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10 Tracer Techniques for Mines

10.1 Why Conduct a Mine Water Tracer Test?

10.1.1 Objectives of Mine Water Tracer Tests

Usually, tracer tests are conducted in or near mines to find connections from the surface to the mine or vice versa. Typical examples are tracer tests conducted in conjunction with numerical models to assess potential radioactive waste disposal sites (e.g. Lee 1984). All tracer tests in mines can be grouped based on their objectives:

- assessing the risk or cause of mine water inrushes/inundations (Skowronek and Zmij 1977; Goldbrunner et al. 1982; Wittrup et al. 1986; Qiang et al. 1992; Lachmar 1994);
- optimising mining strategy (Adelman et al. 1960; Reznik 1990; Williams and Kirschner 1992; Kirschner and Williams 1993);
- evaluating the feasibility or effects of underground disposal of non-radioactive waste (Fried 1972; Himmelsbach and Wendland 1999);
- evaluating potential underground disposal of radioactive waste (Abelin and Birgersson 1985; Brewitz et al. 1985; Galloway and Erickson 1985; Cacas et al. 1990; Lewis 1990; Birgersson et al. 1992; Hoehn et al. 1998; Sawada et al. 2000; hundreds of studies were conducted in the Stripa mine/Sweden, the Grimsel/Switzerland experimental site, and the Yucca Mountain/USA site);
- subsidence studies (Mather et al. 1969); and
- developing remediation strategies (Aldous and Smart 1987; Doornbos 1989; Aljoe and Hawkins 1993, 1994; Davis 1994a, 1994b; Wolkersdorfer 1996; Wolkersdorfer et al. 1997a; Canty and Everett 1998)

Tracer tests have also been conducted to study "heat mining" in geothermal projects (e.g. Gulati et al. 1978; Horne et al. 1987; Kwakwa 1989; Randall et al. 1990; Aquilina et al. 1998). Because such studies are similar to those conducted in fractured rocks (see Himmelsbach et al. 1992; Käß 1998) and are usually done using boreholes, rather than conventional mines, these studies will not be considered further here.

Many tracer tests are not reported in the literature, or are only available as master's theses (e.g. Anderson 1987; Bretherton 1989; Diaz 1990; Hasche 2001). This may imply that they were unsuccessful or that the results were confidential, but may just reflect the fact that no one was willing to take the time to convert the study into a research paper. So far, only a few published tracer tests have been conducted to trace the hydrodynamic conditions of a flooded underground mine (Aljoe and Hawkins 1994; Wolkersdorfer et al. 1997a; Wolkersdorfer and Hasche 2001a), mainly because no suitable method was available to inject the tracer into the mine water at predetermined depths or without contaminating the mine water above the injection point. Most tests therefore injected the tracer at the surface, allowing the tracer to flow into the mine through fractures (e.g. Lachmar 1994) or used boreholes (e.g. Galloway and Erickson 1985; Cacas et al. 1990).

As will be shown in section 11.6, in-situ remediation and treatment methods usually fail because they require a thorough understanding of the flow regime within the flooded underground mine and where underground dams have to be installed before flooding. Tracer tests in flooded underground mines are therefore imperative for such in-situ options.

10.1.2 Aims of Mine Water Tracer Tests

Tracer tests are commonly used to investigate the hydraulic parameters or interconnections of ground water flow (Käß 1998). Most such techniques are well described and a range of tracers or methods can be selected, depending on the aims of the tracer test and the hydrological situation.

Published results of tracer tests in abandoned underground mines are still uncommon, as already stated by Davis (1994b, 1994a). Since less experience exists in tracing mine water, the expected results of an individual mine water tracer test cannot always be predicted. Summarised, the aims are as follows:

- testing the effectiveness of bulkheads dams,
- investigating hydrodynamic conditions,
- tracing connections between a mine and the surface,
- clarifying reasons for inundations,
- assessing contaminant mass flow, and
- estimating the decrease or increase of contaminants

Historically, the first tracer tests conducted in mines were simply to reveal connections between ground or surface waters and the mine (e.g. Skowronek and Zmij 1977). One of the first tracer tests in a deep flooded underground mine was conducted in 1995 to investigate the more complex hydrodynamic conditions of the flooded mine (Wolkersdorfer 1996).

