Intitut für Hydrologie der Albert-Ludwig –Universität Freiburg im Breisgau

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Hydrological and geochemical investigation in a karstified catchment of the Lodowe spring in the Tatra Mountains to estimate water flow components and water resources

> Diplomarbeit unter der Leitung von Prof. Dr. Ing. P. Maloszewski Freiburg im Breisgau, Januar 2008

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Glossary of symbols

Note: Dimensions are given in SI (Système International) units. M is mass, L length and T time

| a | chemical activity |
|---------------------------|--|
| α | aquifer compressibility |
| β | compressibility of water |
| В | spacing between the parallel plane walls of a fracture [L] |
| c(x, y, z) | concentration in three dimensional space |
| С | constant |
| ¹³ C | carbon 13 |
| D | tensor of diffusion coefficients [L ² /T] |
| d | hydraulic depth [L] |
| DIC | dissolved inorganic carbon |
| DM | Dispersion Model |
| δ | isotope ratio |
| $\delta(t)$ | Dirac function |
| Δ | Laplace operator |
| e | goodness of fit |
| EM | Exponential Model |
| f | friction factor |
| \overrightarrow{F} | mass flux vector[M/L ² .T] |
| g | gravitational acceleration [L/T ²] |
| GMWL | Global meteoric Water Line |
| \mathbf{h}_{f} | laminar flow head loss [L] |
| h | total head (pressure head+elevation head) [L] |
| ^{2}H | deuterium |
| ³ H | tritium |
| ³ He | helium 3 |
| i | transfer function |
| IAP | ion activity product |
| j | number of observations |
| K | hydraulic conductivity [L/T], |
| K_1 | equilibrium constant |

| K_{CO_2} | equilibrium constant for the dissolution of CO_2 in water |
|------------------|--|
| K_R | solubility product |
| l | hydraulic radius [L] |
| m | mass of the molecule [M] |
| m | Manning's roughness coefficient |
| М | concentration in meq |
| n | porosity |
| N_{f} | Froude number |
| 14 N | neutrogen 14 |
| ν | kinematic viscosity[L/T ²] |
| ¹⁸ O | oxygen 18 |
| р | hydrostatic pressure [M/L/T ²] |
| p_{CO_2} | CO ₂ partial pressure |
| P _D | dispersion parameter [] |
| PFM | Piston Flow Model |
| Q | discharge [L ³ /T] |
| Q _B | base flow discharge measured [L ³ /T] |
| Q _C | discharge from the conduit aquifer [L ³ /T] |
| Q _{max} | maximum discharge measured [L ³ /T] |
| Q _P | discharge from the porous aquifer [L ³ /T] |
| R | ratio of the isotope of interest to the most abundant isotope of the species |
| Re | Reynolds number |
| REV | representative elementary volume |
| $ ho_{w}$ | density of water [M/L ³] |
| S | term for additional sources or sinks such as biodegradation, radioactive decay |
| | and precipitation |
| SI | saturation index |
| Ss | specific storage [L ⁻¹] |
| Т | mean transit time of water [T] |
| TU | tritium unit |
| τ | dummy variable |
| и | velocity [L/T] |
| U _{max} | threshold above which the studied integral of the REV stabilizes |

| V | Unit volume of earth material [L ³] |
|-------|---|
| V_c | water volume of the conduit aquifer [L ³] |
| Ve | Volume of void space in a unit volume of earth material [L ³] |
| V_p | water volume of the porous aquifer [L ³] |
| V_t | total water volume in storage [L ³] |
| V_w | water volume [L ³] |
| VSMOW | Vienna Standard Mean Ocean Water |
| Z | elevation head [L] |

Abstract

Karst systems are highly heterogeneous aquifer bodies. Additionally to a matrix and a fracture porosity encountered in other water bearing formations, karst carbonate aquifers are characterized by more or less large solutional conduits. These three types of porosity have been regrouped under the term triple porosity. Modeling triple porosity aquifer poses many challenges to the hydrologist. In this thesis, the applicability of physically based and lumpedparameter models in karst hydrosystems are discussed, and their respective advantages and flaws compared. The water chemistry and isotopic composition of the Lodowe karst spring in the Polish Tatra Mountains has been monitored for a duration of three months. One storm hydrograph was analyzed, and modeling techniques were combined with chemical and physical observations to derive a conceptual model, as well as estimates of the water resources and potential for contamination of the karst aquifer feeding the spring. The Lodowe spring is characterized by its rapid response to storm events as well as a discharge dependant variation in its water chemistry and isotopic concentrations. This response can be modeled by a double porosity approach considering the porous matrix and the conduit system as two separate entities in interaction with one another. The porous matrix assumes the storage function of the karst aquifer while the conduit system assumes its transport function. Although the drainage basin of the Lodowe spring is situated in a protected area, diffuse contamination in the form of atmospheric pollution for example could still be a potential contaminant source for the porous reservoir.

Zusammenfassung

Karst Systeme sind sehr heterogene Grundwasserkörper. Dabei unterscheiden sich Karstaquifere von anderen wasserführenden Körpern indem sie, zusätzlich zu einer Matrixund Kluftporosität, von unterschiedlich breiten Lösungskanälen durchzogen werden. Diese drei Porositätstypen fast man unter den englischen Begriff "triple porosity" zusammen. Die Modellierung von Mehrporositätssystemen stellt für Hydrologen eine Vielzahl von Herausforderungen dar. In dieser Diplomarbeit werden die Anwendungsmöglichkeiten von physikalisch basierten- und lumped-Parameter Modellen, sowie ihren spezifischen Vor- und Nachteilen diskutiert. In der Lodowe Quelle, welche im polnischen Tatra Gebirge liegt, wurden drei Monate lang wasserchemische Parameter und Isotopenkonzentration gemessen. Dann wurde ein Konzeptmodel aus der Kombination von Modellierungstechniken und chemischen/physikalischen Beobachtungen erarbeitet. Die Wasserressourcen und das Gefährdungspotential durch Kontamination des Karstaquifers wurden ebenfalls abgeschätzt. Charakteristisch für die Lodowe Quelle sind eine schnelle Reaktion auf Regenereignisse Wasserchemie sowie schüttungsabhängige Schwankungen der und der Isotopenkonzentrationen. Diese Reaktion kann mit dem Ansatz einer Zweifach-Porosität modelliert werden, wobei die poröse Matrix und das Kanalsystem zwei unterschiedliche Einheiten darstellen, die miteinander wechselwirken. Die poröse Matrix fungiert weitgehend als Speicher, während die Kanäle die Transportfunktion übernehmen. Obwohl das Einzugsgebiet der Lodowe Quelle in einem Schutzgebiet liegt, ist eine diffuse Kontamination, zum Beispiel durch atmosphärische Deposition, nicht auszuschließen. Dies stellt eine potentielle Gefährdungsquelle des porösen Grundwasserkörpers dar.

Résumé

Les systèmes karstiques sont extrêmement hétérogènes. En sus d'une porosité d'interstice et d'une porosité de fissure rencontrée dans les milieux poreux et fracturés, les aquifères karstiques se caractérisent par les conduits de dissolution qui les parcourent. On parle alors de triple porosité. La modélisation d'aquifères où se rencontre cette triple porosité pose de nombreux défis à l'hydrologue. Dans ce mémoire, les possibilités des modèles phénoménologiques et de type « boîte noire » et leurs avantages et inconvénients respectifs sont comparés. La composition chimique et isotopique de la source de Lodowe située dans les Tatra polonaises a été mesurée pendant une période de trois mois. Un hydrogramme a été analysé, et différentes techniques de modélisation combinée avec les paramètres physicochimiques mesurés afin de développer un modèle conceptuel de l'aquifère. Les ressources en eau et le potentiel de contamination de la nappe alimentant la source ont également été évalués. La source de Lodowe est caractérisée par une réponse rapide aux précipitations et des changements dans sa composition chimique et isotopique en fonction du débit. Un système à double porosité est à même de modèliser cette réponse en considérant le milieu poreux et le système de conduits comme deux entités séparées et en interaction l'une avec l'autre. Le milieu. poreux assume une fonction de stockage et les conduits une fonction de transport. Bien que le basin versant de la source de Lodowe soit situé dans une zone protégée, les risques d'une contamination diffuse du réservoir poreux, par exemple par deposition atmosphérique, ne peuvent être exclus.

1. Introduction

1.1 General considerations about karst water resources

As a sedimentary rock covering up to 20% of the Earth's continents (Figure 1.1), carbonate rocks and their associated karst systems are of major importance both from a scientific as well as purely practical point of view. Karst systems differ from porous or fractured aquifers in that they are characterized by a hydrological response (i.e. the flow at the spring) not linearly related to its input in the form of rain or snow (Pinault et al., 2001). As Kehew (2000) points out, carbonate-rock systems include some of the most prolific and important aquifers for ground water supply, of which the Edwards aquifer in Texas and the Floridan aquifer in Florida are two prominent examples.



