	2325	2336	2338
2339	2349	2351	2352	2369
2382	2383	2384	2385	2386
2391	2392	2398	2405	2411

**Caves/Speleology**

17	27	33	34	35
36	37	38	39	40
45	50	51	52	53
55	56	57	58	59
60	61	64	65	66
67	68	69	70	71
73	75	76	77	83
84	90	97	98	101
102	108	109	115	128
131	145	147	150	155
161	163	164	165	166
177	178	180	181	182
183	186	197	201	202
205	210	211	212	213
217	218	221	223	230
231	232	233	236	237
240	241	242	245	247
268	273	283	290	293
306	329	332	337	339
341	353	356	361	365
367	368	369	372	373
374	378	404	409	413
416	421	440	441	442
443	444	457	459	463
464	474	476	504	515
516	517	521	525	527
535	570	574	578	588
589	591	598	599	601
611	623	625	626	627
630	639	640	644	645
649	653	654	666	668
670	672	674	680	681
682	683	684	687	692
693	695	696	700	703
706	722	728	736	737
738	739	740	741	742
743	744	745	746	747
748	749	758	760	764
772	773	776	795	796
797	798	805	807	808
813	817	819	821	824
825	826	847	848	849
850	851	852	853	854
864	866	874	882	890
891	894	895	903	905
913	914	915	920	924
927	931	940	946	949
955	957	958	964	971
980	985	995	1016	1023
1025	1030	1031	1052	1053

**Caves/Speleology, continued**

1054	1060	1061	1062	1063
1066	1081	1082	1084	1087
1089	1090	1100	1117	1119
1121	1123	1124	1125	1126
1127	1135	1152	1153	1166
1167	1172	1173	1186	1188
1201	1203	1204	1208	1209
1210	1215	1221	1222	1223
1229	1230	1243	1278	1279
1282	1284	1285	1286	1289
1290	1298	1305	1307	1309
1314	1315	1320	1323	1328
1329	1335	1337	1350	1357
1363	1374	1394	1395	1406
1416	1418	1423	1426	1428
1429	1430	1430	1437	1443
1450	1455	1456	1458	1460
1461	1463	1466	1467	1468
1469	1472	1475	1476	1477
1478	1479	1484	1495	1496
1498	1500	1501	1502	1505
1506	1507	1508	1510	1513
1514	1519	1524	1525	1528
1529	1536	1537	1538	1544
1556	1568	1569	1577	1586
1590	1597	1599	1603	1604
1605	1611	1612	1617	1619
1620	1625	1626	1627	1635
1636	1638	1639	1640	1641
1642	1643	1670	1679	1681
1685	1686	1689	1692	1693
1694	1697	1703	1704	1734
1736	1738	1748	1753	1769
1770	1775	1786	1787	1788
1789	1799	1803	1804	1810
1811	1821	1822	1824	1825
1826	1827	1829	1830	1832
1846	1860	1861	1862	1863
1879	1880	1881	1886	1890
1891	1898	1902	1903	1928
1942	1967	1968	1982	1984
1992	1999	2001	2006	2008
2019	2021	2023	2024	2025
2036	2037	2038	2039	2040
2041	2042	2043	2048	2049
2054	2061	2065	2066	2073
2074	2075	2082	2083	2089
2097	2102	2103	2104	2105
2116	2119	2120	2121	2122
2123	2124	2126	2127	2129
2132	2136	2137	2138	2140
2141	2142	2143	2147	2150
2153	2160	2161	2166	2167
2171	2174	2176	2189	2219
2223	2224	2236	2237	2242

2247	2262	2270	2273	2274
2275	2276	2277	2278	2279
2280	2281	2283	2284	2285
2286	2288	2289	2290	2303
2332	2348	2350	2377	2378
2379	2401	2402	2403	

**Geomorphology**

12	80	81	104	107
159	169	190	209	272
282	338	361	364	377
414	415	419	422	423
424	426	427	428	429
434	494	526	549	566
636	658	676	678	679
783	802	810	812	830
870	876	877	893	986
988	999	1046	1059	1079
1095	1112	1199	1280	1295
1324	1362	1398	1415	1429
1476	1516	1517	1521	1530
1541	1553	1564	1568	1579
1669	1673	1745	1778	1783
1834	1855	1866	1900	1915
1923	1924	1945	1978	1980
1987	2020	2029	2092	2102
2174	2235	2239	2241	2334
2344				