It would be useful in many mining situations to use a multi-tracer approach. Possible candidates for multi-tracer tests are dyes, salts, and solid tracers. Wolkersdorfer et al. (2002) conducted a multi-tracer test in the Austrian Georgi-Unterbau mine (see section 12.13), using rock salt (NaCl), sodium fluorescein, uranine, and different microspheres in the flooded underground mine. Because the number of tracers that can be used in a single mine water tracer test is limited, my working group prefers fluorescent microspheres. Up to eight different colours can be injected and up to six have been used so far, in a mine water tracer test conducted at the flooded Straßberg/Germany fluorspar mine (see section 12.11).

In the future, tracer tests should become a prerequisite for evaluating remediation strategies for abandoned mine sites. Kimball et al. (1999) gave an example of how to use tracer tests and carry out synoptic sampling of trace metals in surface streams to evaluate the environmental impacts of mine effluents on watersheds. This can also be done in other mine closure cases where the hydrogeological situation is unclear and the choice or implementation of remediation strategies will be affected by the water flow.

10.1.3 Possible Mine Water Tracers

Underground mines generally consist of shafts, adits, raises, and stopes; these are comparable to the features found in karstic terrains. Therefore, a flooded mine can be looked on as a karst aquifer in a conceptual model, and numerical models of flow in karst aquifers (e.g. Liedl and Sauter 2000) might also be used to describe the hydrodynamics of underground mines. Furthermore, the tracer techniques developed for karst aquifers (e.g. Gospodarič and Habič 1976; Käß 1998) should be appropriate for flooded mines, too.

According to the literature, including our own investigations, nine types of tracers have been used in mine water tracing (Table 18), though only successful tracer tests (and not even most of them) are usually reported. Therefore, little can be said about tracers that are unsuitable for tracing mine water, though some researchers have investigated tracer behaviour in the mine water environment. Aldous and Smart (1987) conducted research into the absorbance of seven fluorescent tracers on iron hydroxide and kaolinite (sulpho rhodamin B, sulpho rhodamin G, rhodamin WT, lissamine yellow FF, pyranine, Na-fluorescein, and Tinopal CBS-X). As the behaviour of tracers varies in different environments, no general conclusions are possible. Yet, from their studies, sulfo rhodamin G and pyranine appear to be the best tracers in sediment-laden mine water – though neither has been used so far due to analytical or environmental reasons. For Na-fluorescein, which easily adsorbs to organic materials, we know of successful tests as well as unsuccessful ones.

The chemical composition of mine waters can very often involve high TDS, low pH (e.g. Iron Mountain: pH –3.6; Nordstrom et al. 2000), or high metal concentrations (Banks et al. 1997), which consequently limits the number of tracers that can be used successfully. Even conservative tracers, such as Na-fluorescein, might be unsuitable under certain mine water conditions e.g. low pH, high suspension load, wooden supports, free chloride radicals.

Therefore, laboratory tests using the chosen tracer and typical mine water compositions are essential to obtain positive results. All tracers have to be selected based on their expected or known behaviour in the mine water in question. An important consideration when conducting such tests is the duration of the laboratory test. From our experience, mine water flows with mean velocities of 0.3 to 1.6 m min^{-1} (95% confidence interval of 42 tracer tests investigated; see table 19), which can be used to roughly calculate the expected residence time. The stability of the tracer in the mine water must be guaranteed for the whole duration of the tracer test. Preceding the Niederschlema/Alberoda and Straßberg tracer test, we conducted 45 and 28 days of laboratory tests, respectively. Concurrently, the tracer was sampled and visually analysed to identify alterations (Wolkersdorfer 1996; Wolkersdorfer and Hasche 2001a).

10.2 Tracers and their Use

10.2.1 Introduction

Many people in the mine water field want to use tracers for their studies once they hear what tracers can do. However, very often, the basic knowledge about the properties of tracers and the way in which tracer tests have to be planned or conducted are not clear. The following chapters will merely introduce the broad field of tracer investigations; consequently, the language and the theory are expressed in a simple manner. It is meant for the novice with a basic knowledge of environmental sciences or geosciences and mainly covers tracers that can be used in mines. Therefore, some rarely used tracers, such as the promising DNA-tracers (Sabir et al. 1999), will not be discussed. Yet, all the prerequisites for conducting a tracer test are given and the relevant references are provided. A range of publications about tracers or tracer tests has been cited in earlier chapters and will also be referred to in the following sections. Readers who want to know more details should read one or more of those publications (e.g. Aley and Fletcher 1976; Moser and Rauert 1980; Käß 1998; Field 2003).