Figure 1.1 Major outcrops of carbonate rocks (Ford & Williams, 1989)

Of the different tasks facing the hydrologist studying a karst catchment, one can mention:

-The classification of a particular karst aquifer according to its flow system. The aquifer can either consist mainly of a porous matrix with a minor secondary porosity in the forms of fractures, joints and bedding planes not solutionally enlarged; or it can be more similar to a reticulation system, with a well-developed network of pipes and conduits (Shuster & White, 1971).

-The delineation of contamination protection zones (Maloszewski et al., 1998). Often, classical approaches loose relevance due to the heterogeneous nature (both in space and time) of the flow paths and velocities within a karst aquifer. The delineation of the aquifer's watershed in particular is subject to considerable uncertainties, since a subsurface "hydrographic network" may well have developed that differs considerably in its boundaries from the overlying watershed. Such boundaries are indeed known to vary with discharge, as karst conduits "overflow" into another watershed (Fetter, 2001).

- The allocation of permissible annual water extraction volumes. In regard to water resources management, reliable estimates of the long-term sustainable yield are important. A knowledge of the origin and contribution of different water sources to the overall water balance can also be necessary (Herzeg et al., 1997), as their respective water qualities can be either different, or the sources more or less exposed to contamination.

-Water quality. Karst aquifers lack the filtering ability of porous aquifers and can transport large quantities of suspended sediments in karst conduits, not only colloids¹, but larger particles as well (Mahler and Lynch, 1999, Massei et al., 2002). Contaminants sorbed onto these particles can be thus mobilized as "mobile solid phase" (Fetter, 1992). Karst aquifers are also much more vulnerable to pollution than porous aquifers. Although the high transmissivity of karst bodies can facilitate the treatment of contaminated areas, it also makes carbonates aquifers much more vulnerable to large scale contamination (Leibundgut et al., 1998, introduction & Fetter, 1992).

The monitoring of water level or discharge, as well as measurements of isotopic composition and hydrochemistry of groundwater at springs can yield "integrated" information for the entire karst system such as the mean water residence time for various flow paths. Catchment scale modelling may indeed be the most adequate to study and try to understand the system response to precipitation (Pinault et al., 2001).

¹ The term colloid refers to a particle-size range of less than 0.00024 mm, i.e smaller than clay size (Bates & Jackson, 1984)

1.2 Aim of the study

In this study, a high resolution analysis of the hydrochemistry of the Lodowe spring during a single storm event which took place in September 2007 is attempted. The spring, situated in a karstified catchment spring in the Polish Tatra Mountains, was already known for its wide range of variation in flow rates (Barczyk, 2003). This, coupled with the greatly variable water chemistry measured during the present study indicates a rapid mixing of water and conduit-type flow within the karst aquifer (Lee & Krothe, 2001). A quantitative analysis of the breakthrough curve is to be performed with the following aims:

- Separation of the discharge in components with different residence times.

- Estimation of the mean residence time and volume of water stored in each reservoir.

- Development of a conceptual model based on the combination of short term variations in the water chemistry and isotopic concentration with long term tritium observations.

2. Geography, geology and hydrogeology of the Lodowe spring

2.1 Overview

The Lodowe spring is situated in Poland's Tatra National Park (TNP). The Tatra themselves belong to the Carpathian Orogeny, a segment of the Tethyan chain joining the Alps to the west and the Balkans to the south (URL 1). This chain was then incorporated in the younger Alpine belt (Figure 2.1). The Carpathians form a continuous arc 1300 km long from Vienna to the Iron Gates on the Danube, and are subdivided in western and eastern Carpathian, the transition being in the region of Košice in Slovakia where the general strike changes from SW-NE to NW-SE.

The major units of the western Carpathian, to which the Tatra Mountains belong, are, from the central zone outwards (Schönenberg and Neugebauer, 1997):

- A central zone of crystalline basement rocks arching upward and their Mezozoic sediment cover

- The Pieniny Klippen Belt
- A continuous flysch zone 30 to 130 km wide
- A Molasse foredeep

The Tatra National Park was created 1954. It extends over an area of 21,164 hectares and consists of the entire Polish Tatra (Bibelreither and Schreiber, 1989). Its higher peak, Rysy, on the border to Slovakia, reaches 2499 m.a.s.l. The park is largely covered with mixed woodland.



Figure 2.1 Europe's basement belts. The red circle marks the location of the Western Carpathians (Innes Lumsden, 1992)

2.2 Geological and hydrogeological setting

The Tatra Mountains are part of the central zone mentioned above, and consist of granite, as well as metamorphic and sedimentary rocks (Zuber et al., 2007). Among those, carbonates are predominant in the form of limestones and dolomites. Their widespread occurrence "result from the deposition of carbonate sediments and rocks in shallow marine waters"(Kehew, 2000) during the Triassic and Jurassic. Figure 2.1 summarizes the environmental controls of limestone deposition. Each environment has distinct deposits termed "facies" (Ford & Williams, 1989).



Figure 2.2 Depositional facies of carbonate rocks (Ford & Williams, 1989)

The Lodowe spring emerges at the contact zone of two formations, the High Tatra unit of the Wierchowe series and the sub-Tatra unit of the Reglowe series (Figure 2.3). The High Tatra series is found in the highest parts of the Tatra Mountains and is mainly built of Jurassic sandstones, limestones and marls whereas the older Sub-Tatra series consists of Triassic sandstones, limestones and dolomites (Zuber et al., 2007). The Sub-Tatric series, along with the Choč series, occupies the lowest, forested foot of the TNP. In the high Tatra zone, the Trias is characterized by terrigenic delta sediments deposited in shallow sea basins. During the Jurassic, the sea invaded areas occupied by the High Tatras succession. Periods of

transport of clastic material alternated with sedimentation of carbonate and silicate material. The Trias depositional troughs became deeper during the Jurassic, as exemplified by the Kościeliska valley, while ridges became elevated.

The sub-Tatra sedimentary basin was filled during the Trias by alternating clastic and carbonate (mostly dolomitic) sediments in a shallow and steadily subsiding sea basin (Sokołowski et al., 1976).



Figure 2.3 Geology of the Tatra National Park. 1- and 2- springs; 3-wells; 4-flow direction in karstic channels obtained from dye tests; 7-crystalline formation; 8- sedimentary rocks of the High Tatra unit; 9- sedimentary rocks of the sub-Tatra unit; 10- carbonate Eocen; 11- Podhale flysch; 12-fluvioglacial and river-valley sediments; 13-cross section line (Zuber & al., 2007)

The Lodowe spring dewaters part of the Czerwone Wierchy Massif (see figure 2.4). It emerges at the center of a pool of about 5 meters radius at an altitude of 974 m.a.s.l. Three small streams flow from the pool for a few tens of meters to the nearby Kościeliski stream, a perennial surface stream draining the Kościeliska catchment. The Lodowe spring has a mean

discharge of 700 l/s (Barczyk, 2003), the Kościeliski stream a discharge estimated at 5 m³/s. The spring drains the Czerwone Wierchy Massif (Dąbrowski and Rudnicki, in Barczyk 2003) and has verified connections with the Śnieżna, Czarna and Miętusa caves (Barczyk 1998). Its Recharge area is reported to reach beyond the catchment boundary of the Kościeliski stream with a possible catchment area of 17 km² (Barczyk 1998). The general dip and flow direction of the water-bearing formations of the Czerwone Wierchy Massif is to the north into the flysch sediments of the Podhale Basin (Figure 2.4 and 2.5). The Lodowe spring responds quickly to storm events and shows wide variations in flow rate (Barczyk, 1998) indicating that some of the discharge comes from a conduit flow feeder system (Shuster & White, 1971).



Figure 2.4 Geological cross section along the A-B line of figure 2.3



Figure 2.5 Geography and main springs of the Tatra National Park. The inset shows its geographical situation at the southern border of Poland with Slovakia, the arrows show the verified connections between the Lodowe spring and caves on the slope of Czerwone Wierchy (modified from Barczyk & al., 2002)

3. Aquifer hydrogeology

3.1 general characteristics

First of all, the aquifer body must be *characterized*:

- In its spatial extent. The aquifer's thickness and lateral extent are obviously decisive for the amount of water that can enter storage. Emblanch (2003) reports of a karst aquifer consisting of massive reef having an unsaturated zone 800 m thick, which sustained spring discharge during base flow.
- In its relationship to the overlying stratas, i.e. confined or unconfined (White, 1988).
- In its rock type. Water-transmitting properties and storage depend upon the permeability and porosity of the rocks. The ability of a material to transmit fluid, its

intrinsic permeability, depends on physical properties such as pore size, pore shape and distribution within the matrix (Ford & Williams, 1989).

3.2 Carbonate aquifers

Karst features, both in the geomorphological and hydrological sense, develop where the "main water-bearing formations are carbonate rocks" (White, 1988). The particularity of these catchments is indeed the solubility of the aquifer framework, since karstic processes work towards an enhancement of porosity and hydraulic conductivity (Kehew, 2000, Ford & Williams, 1989). Nevertheless, the diversity of flow regimes in karst regions should not be underestimated. The hydrodynamic properties of karst aquifers are very diverse. Where conduits are well developed, the flow, laminar in pores and smaller fractures, can become turbulent, out of the range of validity of Darcy's law. This is of importance for modeling, since other governing equations become necessary (Wang & Anderson, 1982).