**Alpine Karst**

129	945	1099	1107	1123
1160	1585	1896	2407	

**Coastal Karst**

352	1410	1780	1924	1926
1927	1969	1990	2079	2092

**Dolines**

129	215	436	461	1324
1325	1326	1327	1368	1447
1874	1911	1979	1980	2114
2201	2225	2265	2301	2305
2347				

**Genesis**

198	633	634	661	695
696	711	741	795	813
894	895	910	917	918
1066	1159	1168	1242	1266
1267	1335	1360	1492	1527
1602	1634	1668	1820	1879
2101	2262	2369		

Glacial Karst  
 355 449 1441 1746 1815  
 1816 1843 1897 1923 1985  
 2177 2190

Landform Evolution  
 132 170 199 216 338  
 410 411 431 456 543  
 638 671 857 893 1024  
 1369 1566 1621 2093 2235  
 2238

Historical Geology  
 959 2135 2282

Marine Karst  
 195 349 784 2353

Paleokarst  
 28 148 356 468 480  
 542 577 665 691 734  
 962 990 999 1007 1039  
 1292 1385 1503 1678 1743  
 1779 1872 1899 1970 2086  
 2193 2298 2362

Petrology  
 113 141 327 1038 1040  
 1057 1189 1190 1212 1543  
 1551 1739 1971 2030 2104  
 2199

Pseudokarst  
 184 185 729 862 1010  
 1116 1276 1288 1740 1831  
 2144

Salt  
 352 571 572 1073 1910  
 1975 2169

Sandstone  
 179 190 761 842 1773  
 1774 2098 2099 2413

Solution Features  
 216 271 295 369 619  
 630 631 633 634 689  
 1058 1379 1563 1976 1983  
 2232

Structural Geology  
 22 214 708 810 815  
 1017 1026 1027 1079 1432  
 1435 1456 1487 1520 1521  
 1522 1555 1565 1632 1655  
 1710 1726 1835 1916 1931  
 1998

Tectonics  
 261 281 283 342  
 359 469 482 526  
 539 725 777 792  
 803 804 815 816  
 844 876 877 1142  
 1217 1352 1366 1417  
 1548 1554 1555 1606  
 1737 1805 1935 1946  
 2095 2296 2297 2312  
 2339 2400

Tropical Karst  
 21 196 417 418 422  
 430 433 435 781 1331  
 1367 1418 2033 2244

Lakes  
 351 355 504 546 556  
 2097 2226

Mineralogy  
 2 9 108 109 179  
 219 294 310 313 333  
 346 360 362 382 463  
 468 628 691 694 697  
 714 718 734 763 770  
 829 830 856 873 926  
 937 977 1037 1057 1087  
 1119 1134 1146 1173 1178  
 1186 1218 1238 1239 1254  
 1265 1266 1268 1272 1273  
 1294 1316 1414 1453 1459  
 1471 1588 1601 1602 1622  
 1692 1693 1696 1737 1747  
 1749 1759 1762 1819 1848  
 1860 1861 1862 1906 1912  
 1925 1996 1997 2008 2036  
 2045 2057 2164 2220 2221  
 2295 2413

Reefs  
 194 1904

**Sinkholes**

11	14	92	103	119
120	121	122	123	126
132	154	262	332	343
375	393	400	402	412
498	518	524	536	537
573	618	619	620	698
709	710	723	724	726
732	766	858	875	892
909	956	963	1024	1048
1055	1065	1075	1076	1078
1094	1120	1128	1165	1187
1275	1309	1355	1375	1377
1388	1389	1401	1434	1439
1482	1526	1541	1544	1578
1587	1629	1645	1690	1691
1736	1777	1793	1915	1916
1919	1963	1973	2000	2003
2004	2028	2029	2059	2068
2069	2077	2090	2173	2218
2230	2251	2252	2260	2261
2263	2264	2269	2310	2311

**Springs**

16	43	118	152	173
235	239	255	256	269
320	349	354	383	385
490	500	582	716	750
775	784	789	796	799
806	809	817	835	837
872	879	898	934	976
1062	1103	1104	1139	1147
1150	1183	1205	1221	1248
1251	1255	1262	1317	1353
1397	1482	1581	1605	1608
1623	1653	1671	1766	1767
1783	1785	1788	1870	1966
2050	2051	2222	2225	2267
2268	2319	2354	2355	2356
2372	2402			

**HYDROLOGY**

30	93	168	189	207
225	248	377	406	477
624	657	673	827	828
831	1018	1021	1029	1035
1036	1037	1038	1040	1050
1059	1068	1069	1080	1085
1091	1092	1093	1105	1111
1115	1124	1136	1137	1163
1169	1170	1174	1177	1184
1202	1216	1224	1225	1233
1238	1239	1300	1310	1319
1332	1339	1376	1383	1394
1395	1433	1438	1451	1453
1455	1471	1488	1509	1511