10.2.2 What are Tracers?

Tracers or marker substances are used to evaluate characteristic hydrogeological parameters. They can be divided into natural (or environmental) tracers that are “naturally” or unintentionally contained in the water, and artificial tracers. As a rule, the former are already contained in the water, whereas artificial tracers are injected into the water during the field test. Environmental isotopes, environmental chemicals, organisms, or the physical qual-

Table 18. Selection of tracers that have already been used in mine water tracer tests; only selected references are provided.

Tracer	References
NaCl	Mather et al. (1969); Hawkins and Aljoe (1992); Wolkersdorfer (2002b); Wolkersdorfer and Hasche (2004)
Na-fluorescein	Mather et al. (1969); Parsons and Hunter (1972); Nunes et al. (1990); Wirsing (1995)
Rhodamin WT	Canty and Everett (1999)
Club Moss Spores	Wolkersdorfer and Hasche (2001b); Wolkersdorfer (2001); Wolkersdorfer and Hasche (2004)
Microspheres	Wolkersdorfer and Hasche (2001b); Wolkersdorfer (2001); Wolkersdorfer and Hasche (2004)
Sulpho Rhodamin B	Aldous and Smart (1987)
Tritium	Mulenga et al. (1992); Zhou et al. (1993)
CFC chlorofluorohydrocarbon	Parry et al. (2000)
Rare Earth Elements	Worrall (1999); Wolkersdorfer (2002a); Merten et al. (2004)

ities of the water are examples of natural/environmental tracers. Artificial tracers can roughly be divided into water-insoluble (e.g. dyes, phages, microparticles, and spores) and water-soluble tracers (e.g. pigments, salts, and radioactive substances).

The difference between artificial and natural tracers can be clarified by using tritium as an example. Tritium arose from atmospheric nuclear weapon tests and reached ground water naturally in precipitation. Used in this manner, tritium is an *environmental* isotope and is therefore regarded as a *natural* tracer. However, tritium can be injected into the ground water within the scope of a tracer test as a radioactive tracer, and would then be serving as an *artificial* tracer (Geyh and Schleicher 1990).

The increasing environmental awareness of the population and the authorities during the last few decades has led to increasing problems in conducting tracer tests. We have found that it is usually better to use the words "tracer" or "marking substance" instead of the proper tracer names of the tracers, which may sound scary to the uninformed.

Table 19. Distances and mean velocities of worldwide tracer tests in underground mines. Table is given for comparisons only, details concerning geological setting and hydraulic parameters are given in the literature cited. Mean of all 42 tracer tests: 0.3–1.6 m min^{-1} 95% confidence interval of 42 tracer tests; [1] result probably wrong.

Distance, km	veff, m min^{-1}	Reference	Location
0.015	0.0001	Wolkersdorfer unpublished	Rabenstein/Sachsen
0.17	0.0003	Wolkersdorfer unpublished	Rabenstein/Sachsen
0.2	0.001[1]	Aljoe and Hawkins (1993)	Buckhannon/WV
0.044	0.004	Aljoe and Hawkins (1993)	Buckhannon/WV
0.093	0.004	Wolkersdorfer unpublished	Straßberg/Harz Mts
0.093	0.006	Wolkersdorfer and Hasche (2004)	Straßberg/Harz Mts
0.13	0.01	Aljoe and Hawkins (1994)	Buckhannon/WV
0.077	0.01	Canty and Everett (1998)	Red Oak/Oklahoma
0.78	0.01	Wolkersdorfer (1996)	Niederschlema/A.
0.238	0.014	Wolkersdorfer unpublished	Straßberg/Harz Mts
0.048	0.02	Wolkersdorfer et al. (2002)	Brixlegg/Tirol
0.01	0.03	Wolkersdorfer et al. (2002)	Brixlegg/Tirol
1.182	0.07	Wolkersdorfer unpublished	Straßberg/Harz Mts
0.35	0.1	Mather et al. (1969)	Aberfan/South Wales
1.181	0.1	Wolkersdorfer unpublished	Straßberg/Harz Mts
3.539	0.1	Wolkersdorfer unpublished	Straßberg/Harz Mts
0.077	0.12	Canty and Everett (1998)	Red Oak/Oklahoma
0.077	0.14	Canty and Everett (1998)	Red Oak/Oklahoma
0.283	0.15	Wolkersdorfer and Hasche (2004)	Straßberg/Harz
1.773	0.15	Wolkersdorfer and Hasche (2004)	Straßberg/Harz
0.171	0.17	Canty and Everett (1998)	Red Oak/Oklahoma
6.564	0.17	Wolkersdorfer unpublished	Straßberg/Harz Mts
1.7	0.2	Parsons and Hunter (1972)	Ebbw Vale/Mons.
0.229	0.23	Canty and Everett (1998)	Red Oak/Oklahoma
0.4	0.27	Czolbe et al. (1992)	Peißen/Germany
3.6	0.3	Aldous and Smart (1987)	Forest of Dean/Gls.
4.798	0.3	Wolkersdorfer and Hasche (2004)	Straßberg/Harz Mts