The porosity of an aquifer is defined as the void spaces between sediments allowing the movement of water.

For the porosity, Fetter (2001) gives:

$$n = \frac{100V_e}{V}$$

Where V_e is the volume of void space in a unit volume of earth material (L³) and V the unit volume of earth material, including both voids and solids (L³)

A theoretical porosity can be derived considering the possible arrangements in three dimensions of spheres of equal radius, with results of 26% (rhombohedral system), 30%, 40%, and 48% (cubic system) (De Marsily, 1981). Porosity is less when the material is poorly graded, since the grains of smaller diameters "fit in" in the voids left by the larger grains (Fetter, 2001).



Figure 3.1 Cubic (A) and rhombohedral (B) packing systems (Fetter, 2001)

In the case of carbonate formations, the matter is not so simple. In addition to the primary porosity consisting of a packing of mineral grains, the aquifer is riddled with joints, fractures and bedding planes¹, giving it a secondary porosity, and even a conduit porosity if larger cavities, where the flow is turbulent, have developed (White, 1988). This leads to the triple-porosity concept used in karst hydrogeology. The primary porosity of the porous matrix and the secondary porosity due to fractures are where laminar flow takes place and the conduit porosity where the flow is turbulent. The great variability and uncertainty of permeability estimates in karst aquifer is shown in figure 3.2.



Figure 3.2 Variability of measured/effective permeability. Limestone has a wide range left undefined in its upper bound (White, 1988)

3.3 Classification of carbonate aquifers

Carbonate aquifers can be classified as lying somewhere on a line between two "end-member conditions" illustrated on figure 3.3 (Ford & Williams, 1989). Conduit aquifers constitute the first end-member. In such an aquifer, the entire water circulates in solutional pipes, and recharge takes place as point recharge. This end-member is best developed in massive limestones with low primary permeability (Kehew, 2000). The second end-member consists

¹ Fracture is the generic term used in geology to describe any kind of openings in the rock matrix. Faults are fractures which show a relative lateral displacement of the two blocks of rock, which lacks in joints . Bedding planes are extensive structures resulting from an change or an interruption in carbonate sedimentation (Dreybrodt, 1988)

of diffuse flow aquifers, with a diffuse recharge onto carbonate rock having a high primary porosity, as is the case in uplifted coral (Ford & Williams, 1989). Although authors seem to agree upon the idea of two end-members, the exact definition can vary. Shuster & White (1971) for example consider as diffuse aquifers those where the flow takes place along "joints, fractures, partings, bedding planes, and other small interconnected openings measured in centimeters or less", and conduit aquifers those where water flows "often turbulently through solution passages measured in centimeters to meters". Table 3.1 summarizes typical aquifer properties encountered for different types of porosities.



Figure 3.3 The two conceptual end-members of karstic flow systems (Shuster & White, 1971)

It is important to note that this conceptual model for karstic systems carries assumption about spring recharge as well as flow type (Kehew, 2000). For a given hydraulic conductivity, diffuse recharge onto a high primary porosity chalk aquifer will considerably differ in its reaction from one recharged by "breached caprock over massive limestone" (Ford & Williams, 1989).

Another way to consider the two end-members is through the residence time of water (Kehew, 2000). In a "pure" conduit flow aquifer, the residence time of water is relatively short as water has velocities in the range of m/hrs or km/hrs, quite similarly to surface water or water flowing in the pipes of a water supply network (Ford & Williams, 1989). On the contrary, springs fed by diffuse flow aquifers "have time to equilibrate with respect to temperature and water chemistry" (Dreybrodt, p. 80). Long residence time can also mean long flow path, and reciprocally, short residence time, short flow path (Scanlon and Thrailkill, 1987)

| | Primary | Fracture | Conduit |
|-------------------------------------|---|---|---|
| | porosity | porosity | porosity |
| Physical situation | Intergranular pores | Concentrations of joints and fractures | Open channels and pipes of various sizes and shapes |
| | Wugs | Bedding plane partings (may be enlarged by solution) | |
| | Isolated joint and bedding plane partings | | |
| Homogeneity | Usually isotropic | Usually anisotropic because of fracture spacing and preferred orientations | Usually highly anisotropic |
| | | May be statistically isotropic over large volumes | |
| Flow regime | Laminar | Laminar | Turbulent |
| | Darcy flow | May deviate from Darcy flow | Non-Darcy flow |
| Water table | Well-defined water table surface | Irregular surface | Behaves as subsurface drains, which may be at, above, or below adkacent water table |
| Response to short-term events | Slow | Moderate | Rapid |

 Table 3.1 Aquifer properties for different types of Porosities

(White, 1988)

4. Spring monitoring in the Tatra Mountains

4.1 Spring classification

A spring is a discharge point for the subsurface flow (Lee and Krothe, 2001). From a hydrological perspective, it is an output control that "yields qualitative and quantitative inferences about the physical and chemical nature of the aquifer that is [its] source" (Desmarais & Rojstaczer, 2002). The vertical position of the emergence point controls the elevation of the water table upstream of the spring as well as "its variation under different discharge conditions" (Ford & Williams, 1989). We can distinguish (figure 4.1):

- Free draining springs for which gravity is the driving force.

- Dammed springs, where a barrier to the flow path forces the water to overflow.

- Confined springs, where the aquifer is confined at the point of discharge. The point of emergence can be located on a fault plane or at a discontinuity in the confining layer. Another term for these springs is "vauclusian" after the Vaucluse karst spring in southern France.



Figure 4.1 Spring types (Ford & Williams, 1989)

4.1.1 Spring hydrograph

In some cases, the structure of the aquifer can be inferred from its hydraulic response (Dassargues, 1998). Since conduit spring react near instantaneously to the change in pressure head induced by a flood pulse (Dreybrodt, 1988) whereas diffuse flow spring show both a lag and a dampening in their response to changes in recharge rate, the spring hydrograph is a good first indicator of the flow type and can be used as a tool for investigation (White, 1988). Ideally, the unsteady state following a precipitation event can be conceptualized thus:

An intense storm leads to a quick rise in water level in the headwater followed by an increase in the hydraulic head and the hydraulic gradient. This increased gradient "pushes" water out of deep storage, and the increased flux is flushed out of the system at the spring. A lag time is observed and equals to the time needed for the pressure wave to travel to the exit, then discharge increases till a peak is reached, followed by a decrease back to the base flow discharge (corresponding to the receding curve of the hydrograph). The conceptualization of this flow pattern is often called "piston flow".

The hydrograph will tend to be flashy if conduit flow predominates, or more subdued for diffuse flow (figure 4.2).



Figure 4.2 Comparison of the storm response of two karst aquifer: conduit flow for the Rocks Spring, diffuse flow for the Thompson Spring (White, 1988)

Figure 4.3 is a conceptual sketch of the relationship between the conduit and matrix reservoirs. Storm discharge reverses the pressure gradient and partially recharges the porous matrix, which sustains base flow.

White (1988) suggests the ratio of the maximum discharge to the base flow (either annual or event related) Q_{max} / Q_B as a measure for the "flashiness" of a spring (table 4.1). The presence or absence of a plateau value for the discharge and the recession period also characterize the aquifer.

| Spring | Q _{max} /Q _B | t _R (days) |
|-------------------------------|----------------------------------|-----------------------|
| Fast-response springs | | |
| Rocks Spring | 42 | 7.3 |
| Penns Cave | 96 | 19 |
| Davis Spring | 91 | 4.1 |
| | | |
| Intermediate-response springs | | |
| Thompson Spring | 9.5 | 70 |
| Tuscumbia Spring | 7 | 65 |
| Aghia Eleousa | 7.5 | 86 |
| | | |
| Slow-response springs | | |
| San Marco Springs | 1.6 | |
| Silver Spring | 1.5 | |
| Ras-el-Ain | 1.16 | 2070 (5.67 years) |

Table 4.1 Q_{max} / Q_{B} ratio and mean transit time t_R for different karst springs

(modified from White, 1988)

One of the major problems encountered in hydrograph analysis is the rarity of "pulse-like" rain events. More often than not, the ideal localized downpour evenly distributed over the whole catchment rather takes the form of a steady rain event going on for days, or only concerning a subcatchment. In the first case, one can attempt to assume that pseudo steady state conditions have been reached (Desmarais & Rojstaczer, 2002).



Figure 4.3 Exchange of groundwater between conduit and matrix at high and low flow

(White, 2003)

4.1.2 Storage

The amount of water in storage is also of interest. This aquifer property is described by the specific storage Ss. In a saturated aquifer, it is the volume of water released from a unit volume of aquifer per unit decline in head (Bear, 1979). It is given by:

$$Ss = \rho g(\alpha + n\beta) [L^{-1}]$$
(4.1)

Where α is the aquifer compressibility, ρ_w the density of water [kg/l], g the gravitational acceleration [m/s²], n the porosity, and β the compressibility of water

The specific storage is normally found from pumping test scores. In karst, though, the "averaging out" of the aquifer heterogeneities normally achieved through pumping is seldom satisfied, since the wells may have wildly varying yields depending whether they are situated on a fracture zone or not. The analysis of the recession curve of the spring hydrograph can here again circumvent these difficulties. For details, we refer to White (1988) page 186-189.