1518	1550	1552	1563	1564
1594	1595	1630	1661	1664
1673	1717	1722	1738	1766
1784	1845	1856	1859	1886
1890	1892	1894	1920	1951
1952	1969	1970	2002	2090
2101	2115	2128	2145	2146
2157	2158	2196	2200	2228
2234	2237	2240	2245	2249
2253	2255	2256	2299	2322
2323	2337	2370	2371	2373
2375	2397	2399	2401	2409

**Geothermal Sources**

585	1733	1762	1996	1997
2137	2144	2370	2371	2408

**Hydrogeology**

20	41	44	62	85
94	95	96	99	100
110	118	135	143	156
157	171	174	175	176
199	214	243	244	254
255	257	259	263	266
267	274	275	277	278
284	288	296	297	299
300	301	303	304	305
308	309	311	312	314
315	316	317	318	319
322	323	324	326	330
331	340	345	346	347
351	357	358	360	366
370	371	376	380	381
386	387	389	390	394
395	396	397	398	399
403	407	466	470	473
474	486	487	489	499
500	503	505	506	507
509	511	512	513	520
523	529	531	545	547
548	551	552	563	564
575	579	580	581	582
591	593	607	609	611
612	631	632	635	637
638	641	642	646	652
663	664	672	688	689
692	693	697	701	713
716	720	721	751	753
754	755	756	757	762
765	769	771	774	785
787	790	800	811	818
822	823	833	834	838
840	845	846	859	860
878	880	881	883	884
886	888	896	897	899
901	902	906	919	928

Hydrogeology, continued

929	947	948	951	952
953	954	972	974	975
982	983	984	987	991
993	994	998	1000	1006
1012	1014	1042	1049	1052
1054	1074	1075	1096	1098
1099	1100	1101	1102	1104
1106	1107	1108	1109	1110
1118	1122	1130	1132	1133
1134	1138	1140	1142	1145
1148	1149	1150	1159	1175
1176	1177	1178	1179	1180
1181	1182	1183	1199	1200
1207	1219	1226	1227	1231
1236	1237	1240	1241	1245
1246	1248	1250	1251	1252
1255	1257	1258	1259	1261
1263	1264	1269	1272	1273
1274	1291	1293	1299	1301
1302	1303	1304	1308	1312
1313	1330	1343	1344	1349
1353	1354	1356	1364	1365
1367	1378	1380	1382	1386
1387	1390	1391	1393	1396
1399	1400	1402	1403	1404
1405	1406	1407	1408	1409
1411	1431	1440	1442	1445
1446	1448	1480	1483	1485
1486	1491	1497	1520	1522
1534	1536	1540	1542	1558
1566	1571	1579	1581	1583
1584	1586	1589	1600	1608
1614	1619	1633	1654	1657
1659	1662	1663	1671	1672
1676	1682	1687	1688	1689
1755	1756	1758	1759	1760
1763	1763	1765	1780	1781
1806	1812	1813	1842	1849
1852	1854	1857	1867	1868
1870	1873	1888	1902	1909
1910	1911	1917	1921	1947
1949	1950	1955	1962	1966
1977	1986	1995	2012	2021
2022	2032	2034	2035	2047
2055	2056	2058	2060	2078
2080	2091	2094	2155	2163
2165	2178	2179	2180	2182
2183	2192	2193	2195	2207
2216	2217	2238	2247	2248
2250	2251	2265	2269	2294
2306	2307	2308	2313	2315
2318	2324	2329	2330	2331
2332	2333	2341	2343	2353
2359	2360	2361	2363	2364
2365	2366	2367	2368	2376

2377	2378	2380	2387	2388
2389	2390	2393	2394	2395
2408	2412			

## Drainage

6	170	325	340	507
568	632	635	637	703
832	1047	1051	1198	1206
1415	1448	1561	1664	2017
2018	2033	2321	2326	

## Geochemistry

4	5	42	98	100
144	191	192	193	208
247	275	276	364	401
471	477	487	508	522
565	579	624	641	648
663	701	754	770	775
776	868	872	879	885
887	911	930	951	957
1088	1089	1090	1092	1114
1140	1213	1214	1281	1292
1318	1357	1376	1414	1436
1480	1481	1486	1527	1552
1557	1573	1733	1752	1764
1791	1798	1857	1906	1928
1961	2005	2009	2035	2044
2051	2062	2087	2151	2152
2208	2236	2404		