Table 19. Continued. Niederschlema/A.: Niederschlema/Alberoda; Ebbw Vale/Mons.: Ebbw Vale/Monmouthshire; Gls.: Gloustershire.

Distance, km	veff, m min^{-1}	Reference	Location
0.15	0.4	Mather et al. (1969)	Aberfan/South Wales
0.172	0.4	Wolkersdorfer et al. (1997a)	Niederschlema/A.
0.216	0.5	Wolkersdorfer et al. (1997a)	Niederschlema/A.
0.22	0.5	Wolkersdorfer et al. (1997a)	Niederschlema/A.
0.2	0.6	Mather et al. (1969)	Aberfan/South Wales
3.18	0.7	Wolkersdorfer and Hasche (2004)	Straßberg/Harz Mts
0.5	1.3	Aldous and Smart (1987)	Forest of Dean/Gls.
2.25	1.5	Wolkersdorfer and Hasche (2004)	Straßberg/Harz Mts
0.776	1.6	Wolkersdorfer et al. (1997a)	Niederschlema/A.
0.04	1.7	Wolkersdorfer et al. (2007)	Freiberg/Sachsen
0.736	1.8	Wolkersdorfer et al. (1997a)	Niederschlema/A.
0.78	2	Wolkersdorfer et al. (1997a)	Niederschlema/A.
2.159	5.7	Wolkersdorfer et al. (1997a)	Niederschlema/A.
2.723	7.9	Wolkersdorfer et al. (1997a)	Niederschlema/A.
0.5	11.1	Aldous and Smart (1987)	Forest of Dean/Gls.

10.2.3 What are Tracers used for?

Tracers are used to characterise flow paths in many different disciplines like geology, hydro(geo)logy, chemistry, physics, water supply and distribution, hydraulic engineering, limnology, or biology. Tracers have been used to pursue underground watercourses since Roman times. Today, tracers are also used in flooded mines, at site investigations of radioactive repositories, and in living beings.

The prime aim of tracer tests is to trace back flow paths, and determine flow velocities, mass transfer, and hydrogeological parameters. By evaluating tracer tests, the following information and characteristic quantities can be determined:

- hydraulic connections of flow pathways,
- ground water flow directions,
- ground water velocity, average interstitial velocity, and mean residence time,

- hydrodynamic dispersion,
- flow and mass transfer rates,
- variability of hydrogeological properties, and
- transport behaviour of dissolved or particulate water constituents as well as their interactions

10.2.4 Requirements for Tracers

A tracer is described as a conservative or ideal tracer in the subsurface medium if it exhibits:

- inert behaviour not prone to chemical reactions with immobile solids,
- unchanging physical qualities, and
- is transported at the same velocity as the flowing water.

In addition, as many of the following criteria as possible should be met:

- no natural occurrence of the tracers in the transport medium,
- good analytical detectability even at great dilution,
- water-soluble or dispersible,
- robust chemically stable,
- no interactions between tracer and medium,
- reasonably priced in terms of acquisition, handling, and analysis,
- physiologically safe (not toxic), and
- no lasting effect on ground water composition

No tracer satisfies all the aforementioned conditions equally well. Rather, the most suitable tracer has to be selected based on the question to be answered. Based on its transport behaviour, tritium would fulfil most of the ideas of a conservative tracer, yet, for reasons of cost effectiveness and analytical procedures, fluorescent dyes are the most common tracers used.