4.1.3 Sources

More recent studies have addressed the issue of the sources of base flow. Is it only sustained by water from the saturated zone, or does the unsaturated zone (the epikarst in particular) participate as well (Emblanch, 2003, Lee & Krothe, 2001) ? These questions can be best answered using separate mixing components and a mixing-cell model (Emblanch, 2003), more of which below (5.5.1). Since a definition of the saturated zone in karst is not as straightforward as in porous media, it may be helpful to consider that base flow is derived from phreatic diffuse flow water (Lee & Krothe, 2001).

4.2 Field investigation: hydrogeochemical monitoring

The spring was sampled hourly from the 6th to the 9th September 2007, during and after a regional storm which affected southern Poland. The storm having begun four days earlier, only the recession could be sampled. Base flow sampling was undertaken in the previous month, and until the end of October. Samples were taken as close to the supposed emergence point as possible using standard PVC softdrink 500 ml bottles. Water temperature, pH and electric conductivity were measured in the field. The discharge proved impossible to measure with any degree of accuracy, either using an artificial tracer or a current meter, and even ADCP measurements would have been doubtful, had one been available. The spring being situated within the TNP, installing a weir for each outflow was out of the question, and would have proven difficult for one of the channel, where no clear cross-section can be defined. The discharge data used in this study was provided by Dr. Barczyk from the Institute of Hydrogeology of Warsaw University, who monitors the water stage hourly by means of a pressure transducer. The measured values are converted with the help of a rating curve. The tritium data was provided by Drs Różański and Rzonca from the Institute of Hydrology of the Jagiellonian University in Cracow.

The chemical analysis was undertaken at the Institute of Hydrology of the Jagiellonian University using a DIONEX ICS-2000 ion chromatograph, the isotope analysis was done at the Institut für Grundwasserökologie at the Helmholtz Zentrum in Munich.

Two words of caution concerning the quality of the data seem here necessary. Firstly, no measurement of alkalinity was undertaken in the field. The study uses alkalinity values obtained from the lab, which may or may not come close to the true field values. Secondly, the discharge data should be viewed with caution. They probably rather give the order of magnitude of the flow than reliable estimates of the actual discharge at any given time.

5. Modeling of water resources in the Lodowe catchment

The aim of a groundwater study is the determination of *parameters* with which to model a *system*, either for prediction in an engineering project, or to understand natural processes. As Massei et al. (2006) put it, these parameters (hydrodynamic, hydrodispersive) help to determine the structure/function relationship of karstic hydrosystems. Due to their ubiquitous nature within the catchment, chemical species are a useful tool of investigation.

5.1 Continuum approach to flow through porous media

In order to model and subsequently solve a groundwater problem, one has to translate observations made in nature into a conceptual model (Motyka, 1998). During this process, the main features of the model are recognized, and a certain number of assumptions are made. These cannot be verified, but constitute so to speak the *axioms* of the model (Kitanidis, 1999). In the continuum approach, a Representative Elementary Volume (REV) is defined through averaging of all microscopic flow paths forming"a complex network of interconnected pores within the aquifer" (Bear, 1979). Following conditions must be met:

- The control volume should be large enough to contain a sufficient number of pores necessary to define global mean properties.

- The volume should be small enough to make sure that variations in parameters can be approximated by smooth, or at least continuous, functions (de Marsily, 1981).

It is in this fictitious continuum that we may assign values of properties to any mathematical point (Bear, 1979). Macroscopic parameters like the hydraulic conductivity "represent" microscopic behaviour (Ford p.142).

This classical modeling method can prove difficult to apply to mixing problems in a karst aquifer due to the heterogeneity of the system and its departure from laminar flow (Lee et al., 2001). For karstic systems, the problem is how to define the REV for modeling purposes, since the existence of a threshold U_{max} above which the variations of the studied integral stabilizes around a mean value (figure 5.1) is not certain as is the case in porous media (de Marsily, 1981).



Figure 5.1 Volume definition of the REV (Bear, 1979)
The modeling of discontinuities like fractures and bedding planes poses another problem. At the boundary, instead of the stepwise variation observed in nature, the function varies continuously.

Dassargues (1998) reports of efforts made to reconcile the "highly heterogeneous reality [of karst] with the REV concept". The non-acceptable values for porosities needed during calibration lead some modelers to consider that the mathematical model is no longer physically consistent but still useful as black-box type model (see 5.5).

5.2 Physically-based approach: Hydrodynamic of flow

Flow in Karst cover a wide field of hydrodynamic conditions, both laminar and turbulent flow regimes are encountered. Conceptually, laminar flow can be seen as a an ordered set of streamlines parallel to one another, whereas turbulent flow is made up of eddies (Chadwick & Morfett, 1998). As illustrated by figure 5.2, the change from laminar to turbulent flow is not brutal, but goes through a transitional period. Transitional flow is characterized by variations in the velocity components perpendicular to the direction of flow around a mean value, as illustrated by figure 5.3.



Figure 5.2 Laminar, transitional and turbulent flows. (Chadwick & Morfett, 1998)



Figure 5.3 Variations in the velocity components perpendicular to the flow direction for transitional and turbulent flows (Chadwick and Morfett, 1998)

Three forces act on the REV: inertial, gravitational, and viscous. Their action can be summed up using two numbers, the Reynolds number, which is the ratio of the inertial to the viscous forces, and the Froude number, the ratio of the inertial to the gravitational forces. The Reynolds number is used to predict the onset of turbulent flow (Chadwick & Morfett, 1998):

$$\operatorname{Re} = \frac{ul}{v} \tag{5.1}$$

Where u is the velocity [L/T], l the hydraulic radius [L], and v the kinematic viscosity [L/T²]

)

The flow in natural conduits is laminar for Re<1 to 10, transitional for Re<100, and turbulent above a Reynolds number of 100 (Bear, 1979).

5.2.1 Equations for conduit type flow

Conduit type flow in karst aquifers is similar to conduit flow and open channel flow as they are defined in hydraulics (figure 5.4). The law of Bernoulli relates flow velocities in a conduit to pressure and elevations (Ford & Williams, 1989). Modified to account for the head loss (water is a non-ideal fluid), we have (Chadwick & Morfett, 1998):

$$\frac{p_1}{\rho g} + \frac{v_1}{2g} + z_1 = \frac{p_2}{\rho g} + \frac{v_2}{2g} + z_2 + h_f$$
(5.2)

With p is the hydrostatic pressure $[M/L/T^2]$, v the velocity [L/T], z the elevation head [L], and h_f the Laminar flow head loss [L]

Formulas to compute h_f for different geometries are given in White (1988) page 162.

When the conduits are only partially full, the flow is similar to open channel flow.

The Froude number characterizes such a flow type (White, 1988):

$$N_f = \frac{u}{\sqrt{gd}}$$

Where *d* is the hydraulic depth [L], *u* the velocity of flow[L/T], and g the gravitational acceleration $[L/T^2]$

For $N_f < 1$, the flow is subcritical. For $N_f > 1$, it is supercritical. Most flows are in the subcritical-turbulent regime (White, 1988). At the transition zone from super to subcritical flow, a hydraulic jump forms, and a large amount of energy is released. These zones have a high erosion potential.

Open channels are not pressurized, so the hydraulic gradient is determined by their channel slope and Manning-type formulae can be used to calculate the mean flow velocity (Chadwick & Morfett, 1998):

$$u = \frac{1}{m} l^{\frac{2}{3}} S^{\frac{1}{2}}$$
(5.3)

Where u is the velocity of flow[L/T], m Manning's roughness coefficient, l the hydraulic radius [L], and S the channel slope



Figure 5.4 Longitudinal and cross section for pipe and channel flows (Chadwick and Morfett,

5.2.2 Equations in porous media

Combining the continuity equation and Darcy's law yields a second order partial differential equation which is the general equation for flow in three dimensions for an isotropic, homogeneous, porous medium (Bear, 1979):

$$K\left(\frac{\partial^2 h}{\partial x^2} + \frac{\partial^2 h}{\partial y^2} + \frac{\partial^2 h}{\partial z^2}\right) = (\alpha \rho_w g + n\beta \rho_w g)\frac{\partial h}{\partial t}$$
(5.4)

Where K is the hydraulic conductivity [L/T], h the total head (pressure head+elevation head), α the aquifer compressibility, ρ_w the density of water [M/T³], g the gravitational acceleration [L/T²], n the porosity, β the compressibility of water, and x,y,z and t the coordinate axis of the 4D space.