## Ground-Water Movement

18	26	134	254	305
308	309	322	323	403
483	501	502	505	506
511	569	592	603	646
715	755	756	762	765
823	832	835	841	897
898	899	906	908	987
991	1012	1121	1131	1139
1141	1143	1341	1342	1417
1442	1454	1457	1565	1633
1660	1684	1754	1755	2013
2047	2050	2181	2197	2209
2226	2381			

## Ground-Water Withdrawal

1990

## Recharge

43	142	265	1098	1274
1958	2191			

**Sedimentation**

8	32	114	148	196
212	213	249	250	251
287	292	321	329	363
391	409	432	459	482
484	485	491	530	532
540	543	594	601	605
643	667	680	712	717
721	733	736	737	738
739	740	742	743	744
745	746	747	748	749
809	824	825	848	849
989	1002	1003	1004	1005
1041	1086	1125	1126	1127
1172	1196	1212	1260	1265
1267	1305	1306	1322	1343
1360	1373	1452	1496	1502
1523	1531	1532	1538	1545
1548	1556	1575	1616	1618
1631	1650	1651	1668	1743
1834	1850	1851	1939	2001
2019	2049	2086	2199	2252
2323				

**Carbonate Stratigraphy**

105	194	195	286
287	438	677	712
1192	1345	1677	1914
2163	2200	2295	2387
2388	2398	2404	

**Temperature**

1524	2070	2189
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**Water Level**

666	840	1512	1871	1388
1389	1820			

**Modeling**

49	95	136	277	279
297	298	307	335	383
385	510	519	605	702
974	1028	1070	1143	1262
1264	1281	1338	1433	1513
1567	1574	1623	1683	1729
1777	1785	1793	1808	1844
1873	1892	1918	1919	1979
1981	1982	1985	2000	2007
2013	2014	2059	2072	2162
2233	2326	2335	2345	2354
2358	2395	2397	2410	

**Water Quality**

106	130	139	560	778
1144	1219	1231	1232	1403
1488	1490	1542	1591	1607
1646	1690	1887	1953	1954
1959	2154	2227		

**INVESTIGATIVE METHODS****Geophysical Surveys**

124	125	203	334	344
348	405	488	492	493
610	643	861	932	933
966	1045	1151	1152	1165
1195	1206	1234	1256	1275
1277	1412	1423	1864	1865
1876	1930	1964	1965	1988
2071	2085	2214	2243	2263
2293	2374	2400		

**Magnetics**

8	158	467	1271	1277
1278	1306	1315	1351	1449
1483	1491	1531	1532	1575
1963				

**Microscopy**

787	1549
-----	------

**Radiocarbon Dating**

1283	1869
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**Remote Sensing**

47	925	1141	1583
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**Resistivity**

46	203	676	927	1034
1675	1741			

**Seismic Methods**

479	1129	1194	1427	1631
1632	1648	1907	2325	

**Tracing Techniques**

15	82	151	446	580
682	814	971	992	1083
1093	1147	1224	1307	1358
1365	1371	1490	1537	1607
1665	1740	1802	1893	1895
1896	1905	2002	2254	2266
2373				

**Fluorescent Tracing**

801	806	948	1666
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**Statistical Analysis**

375 1011 1311 1340 1730

**LIFE SCIENCES****Archaeology**

404 426 1208 1209 1210  
1234 1279 1321 1329 1424  
1494 1922 1942 2053 2278

**Biology**

164 773 901 961 989  
1067 1268 1789

**Botany**

772

**Ecology**

264 559 2257

**Paleontology**

2 217 333 598 599  
855 1156 1185 1296 1392  
1533 1543 1547 1562 1570

**Zoology**

460 1022 1381

**RESEARCH**

1081 1082 1337 1459

**Geographical Survey**

350 379 420 793

**History**

111 1569 2406

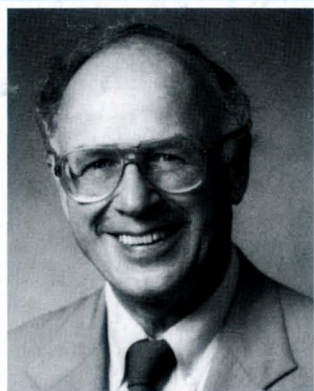
**Maps**

7 10 14 81 117  
284 311 312 326 336  
341 400 405 492 575  
665 769 805 807 900  
925 936 1077 1078 1117  
1160 1193 1228 1304 1398  
1516 1652 1714 1741 1776  
1878 1981 2083 2376









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