10.2.5 Types of Tracers

"Natural" or "Environmental" Tracers

Stable Isotopes

Environmental isotopes are nuclides of elements that occur in water without having been added or injected on purpose to conduct a tracer test. They are therefore natural tracers. Usually, their concentrations are low and the analysis and the interpretation subsequently turns out to be difficult. In distinction to artificial tracers, they can be used over large areas and long time scales. Besides geohydraulic parameters, environmental isotopes allow the age and temperature evolution of the waters to be traced (e.g. Lippmann et al. 2003). Fractionation of certain stable isotopes also allows the identification of certain biogeochemical processes (e.g. bacterial sulphate reduction; Fauville et al. 2004).

Environmental Chemicals

Environmental chemicals are substances that enter the water cycle accidentally or by slow contamination. They might be the same substances as in the case of artificial tracer tests, but because they reach the water cycle unintentionally they are categorised as "natural" tracers.

Sodium fluorescein or pyranine are two commonly used dyes in cosmetic articles, though a test with several different cleaning detergents showed that other chemicals are now being substituted for sodium fluorescein. Seeping boric acid from house waste disposal sites can be considered a good tracer (Neal et al. 1998). Increased boron concentrations in water analyses usually point to nearby house waste disposal sites or, in certain areas, to naturally elevated boron concentrations e.g. Col and Col (2003). Chlorides are found in the vicinity of streets or airfields, where salt is used for de-icing, or downstream of potash pits. Kolpin et al. (2002) investigated the background concentrations of 95 organic wastewater contaminants in the USA, thereunder caffeine, hormones, and antibiotics. Very good environmental tracers are sulphur hexafluoride (SF_6) or chlorofluorocarbons (CFCs), which are abundant in nearly every water. The same substances can also be used as artificial tracers.

Metals and semi-metals (e.g. Cd, U, As, Cu, and Sb) can be considered as natural tracers downstream of mine water drainage tunnels. One of many examples worldwide is the river Erft in the Eifel/Germany, which receives mine water from the abandoned Mechernich mine (Schalich et al. 1986). Such natural tracers are commonly used in the exploration for ore deposits (Grimes et al. 1995).

One of the most expensive and outstanding "natural" tracer tests happened on 12 August 1901 (Anonymous 1901), when lightning hit the Pernod factory at Pontarlier and about 1 million litres of absinth were flushed down the river Doubs. Two days later, André Berthélot noticed the absinth at the Loue Spring, 50 km north-north-east of Pontarlier.

Organisms

Organisms are rather exotic tracers. Common natural tracers are bacteria, which can be used to trace the environmental influence of excrement. Eels or ducks were also used successfully as tracers, though they should perhaps be listed as “artificial” tracers in the example cited, because the organisms were marked (Käß 1998).

Physical Influences

A physical influence that plays a major role in ground water investigations or the judgement of ground water contaminations is a change in water temperature. New fibre optic measuring methods make it possible to receive a high spatial resolution of temperature differences. Schreck et al. (1998, 1999), and Stoddart et al. (2005) used this method to monitor temperature variations in mine dump sites. Van Berk (1987) was able to show that downstream of a coal mine waste dump, the ground water temperature increased by 3–6 K, consistent with the exothermic pyrite weathering reaction.

Changes in electrical conductivity were used to trace the sources of highly mineralised waters emanating from potassium mine waste rock piles in the German Rhine river valley.

Artificial Tracers

Water-soluble Tracers

Dyes

Dyes are the most frequently used artificial tracers, amongst which fluorescent dyes are today the first choice when carrying out tracer tests. The dyes used are largely non-poisonous apart from the rhodamines and can easily be detected by fluorometers, fluorescence chromatography, or with the support of HPLC (high pressure liquid chromatography). Transportable fluorometers and other sophisticated techniques (e.g. MORES: micro optical remission micro sensors; fibre optics) are now available and allow continuous monitoring of fluorescence intensity. Both the easy analytical verification and relatively low cost have considerably contributed to the distribution of fluorescent dyes as tracers in hydrogeological investigations. They are also used to dye drift particles e.g. spores, microspheres to increase their detectability. Non-fluorescent dyes are of minor significance since they are often sorptive and their analytical verification is less precise than fluorescent dyes.