When there is no change of head with time (steady-state flow), equation (5.4) simplifies to the Laplace equation:

$$\Delta h = 0 \tag{5.5}$$

Where Δ is the Laplace operator

But as mentioned above, Darcy's law looses its validity for turbulent flows, that is, when the flow velocity ceases to be linearly proportional to hydraulic head (figure 5.5). For turbulent flows, equations (5.4) and (5.5) cease to be valid.



Figure 5.5 Departure from Darcy's linear relationship between the hydraulic gradient and the specific discharge at high Reynolds numbers (White, 1988)

5.2.3 Equation for fracture flow

If the flow is laminar, Darcy's law is applicable to fracture flow using a hydraulic conductivity given by (White, 1988):

$$K = \frac{gB^2}{12\nu} \tag{5.6}$$

Where B is the spacing between the parallel plane walls of the fracture

The discharge is then given by the following "cube law" equation (White, 1988):

$$Q = \Delta h \frac{C}{f} B^3 \tag{5.7}$$

Where f is a friction factor and C a constant []

Modeling a whole network of such fractures is much more complex, because of their unknown interconnection, the variation in the aperture B from fracture to fracture and along one single fracture, and the onset of turbulence for the larger ones, or at fracture intersections. Sudicky & Frind (1982) approximate the aquifer with a network of parallel, equally spaced fissures with same aperture. For short residence time, the karstic system can be further approximated by one single fissure "situated in the infinitely extended matrix" as proposed by Maloszewski & Zuber (1985) in their Single Fissure Dispersion Model (SFDM). The rationale is that water and substances in solution penetrating the porous matrix through diffusion have no time to reach adjacent fractures, which means that every flow path stays independent of the others. Figure 5.6 illustrates the double porosity concept with exchange between the fissures and the matrix. Further models for karstic aquifers are discussed in 5.5 below.



Figure 5.6 Conceptual model of a double porosity aquifer with convection in the fractures and diffusion driven exchange with the porous matrix (Maloszewski et al., 1998)

5.2.4 Equations for diffusion phenomenon

The hydrodynamic of flow is not only relevant for water discharge. We mentioned earlier that one karst particularity is to have a soluble framework. One last phenomenon of importance in karst systems is the mass exchange between the solid and liquid phases in the form of dissolution and precipitation which we will discuss in 4.3. The mass transport mechanism coupled to the solid-liquid exchanges in limestone rocks is twofold (Dreybrodt 1988, chapter 3)

- Convection, understood as a "flow of liquid under the influence of an external force" (Dreybrodt).
- Diffusion, which is the random (in the statistical sense) movements of particles such as Brownian motion or eddies.

The total flux is given by the sum of the diffusion and convection terms (Fetter, 1992):

$$F = -D\nabla c(x, y, z) + \vec{u}.c(x, y, z)$$
(5.8)

Where \vec{F} is the mass flux vector [M/L².T], D the tensor of diffusion coefficients [L²/T], c(x, y, z) the concentration in three dimensional space, and \vec{u} the velocity vector

Once the flux is known, the general equation for mass transport, the advection-dispersion equation can be derived (Fetter, 1992):

$$\frac{\partial c(x, y, z, t)}{\partial t} + \vec{u} \nabla c(x, y, z, t) = D\Delta c(x, y, z, t) + S$$
(5.9)

Where S is a term for additional sources or sinks such as biodegradation, radioactive decay and chemical precipitation

The solutions of these equations depend on the boundary conditions. The advective term $\vec{u}\nabla c(x, y, z, t)$ is necessary for modeling dissolution in moving water bodies. This constitutes the difference between laminar and turbulent flow for mass transport. In laminar flow, the only mixing taking place between streamlines is due to molecular diffusion, whereas turbulent flow adds the effect of mechanical, eddy-driven diffusion. Thus, turbulent flow favorizes dissolution.

All the equations in this paragraph are data intensive. When one also takes into account that high and low discharge in karst may be governed by different hydrologic flow laws and that the porous modeling approach may anyway be inadequate to deal with the heterogeneity of karst (Pinault et al., 2001), physically-based modeling may seem an inappropriate approach. Modeling the aquifer at catchment scale with the help of lumped-parameter models can lead to more accurate results. These models are discussed in 5.5.

5.3 Hydrogeochemistry

As can be taken from Fetter, 2001: "Natural waters are never pure; they always contain at least a small amount of substances dissolved in the water". In the case of karst aquifers, one, if not the main source of dissolved substances, is the carbonate matrix itself.

5.3.1 Reactions within the carbonate system: acid-base reactions

The weathering of limestone rocks is basically a series of redox reactions between carbonates and atmospheric carbon dioxide dissolved in water. The products are divalent metal and bicarbonate ions.

The general reaction for calcite and aragonite is (Ford & Williams, 1989):

 $CaCO_3+CO_2+H_2O \rightarrow Ca^{2+}+2HCO_3^{-1}$

And for dolomite (Ford & Williams, 1989):

 $CaMg(CO_3)_2 \rightarrow Ca^{2+} + Mg^{2+} + 2CO_3^{2-}$

Evaporite rocks such as gypsum and anhydrite may also be present in carbonate rocks.

5.3.2 Reaction of the calcite system with H₂O-CO₂

The dissolution and precipitation of calcite is controlled by the equilibrium of three reactions (Ford & Williams, 1989):

 $CaCO_3+H^+ \rightarrow Ca^{2+}+HCO_3^-$

 $CaCO_3+H_2CO3 \clubsuit Ca^{2+}+2HCO_3^-$

 $CaCO_3+H_2O \rightarrow Ca^{2+}+H_2O+CO_3^{2-}$

 $CO_2(g)$ dissolves to $CO_2(a)$ in water. In solution, $CO_2(a)$ reacts with water to form carbonic acid:

 $CO_2(g)+H_2O \rightarrow H_2CO_3^{1}$

Carbonic acid is a diprotic acid (Kehew, 2000), i.e. it can dissociate twice, first to bicarbonate, then to carbonate, and give away two hydrogen cations, according to the following reactions:

 $H_2CO_3 \rightarrow H^+ + HCO_3^-$

$$HCO_3^{-} \rightarrow H^+ + CO_3^{2-}$$

It follows that the three species encountered in solution when CO_2 dissolves are H_2CO_3 , HCO_3^{-} , and CO_3^{-2-} .

A Bjerrum diagram summarizes the pH domain of predominance of each species under closed system conditions (Figure 5.7).



Figure 5.7 Bjerrum diagram of the carbonate species (Kehew, 2000)

As shown by figure 5.7, HCO_3^- is the predominant ion a pH range from 6 to 8.

¹ As a convention, all the CO2 present in solution is considered to be carbonic acid (Kehew 2000)

5.3.3 Open and closed systems

A system is called open if it is in contact with its surrounding and can exchange constituents with it. In shallow groundwaters, where open system conditions are often encountered, water is in contact with atmospheric oxygen and carbon dioxide. Close system conditions develop in confined aquifers further away from the recharge area (Kehew, 2000).

5.3.4 Alkalinity

Water is electrically neutral, which means that the normalities¹ of cations must equal the normalities of anions.

For a solution in contact with CO₂, we can write the following charge balance equation (Davis & Cornell, 1998):

$$Alkalinity = M_{HCO_{2}^{-}} + 2M_{CO_{2}^{2^{-}}} + M_{OH^{-}} - M_{H^{+}}$$
(5.10)

Where M is the concentration of the considered species in meq²

This charge balance is the sum of all nonconservative ions in solution. The concentration of nonconservative ions would change if an acid were added to the solution, hence their name. Thus, the alkalinity of a solution represents its capacity to resist to pH changes induced by adding an acid or a base to it (Davis & Cornell, 1998). In a word, alkalinity buffers the solution. Alkalinity should always be measured in the field to obtain accurate values. Long storage times of the samples increase the chance of atmospheric CO2 dissolution or degassing (Clark & Fritz, 1997).

In this paragraph, the kinetic of dissolution of carbonate rocks, which depends on the crystallography of the carbonates, the temperature of the water, its flow rate and flow regime has not been discussed. For details, see Kehew (2000) or Ford & Williams (1989).

5.3.5 Saturation index

For a solid-liquid reaction $AB_{(solid)} \longleftrightarrow A_{(a)} + B_{(a)}$, the saturation index is defined as (Merkel & Planer-Friedrich, 2005):

$$SI = \log(\frac{IAP}{K_R}) \tag{5.11}$$

Where IAP is the ion activity product of the solution, i.e. the sum of the activity of all the species in solution in meq/l, and K_R the solubility product of the reaction

¹ The normality of a species is its concentration given in meq/l (see footnote 2)

² The concentration in meq of a species is found by multiplying its concentration in moles/l by its valence (Kehew, 2000)

A positive saturation index means a supersaturated solution relative to the considered species, a negative value, undersaturation, and a value of zero, thermodynamic equilibrium. Conduit flow water is well below saturation at all times because of the short flow/residence time (Shuster & White, 1971, Kehew, 2000). "Older" water held in the porous matrix is nearer equilibrium.