Salts

The salt most frequently employed for tracer tests is rock salt (NaCl), though potassium chloride, lithium chloride, and bromide salts are also used. Though most salts are comparatively cheap and their detectability is reasonably good, large quantities (up to several tons) of salt may be required, and therefore cost might hinder their use in mine water tracer tests. For a tracer test at the abandoned Straßberg/Germany fluorspar mine, 20,000 L of saturated NaCl brine were injected (Fig. 77).

Radioactive and Neutron Activatable Tracers

Radioactive tracers can easily be detected with field or laboratory equipment and though their use requires that radiation protection procedures and regulations be followed, in other ways their handling is no different from that of other tracers used in hydrogeology. However, at present, it is difficult to get permits to conduct tests using radioactive tracers, although they are effective for determining various geo-hydraulic parameters. Neutron-activatable tracers are non-radioactive elements that can be neutron activated after they are sampled in the field (Jester and Raupach 1987). Commonly used elements are ^{80}Br, ^{116}In, ^{165}Dy, ^{152}Eu, ^{140}La, and ^{56}Mn. They can be measured at very low concentrations because the analytical procedure is very sensitive.

Fig. 77. Sampling of saturated NaCl brine used for the Straßberg/Harz/Germany tracer test.

Water Insoluble Tracers

Solid Tracers

A solid substance was used in one of the first tracer tests ever reported: chaff to examine the springs of the river Jordan in the year 10 AD (Käß 1998). However, solid tracers are less suitable for conducting quantitative tracer tests. Should only a qualitative assessment be necessary, solid tracers may still be useful. The semi-quantitative LydiA-method, which uses filter nets and auto-samplers, was developed for mine water tracer tests, and is described elsewhere in this book (Fig. 78).

Phages

Phages are viruses with sizes between 20 and 300 nm. They are inactive when outside of bacteria and consequently, they do not have any active metabolism, which means that their number cannot increase during the tracer test. Their qualities as tracers are very good, but their analysis requires special laboratories. Due to the number of different phages known, they are suitable for tracer tests with multiple injection sites. Like all solid tracers, the

Fig. 78. *Lycopodium* Apparatus (LydiA) for injecting solid tracers into flooded underground mines. Diameter 120 mm.

number of particles found after the sample preparation are counted and used for the interpretation.

Bacteria

Because of hygienic issues concerning drinking water protection zones, bacteria play an important role in certain tracer tests (e.g. 50-day-time-of-travel-line). Numerous bacterial genera have proved suitable for hydrogeological tracer tests. They can be used in ground water, column tests, surface waters, and in coastal waters (e.g. Harvey et al. 1989, 1993; Vega et al. 2003).

Micro Particles: Microspheres

Micro particles are microscopically small polystyrene beads of 0.6–100 µm diameter which are coloured with fluorescent dyes (Fig. 79). In hydrogeological tracer tests, their surface should be neutrally charged to prevent sorption. For special investigations, microspheres with positive and negative surface charges can be purchased. Originally, polystyrene beads were developed for physiological investigations. However, several investigations confirmed that they can also be used as hydrogeological tracers in which the good experiences of the numerous physiological investigations can be used with advantage.

Recently, micro particles containing a rare earth element cocktail were developed. Those tracers can be used at sites where dyes might be destroyed due to certain physico-chemical conditions. Microspheres were used in several mine water tracer tests with generally positive results e.g. Straßberg/Harz

Fig. 79. Selection of microspheres used in the Straßberg/Harz 2003 tracer test.

Mountains, Königshütte/Harz Mountains, Ehrenfriedersdorf/Erzgebirge, Georgi Unterbau/Tyrol, Schlema/Saxony (the latter: Werner Käß, pers. comm.).

Spores

The spore tracer method uses club moss (*Lycopodium clavatum*) spores with diameters about 50 µm and is one of the most important methods used in karst examinations. They can be coloured with different fluorescent and non-fluorescent dyes so that several injection places can be examined in a single test. The evaluation is laborious since the spores found must be counted microscopically. Besides their use in karst areas, spores have also been used successfully in mine water tracer tests to investigate hydraulic connections and parameters as well as effective velocities underground e.g. Niederschlema/Alberoda/Erzgebirge, Straßberg/Harz Mountains.