5.3.6 Piper diagram

Piper diagrams can be used to classify water in hydrochemical facies and to recognize shifts in these facies due to the arrival of less mineralized meteoric water during unsteady state discharge (Massei et al., 2002). A piper diagram is the combination of two trilinear diagrams, one for anions, and one for cations. Each observation is plotted as one point on these two diagrams and projected on the upper losange. Species concentrations in meq are given in percent (Helsel & Hirsch, 1992).



Figure 5.8 Piper diagram

5.3.7 CO₂ partial pressure

If the pH and the bicarbonate concentration are known, the CO2 partial pressure can be computed from (Kehew, 2000):

$$p_{co_2} = \frac{a_{H^+} a_{HCO_3^-}}{K_1 K_{CO_2}}$$
(5.12)

Where p_{CO_2} is the CO₂ partial pressure, *a* the activity of the species, and with the equilibrium constants $K_1 = 10^{-6.35}$ and $K_{CO_2} = 10^{-1.46}$ at 25 °C

Higher partial pressures can mean either that CO_2 is produced in the aquifer or that water has been in contact with a gas phase having a higher CO_2 concentration that atmospheric before its arrival in the saturated zone (Kehew, 2000^1).

5.4 Isotope hydrogeology

Isotope hydrogeology is based on the measure of variations in the number of neutrons in elements. These isotopes have the same chemical properties, but due to their differing mass, different physical properties. Isotopes are used to interpret the history of the geochemical evolution of water. Fractionation, which occurs during redox reactions, solid-liquid interaction, etc, can give information on the state of a system, the rate of reaction, or the source of the solutes (Clark & Fritz, 1997).

In this study we used one stable isotope of oxygen, ¹⁸O, and two isotopes of hydrogen, the first stable, ²H (deuterium) and the other radioactive, ³H (tritium).

5.4.1 Tritium

Tritium has a half-life of 12.43 years. It is measured in TU, which is defined as one tritium atom per 10^{18} hydrogen atoms. Tritium is produced in the higher atmosphere by ionizing particles following the reaction:

$$^{14}N(n,^{3}H)^{12}C$$

And decays to ³He:

 $^{3}\text{H}\rightarrow$ $^{3}\text{He}+\beta^{-}$

Concentrations of up to 6000 TU (the so-called "bomb peak") were measured in 1963 after the atmospheric weapon tests of the 1950-1960's (Maloszewski & Zuber, 1996). Atmospheric concentrations have since the Soviet-American test ban treaty of 1963 sank back

¹ Higher CO_2 partial pressure in the vadose zone can be the result of biological production, often called soil respiration (Kehew, 2000)

exponentially to natural background level. In the Lodowe spring, the tritium concentration was 11.6 TU in 2001 and 10.6 five years later.

5.4.2 Stable isotope measurement

The concentration of stable isotopes is given as a ratio. The standard notation is (Lee & Krothe, 2001):

$$\delta_{sample} = \left(\frac{R_{sample} - R_{s \tan dard}}{R_{s \tan dard}}\right) .1000 \text{ \%VSMOW}$$
(5.13)

Where R is the ratio of the isotope of interest to the most abundant isotope of the species, and VSMOW (Vienna Standard Mean Ocean Water) the name of the reference used worldwide Figure 5.9 gives a schematic representation of a dual inlet mass spectrometer used to measure the isotope ratio. The dual inlet allows to measure alternatively ratios in the sample and in a standard reference.



Figure 5.9 Schematic representation of a mass spectrometer (modified from Clark & Fritz,

1997)

5.4.3 Fractionation

Fractionation is a change in the isotopic ratio due to the redistribution of the isotopes between two reservoirs. We can distinguish two types of fractionation (Clark & Fritz, 1997):

- An equilibrium fractionation due to the difference in the strength of bonds. Heavier isotopes have stronger bonds than lighter (figure 5.10), so during phase change for example, the stronger bond will statistically survive longer. The heavy isotopic species is then partitioned into the denser phase. This effect is encountered during evaporation and condensation processes.



Figure 5.10 Difference in the strength of bonds between the light and the heavy isotope of an element (Clark & Fritz, 1997)

- Kinetic fractionation is due to a difference in diffusivity velocity. Diffusion is driven by a concentration gradient according to the Fick's first law (Fetter, 1992):

$$\vec{F} = -D(\frac{dc}{dx}) \tag{5.14}$$

Where \vec{F} is the mass flux vector [M/L².T], D the tensor of diffusion coefficients [L²/T], c the solute concentration [M/L³] and $\frac{dc}{dx}$ the concentration gradient [M/L³/L]. The diffusion coefficient is inversely proportional to the mass of the molecule, since we have, according to the gas molecular theory (Clark & Fritz, 1997):

$$u \propto \frac{1}{\sqrt{m}}$$

where m is the mass of the molecule

Thus, lighter molecules will diffuse faster with a fractionation factor given by the mass ratio of the two isotopes.

5.4.4 Variation in precipitation

 δ^{18} O measured during base flow reflects the mean yearly concentration in precipitation (Emblanch, 2003). The δ^{18} O and δ^{2} H input concentration in precipitation vary both regionally and over time. The air temperature controls the partitioning of isotopes in precipitation. Local meteoric water lines provide a baseline for groundwaters. The position of a sample on the line depends on temperature-based processes during the rainout process. Of the different fractionation effects (topographic, latitude, continental), only the seasonal component of isotopic variation in precipitation is relevant for the present study (figure 5.11).



Figure 5.11 Annual variation in δ^{18} O and tritium at three monitoring stations. The Pas station illustrates the variations in δ^{18} O typically encountered in the continental mid-latitudes (Clark & Fritz, 1997)

The amplitude of isotopic variation increases with increasing seasonal extremes in temperature within the catchment, and can be used as variable input to infer groundwater recharge time or aquifer response to precipitation.

5.4.5 Craig's Global Meteoric Water Line

On an annual basis, the global flux of water at the surface of the earth can be considered to be a closed cycle near dynamic equilibrium, unless a major climate shift takes place that modifies the volume of the different storage components (glaciers, ground water and surface water). Craig (1961, in Clark & Fritz, 1997), gives the following relationship between hydrogen 2 and oxygen 18, called the Global Meteoric Water Line (figure 5.12):



Figure 5.12 The Global Meteoric Water Line and kinetic evaporation effects for the original vapour mass (Clark & Fritz, 1997)

Kinetic processes such as evaporation taking place after or during rainout can be recognized by plotting the surface or groundwater data against the GMWL. Kinetic evaporation results in the data having a smaller slope than the GMWL.

Local Meteoric Water Lines only take into account the $\delta^{18}O$ and $\delta^{2}H$ of the region or catchment under study and can differ from the GMWL. Vapour masses of local origin can differ in their intercept (called the deuterium excess) as well as in their slope. The Eastern Meteoric Water Line used in the Eastern Mediterranean region for example has a deuterium excess of 22%, reflecting the higher fractionation during evaporation from the Mediterranean Sea due to higher mean temperatures.

5.5 Black-box models

Whenever a distributed-parameters approach cannot be applied because of a lack of detailed spatial data concerning the system to be modeled, lumped-parameters (or black-box) models can be used instead for interpretation (Malosewski & Zuber, 1996). Such models ignore spatial variations, which in the case of karst modeling may prove to be an advantage, since the aim is the identification of overall transport properties and/or the differentiation of various reservoirs constituting the karstic system. To this end, parameters such as electrical conductivity, turbidity (Massei et al., 2006), or isotopes, as is the case in this study, can be used for model calibration. Pinault et al. (2001) for example use impulse response functions to derive unit hydrographs for several karst catchments in southern France.

5.5.1 Mixing cell models

The idea of mixing cell models is to subdivise the catchment into reservoirs, each with its specific tracer composition, and to calculate the contribution of each to the total discharge. The different reservoirs can be for example the vadose zone and the saturated zone, or prestorm water and event water. Lee and Krothe (2001) propose a four component model comprising a reservoir for rain, one for soil water, one for epikarstic water, and one for phreatic diffuse flow. The number of independent tracers necessary is equal to the number of components identified minus one.

Different tracers are used to differentiate reservoirs. We will mention two of them here. ¹⁸O gives information as to whether the hydrodynamic system acts as piston flow or as well mixing model. ¹³C portion of DIC allows to better differentiate the unsaturated zone (Emblanch, 2003). Mixing cell models are also very useful to determine the portion of discharge coming from different units of the aquifer, provided end-members can be determined in the field. The calcium to magnesium ratio is a good first indicator of the relative importance of calcite and dolomite formations for the discharge. A ratio higher than 1 means water is mainly discharging from limestone, a ratio near 1 indicates recharge water flows through dolomite (Hem, 1985).