10.3 Preparation

10.3.1 Hydrogeological examination

The aim and purpose of a tracer test must be defined precisely before a tracer test is carried out. A preliminary hydrogeological investigation is imperative and all available geological and hydrogeological data of the investigation area have to be considered in developing a basic conceptual model. Special attention has to be given to the heterogeneities of the aquifer and the mine layout. Geological maps and existing borehole or pump data must be evaluated for that purpose, because such heterogeneities can have a decisive influence on the selection of injection and observation sites. There are several hydrogeological text books available (e.g. Fetter 1988; Jordan and Weder 1995; Domenico and Schwartz 1998; Brassington 1999; Deming 2002; Hiscock 2005; Hölting and Coldewey 2005). It is beyond the goals of this book to repeat what these authors have already written about good hydrogeological practise.

Occasionally, there is insufficient information to establish a conceptual model of the investigation area or to plan the order of potential injection at observation sites. In those cases, further geological or hydrogeological investigations are essential. If necessary, pumping tests or measuring ground water levels will provide further information (Doherty 1990). In all cases, one or more field inspections should be conducted to get an impression of the examination area and the accessibility of the injection and sampling sites. If necessary, the client or the mine operator may have to modify sampling and injection sites to fulfil the needs of a proper tracer test.

The following data, or at least an idea of their order of magnitude, should be available for the planning of a tracer test:

- ground water contour maps and interfered ground water flow directions,
- ground water flow velocity,
- dilution,
- lithology and hydrogeochemical parameters, and
- water use.

The most suitable tracer has to be chosen based on the results of the laboratory tests, the cost of the tracer, and the analytical requirements for the tracer. In addition, a detailed hydrogeological investigation should clarify the most suitable injection and sampling points, based on a conceptual model of the site. Inadequately prepared tracer tests are the most frequent reason for poor results; preliminary investigations are an essential part of a tracer test, even if, and perhaps especially, when the area of investigation is not well characterised. A lack of knowledge about the hydrogeological situation can lead to poor selection of injection and sampling sites; this topic is addressed below.

10.3.2 Selection of Injection and Sampling Sites

A decisive criterion for whether a tracer test turns out to be successful or not is the correct selection of the injection and sampling sites. At least one of the injection sites must be located so that the tracer will flow through the examination area, satisfying the objectives of the investigation. Although this demand seems trivial at first, unsuccessful tracer tests show that this prerequisite is not always met!

Since tracer tests often bring new and surprising knowledge, it makes sense to choose one or two more sampling sites rather than to fail in finding the tracer injected. As a rule, tracer tests are cost-intensive, and a failed tracer test due to not enough sampling sites is dissatisfying for both contractors and customers! Underground and surface watersheds frequently do not correspond and this fact has to be considered when selecting the sampling sites. When there are uncertainties in the correct location of sampling sites, a simple numerical model that assesses hydrogeological parameters can be helpful.

One of the most unpleasant situations for both contractors and customers occurs when no tracer is found *at all*. Such tests simply cannot be evaluated; it may indicate complete sorption or degradation of the tracers, too low a transport velocity, or no hydraulic connection between the injection and sampling sites. You can at least rule out the last possibility if you use a sufficiently large number of sampling sites! Always include boreholes or shafts directly downstream from the injection site. In addition, do not allow yourself to be so convinced that your working hypothesis or conceptual model is correct that you fail to place a sampling site at locations that do not support that belief. It *is* appropriate to place a sampling site at a location that, according to the pre-considerations, might not be possible at all.

Besides the technical criteria, the relative spatial position of the injection and sampling sites and their accessibility play an important role. Sites that might be necessary from a technical point of view but that can only be reached with a disproportionately large effort should generally be omitted in favor of sites that are slightly less ideal but much more accessible. Finally, you can assume that the client will decide to add more injection and sampling sites the week before the test starts!