5.5.2 Hydrograph separation

Hydrograph separation has been used to quantify the instantaneous amount of water discharged from different reservoirs (Sklash & Farvolden, 1979). Whereas artificial tracing methods are "difficult to apply to mixing problems in karst aquifer due to the heterogeneity of the system" (Lee and Krothe, 2001), the use of environmental tracers is particularly appropriate to the construction of hydrograph separation curves. Deuterium and ¹⁸O behave conservatively in low-enthalpy environments and can be used to determine the mixing ratio of

storm/prestorm water in karst terrain. A two components mass balance equations has the following form (Lee and Krothe, 2001):

$$Q_m = Q_r + Q_{ps} \tag{5.15}$$

$$Q_m \delta_m = Q_r \delta_r + Q_{ps} \delta_{ps} \tag{5.16}$$

Combining 5.15 and 5.16 yields:

$$Q_r = Q_m \frac{\delta_m - \delta_{ps}}{\delta_r - \delta_{ps}}$$
(5.17)

Where Q is the discharge [L³/T], δ the isotope concentration [‰], and the m, r, ps subscripts stand for measured, rain, and pre-storm values.

5.5.3 Mean flow time

The assumption behind black-box models is that the "transit time distribution function adequately represent the distribution of flow lines" (Maloszewski et al., 2004). For single porosity aquifers or for sub-systems, different transit time functions are available, each corresponding to a specific recharge situation and flow pattern (figure 5.13).



Figure 5.13 Possible applications for each transit time function. 1) Piston Flow Model 2) Exponential Model 3) Dispersion Model (Maloszewski & Zuber, 1982)

The Piston-flow-model (PFM) is used when each recharge event "pushes" the previous one towards the hydrological outlet (Emblanch, 2003). The Exponential model (EM) can be applied to unconfined aquifers recharged from a large area (Maloszewski et al., 2004). The Dispersion model (DM) describes the advection-dispersion transport. If the hydrodynamic dispersion is zero (see 5.4.3.1), the Dispersion Model reduces to the Piston Flow Model. The three models can be combined to simulate more complex situations. Figure 5.14 gives three examples of possible conceptual models: model 1 has a single reservoir, whereas model 2 and 3 allow the use of more end-members.



Figure 5.14 Conceptual models combining different transit time functions (Maloszewski et al., 1983)

For karstic systems, model 2 could represent conduit flow (direct runoff) and diffuse flow, and model 3 could also take into account diffusion processes between the fissured/conduit reservoir (upper reservoir) and the porous matrix (lower reservoir).

5.5.4 Transit time functions

Each model is characterized by a transfer function relating the input and output signals through a convolution integral (Maloszewski et al., 2004):

$$c_{out}(t) = \int_{0}^{\infty} c_{in}(t-\tau)i(\tau)d\tau$$
(5.18)

Where c(t) is the tracer concentration, *i* the transfer function and τ a dummy variable. The transfer functions for the dispersion model and the piston flow model are:

Piston flow model

$$i(\tau) = \delta(\tau - T) \tag{5.19}$$

Where δ is the Dirac function

Dispersion model

$$i(\tau) = \frac{1}{\sqrt{4\pi P_D \tau / T}} \frac{1}{\tau} \exp\left[-\frac{(1 - \tau / T)^2}{4P_D \tau / T}\right]$$
(5.20)

Where P_D [] is a dimensionless dispersion parameter and T [T] the mean transit time of water

 P_D is the inverse of the Peclet number used in fluid dynamics to relate the rate of convection of a flow to its rate of diffusion (Wang & Anderson, 1982).

T is related to the water volume V_w (L³) in the reservoir and the outflow rate Q(L³/T) by the formula:

$$V_{w} = QT \tag{5.21}$$

5.5.6 Discharge from the conduit aquifer

Double porosity aquifers contain mainly stagnant water in the porous matrix, where the hydraulic conductivity is smaller by orders of magnitude (Motyka, 1998). For artificial tracer tests it is not necessary to take into account this stored water, since the tracer does not diffuse deeply into the stagnant zone matrix (Maloszewski et al., 2004). For environmental tracers though, where diffusion-driven exchange between fissure water and matrix water take place, a more complex model should be used. The Parallel Fissure Dispersion Model (PFDM) proposed by Maloszewski et al. (2004) has 4 fitting parameters, so that no unique solution can be derived from it. A further simplifying assumption is to consider that the fissure network is isolated from the porous matrix during high flow and the flow through it pure piston flow.

Another problem to address is the unsteady state flow prevailing during sampling. Zuber showed (1986) that both the analytical solution and the determined transport parameters are meaningless if steady state conditions were not present at the time of measurement. Werner et al. (1997) propose a numerical algorithm to cope with that situation.

6. Results and discussion

6.1 Base flow characterization and physical parameters

A well marked base flow level previous to a storm helps to characterize the base flow signal and to understand the hydrodynamic of the karst system (Emblanch, 2003). The month prior to the September storm had been dry, and the discharge relatively low when the first sampling took place on 17th August. The recession period was little disturbed by rain events. The October data is probably quite representative of winter base flow hydrochemistry. The various physical parameters measured are first indicators of the spring response to loading.

-Conductivity: The electric conductivity is a measure of the concentration of charged ionic species in solution (Hem, 1985). During the flood, an increase followed by a steady decrease below base flow level, followed by a recovery back to base flow level was observed.



Figure 6.1 Electrical conductivity measured in the field and in the lab

- Temperature: Even though the variation range measured is only 0.3 °C, there seems to be a genuine trend above measurement noise, with a cooler base flow water being mixed

with warmer precipitation water during the flood. No measurement of the precipitation temperature was done, so temperature cannot be used as tracer for hydrograph separation (see 6.5.3 below). The high level of noise would have been problematic anyway.

-Discharge: The observed ratio Q_{max} / Q_B (see 4.1.1) for the September storm was 10, thus characterizing the Lodowe spring as an intermediate response spring.

-Turbidity: This parameter was not measured. Turbidity can indicate that some of the discharge is fed by conduit flow (Desmarais & Rojstaczer, 2002). Higher turbidity was observed on 8th September, the second day of sampling of the September storm.

6.2 Additional information yielded by the water chemistry

Knowledge of the Lodowe karst aquifer and its response to loading can be deepened by considering the variations in the chemical parameters. The Lodowe spring has a calciumbicarbonate hydrochemical facies (Hem, 1985). No significant shift in the facies was observed as the discharge changed (figure 6.2).



Figure 6.2 Piper diagram of the Lodowe spring. All 26 observations plot at the same point

The CaMg ratio varies between 5 at base flow and 9 at high discharge (figure 6.3). According to Shuster & White (1971), this shift indicates a change in the water sources. A ratio near 1 indicates that most of the recharge comes from dolomite whereas a ratio higher than 1

indicates that water is mainly discharged from limestone. The observed increase in the CaMg ratio during high flow means a decrease in the contribution from dolomite formations. Without a detailed geological study, only educated guessing can be done concerning possible calcite and dolomite end-members and their location in the catchment.

The saturation index (SI) was computed using the PHREEQC computer code (Parkhurst & Appelo, 1999). Calcite and aragonite were at equilibrium at all times, dolomite and gypsum undersaturated. This means that dolomite and gypsum are being dissolved in the aquifer. A sensitivity analysis has indicated that the saturation index is sensitive to the alkalinity value given as input. Since alkalinity was not measured in the field, but weeks later in the lab, one should be careful when considering the SI values for calcite and aragonite.



Figure 6.3 Saturation index for dolomite and CaMg ratio

A high CaMg ratio and the apparent saturation of the water with regard to limestone for all water stage as well as the absence of change in the hydrochemical facies of the Lodowe spring tends to indicate that no major change in sources and flow paths take place as the discharge volume changes.

The computed CO_2 partial pressures, all in the 2.10⁻³ range, are higher than atmospheric, even during low flow (figure 6.4). The lower partial pressures observed during the recession period may indicate that event water has a shorter residence time in the vadose zone due to a quicker

infiltration rate. A word of caution is appropriate, though. Sensitivity analysis revealed that an increase of 50% in the alkalinity value would yields atmospheric partial pressures of $10^{-3.5}$. Since alkalinity was not measured in situ, but later in the lab, the need for such a correction is not unrealistic.



Figure 6.4 CO₂ partial pressure

6.3 Conceptual model of spring response to precipitation

Desmarais and Rojstaczer (2002) proposed a conceptual model of flow for the karstic aquifer of the Maynardville limestone in Tennessee which seem to fit well to the chemistry observations made at the Lodowe spring. Three stages can be distinguished: 1) flushing 2) dilution 3) recovery

- The initial increase in conductivity, i.e. an increase in the concentration of dissolved species is the indicator of an increased hydraulic gradient which mobilizes the "old" water trapped in small pores and fractures. This is the response of the system to loading.
- 2) The onset of the conductivity decrease announces the arrival of storm water to the spring. Discharge decreases. Warmer storm water causes water temperature to increases for a while before it levels off to base flow level as the amount of event

water becomes less and has more time to exchange heat with the cooler aquifer water. This phase is a "competition between the velocity at which recharge water is moving through the system, how fast it dissolves carbonates and gains the same chemical signature as the "old" aquifer water, and the amount of mixing that takes place between these two water sources" (Desmarais & Rojstaczer, 2002). CO₂ partial pressures are higher than at base flow due to the increased rate of infiltration leaving less time to recharge water to equilibriate with soil CO₂. The dilution effect caused by the arrival of meteoric water increases the undersaturation of dolomite and gypsum.

3) The recovery phase begins when conductivity reaches its minimum. The concentration of dissolved carbonates in the recharge water reaches that of the aquifer water. The SI for dolomite and gypsum increase. The system strives towards its base flow equilibrium again.

6.4 Isotopes of the Tatra springs

In August 2007, a sampling campaign of the entire Tatra National Park took place under the aegis of the Department of Geography of Cracow's Jagiellonian University. A subset of thirty springs samples were analyzed isotopically. These samples were pooled with those from the Lodowe and plotted (Figure 6.5).

Pearson's correlation coefficient, which is an acceptable measure of linear correlations in the absence of outliers (Helsel & Hirsch, 1992), is 0.97 for the regression line and indicate a very reliable regression. Both end-members "precipitation" and "mean ground water concentration" fall onto the regression line indicating no notable evaporation of meteoric water before infiltration. Both the slope and the intercept of the regression are not significantly different from Craig's GMWL with p values of 0.50 and 0.56 respectively¹.

¹ p values give the probability that the test statistic used for the t-test has the computed value, under the assumption that the slopes/the intercepts do not differ from one another (the null hypotheses). A p value smaller than the significance level leads to a rejection of the null hypotheses (Helsel & Hirsch, 1992)



Figure 6.4 Plot of the Tatra spring data against the GMWL

6.5 Modeling the karst aquifer

6.5.1 Double porosity aquifer

Contrasting information using different isotopes can help to the characterization of an aquifer system (Emblanch, 2003). As proposed by Maloszewski et al. (2002) for the Schneealpe karstic massif, the Lodowe karst aquifer is split into two parallel systems (figure 6.6). Base flow is sustained by discharge Q_P from the porous aquifer with a volume of water in storage V_P . The conduit flow system, activated during a storm, contributes a discharge Q_C to the total spring discharge Q. Its volume of water in storage is V_c .



Figure 6.6 Conceptual model for the Lodowe spring (modified from Maloszewski et al., 2000)

The discharge from the slow-flow, porous aquifer was modeled with tritium using the Dispersion Model (DM) (see 6.5.2) and the quickflow discharge with ¹⁸O using the Piston Flow approach (see 6.5.3).

6.5.2 Lodowe water resources: the tritium data

The tritium input function was calculated from the long-term precipitation input measured at the meteorological station of the Meteorological institute in Cracow, and corrected for by the estimated ratio of winter to summer infiltration coefficient as recommended by Grabczak et al. (1984).

Four tritium measurements were available for the fitting procedure, three taken at low flow (1984, 1987 and 2006) and one at high flow (2001). For that reason, the latter was not included in the modeling procedure. Modeling was performed with the FLOWPC software (Maloszewski & Zuber, 1996) using the Dispersion Model (figure 6.7). Table 6.1 summarizes the results obtained.

 Table 6.1 Tritium modeling

| beta | PD | Mean Water Age T _P (yrs) | е |
|------|------|--|-------|
| 0 | 0,12 | 5,5 | 0,998 |

Beta is a tritium free older flow component, P_D the dispersion parameter and e gives the goodness of fit of the model

e is defined by the equation:

$$e = \frac{\sqrt{\sum_{i=1}^{j} (c_{mi} - c_i)^2}}{j}$$
(6.1)

where c_{mi} is the i-th measured concentration, c_i is the i-th fitted concentration for the time step t_i , and j is the number of observations



Figure 6.7 Best fit curve of the observed tritium concentration of the Lodowe spring. The error bars are in the +/-1 TU range

The Lodowe spring has a mean low flow discharge of 350 l/s. A mean water age for the porous aquifer of 5.5 years yields a volume of water in deep storage (equation 5.21) V_P of $60.7*10^6$ m³. That means a water column 3.57m for a catchment area of 17 km², or, assuming a porosity of 0.033, a saturated zone 108 meters thick. This value seems reasonable. A thickness of 100 meters would fits into the massif, but without additional hydrogeological information concerning the thickness of the water bearing formations around the Lodowe spring, there is no possibility to verify the validity of the values obtained.

6.5.3 Event water: direct flow

Since the sampling missed the beginning of the storm, only the recession curve was measured. In the absence of the rising limb of the hydrograph and chemograph, it was not possible to fit the piston flow model to the data.

The event and pre-event components of the discharge were computed using formula (5.17). Two hydrograph separation curves using ¹⁸O and Ca²⁺ gave very different results (figure 6.8). The δ^{18} O curve shows event water portions as high as 28%. Computations with calcium yielded lower values, indicating that the residence time of event water is probably too long to neglect limestone dissolution. Hydrograph separation using non-conservative species like calcium gives only a minimum estimate of the proportion of new water entering the spring after a storm event.



Figure 6.8 Hydrograph Separation curves with ¹⁸O and Ca²⁺ as tracers

The additional spring discharge during the flushing phase comes from the conduit reservoir. Its volume can be inferred from:

$$V_c = Q_c t \tag{6.2}$$

Where V_c [m³] is the volume of the conduit aquifer, Q_c [l/s] its discharge, and t [hrs] the time interval

 Q_c is equal to the total discharge until event water arrives at the spring, and t is the time period between the beginning of the storm and the peak in conductivity (Desmarais & Rojstaczer, 2002). It is only possible to calculate an upper bound, since sampling began too late to include the conductivity peak. Assuming a four day long constant discharge of 4000 l/s, the volume of fissure water amounts to1.4*10⁶ m³. This agrees well with the volume of 2*10⁶ m³ obtained from recession analysis performed using Mangin's formula (Barczyk et al., 2002).

6.5.4 Water in storage

The total amount of water in storage is equal to the sum of water in storage in the porous and conduit reservoirs:

$$V_t = V_p + V_c = 62.1 * 10^6 \,\mathrm{m^3} \tag{6.3}$$

And the relative amounts are:

$$r_{V_c} = \frac{V_c}{V_t} = 97.25\% \tag{6.4}$$

$$r_{V_p} = \frac{V_p}{V_t} = 2.25\% \tag{6.5}$$

The porous aquifer's storage capacity accounts for nearly 98% of the total aquifer water volume. In that case, it is not surprising to have discharge water saturated with respect to calcite and aragonite at base flow, since the mean transit time of 5.5 years through the porous aquifer leaves ample time to reach equilibrium.

7. Conclusions

Although the lack of data make validation impossible, the results obtained are plausible. The modeling of two parallel systems appears appropriate, since no clear cut classification between conduit flow and diffuse flow emerges from the parameters measured. Some like the variability of the hydrochemistry, the high event water component during storm flow or the flashiness of the spring point towards a conduit flow type. Others like the saturation of calcite and aragonite for all water stages or the near constant water temperature are more indicative of a large diffuse flow reservoir. The use of stable isotopes is a reliable way to determine the ratio of event water to "old", pre-event water. The hydrograph separation curve clearly shows the existence of a large quick flow component to the discharge during a flood. As shown by the regression line of figure 6.4 running parallel to the GMWL, recharge is quick, either through swallow holes, or through the soil horizon. The Lodowe spring seems to occupy an intermediate position between a conduit type and a diffuse aquifer. Although very crude, the discharge ratio Q_{max} / Q_B proposed by White gives a good first characterization of the aquifer. The observed ratio of 9 points to an intermediate response spring (table 4.1), that is, one where no end members dominates completely the flow and both participate significantly to the total discharge. Each subsystem probably assumes a different function. The porous matrix constitutes the main reservoir, with 98% of the total water in storage. On the other hand, the large amount of event water quickly transported to the spring during and shortly after a storm indicates the significant development of the conduit system. This would agree with the conceptual model of flow of figure 4.3. According to it, the porous aquifer feeds discharge through the conduit system at base flow, while the conduit aquifer recharges the porous reservoir and transports event water directly to the spring during storm flow. Due to the heterogeneities in conduit radius and inter- conduit connections, this reversal in the hydraulic gradient is not homogeneous, so that parts of the porous aquifer still contribute to the discharge during high flow, as shown by the hydrograph separation curve. Hence, diffuse and continuous contamination, for example atmospheric, would pose a long term threat to the Lodowe spring aquifer by diffusing into the porous matrix where the mean transit time is long and the mean flow velocity low. On the contrary, a single contamination event from a point source could be flushed quickly to the spring. This, of course, also depends on the type of contaminant reaching the aquifer. DNAPL, being denser than water, would probably sink into

the siphons of the conduit system and start diffusing from there into the porous matrix, rendering remediation strategies virtually impracticable (Fetter, 1992).

The role of the unsaturated zone and the epikarst, crucial in regard to contamination, could only have been addressed by additional sampling. Pinault et al (2001) used DIC and ¹³C in combination with turbidity measurement at the spring to study the transport mechanisms through the epikarst and its contribution to the spring discharge.

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Hiermit erkläre ich, dass die Arbeit selbständig und nur unter Verwendung der angegebenen Hiflsmittel angefertigt wurde.

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