10.3.3 Which Tracers shall be used?

Just as important as the selection of the injection and sampling sites is the choice of the correct tracers. This choice is mainly determined by the question to be solved. Besides this, the hydrogeological and geochemical conditions, the required sensitivity, available analysis methods, and restrictions of use (e.g. permit of the authority, water protection areas) play a role in tracer selection. Occasionally, it is required to use several tracers in a multi-tracer approach. However, compromises have to be made, addressing potenial problems as optimally as possible (e.g. considering costs, transport, permits, and analytical procedures). Käß (1998, 2004) lists the following questions that have to be considered when selecting the optimal tracer:

- sorptivity and ion exchange,
- pore distances,
- chemical and physical water parameters,
- influence of light,
- water use,
- analytical criteria,
- effort of obtaining, transporting, injection, sampling, analytics,
- injection sites,
- sampling sites, and
- long-term behaviour of the tracers.

Although an optimal tracer should behave conservatively, depending on the terms of reference, it might be feasible to use a non-conservative tracer, such as when investigating the transport behaviour of characteristic substances. Table 18 gives a selection of tracers that have already been used successfully in mine water investigations.

10.3.4 How much Tracer must be used?

Numerous equations are specified in the literature for calculating the optimal tracer amount independently of the tracer and the investigation area. In detail, some factors might be contradictory, and therefore, the choice of the correct tracer amount is sometimes tricky. The preliminary values provided by these equations should be regarded as starting points for site-specific considerations.

A comparison of two equations for otherwise identical boundary conditions shall clarify this statement:

$$m = L \times k \times B \tag{68}$$

with m tracer amount, kg
L Distance to the most important sampling point, km
k Coefficient for the tracer substance, if not sodium fluorescein 0.1–20,000
B Factor for general set up of tracer test 0.1–10

and $L = 2.4$ km; $k = 1$; $B = 3$ yields $m \approx 7$ kg for sodium fluorescein (Käß 2004)

$$m = L \times K \tag{69}$$

with m tracer amount, kg
L Distance to the most important sampling point, km
K Coefficient for the aquifer 0.2–2

and $L = 2.4$ km; $K = 1.5$ yields $m \approx 3$ kg for sodium fluorescein (UNESCO 1; Käß 1998)

k, *B*, and *K* are tabulated values that can be found in Käß (1998). They will not be further discussed here, because the two equations are only provided to exemplify how tricky the calculation of a correct tracer amount might be.

The values given in Käß (1998) and Field (2003) differ over a range of three orders of magnitude. In general, the empirical values deduced from the experiences of the working group play an important role in calculating the necessary tracer amount. Käß (2004) concluded that expert knowledge is more important than a list of equations and therefore he only refers to equation 68. With respect to this shortage of reliable equations to calculate the necessary tracer amount, Field (2003) published the EHTD (Efficient Hydrologic Tracer-Test Design) computer code, which can be used to calculate the necessary tracer amounts for various hydrogeologically relevant scenarios if one provides values for 12–13 aquifer and tracer parameters. EHTD can also be used to calculate optimised tracer sampling intervals and predict the breakthrough curve. Yet, a mine water scenario is not yet included in the code.

Therefore, in mine water tracer tests, the empirical data can be backed by the following calculation, which gives a good approximation of the solid tracers needed for a tracer test in a quasi-closed system (the formula given in Wolkersdorfer et al. [1997a, 1997b] is faulty, as r_r is given in % instead of the rate):

$$m = \frac{1}{55{,}000} \times \frac{V_\mathrm{m}}{r_\mathrm{r} \times q} \times f \tag{70}$$

with m	total mass/volume of spores/microspheres, g
V_m	volume of enclosed fluid in the mine, m³
r_r	recovery rate of spores or microspheres, – (not more than 0.02–0.1 might be expected)
q	pumping capacity, L min^{-1}
f	factor (spores: 1; 15 µm microspheres with a concentration of $1 \cdot 10^6$/mL: 0.25), g L m^{-3} min^{-1}

Equation 70 considers water of volume, V_m, in a mine or another enclosure without a discharge into a receiving watercourse. During a tracer test, the water is pumped out of the mine at a pumping capacity q, which must be relatively small compared to the total water volume. The recovery rate for spores or microspheres is based on experience and usually does not exceed 2–10 %.

Yet, we also used other equations to verify the necessary tracer amount. So far, we have had good experiences with the following procedure: given the detection limit of the tracer is c_min, then the discharging mine water must have at least this tracer concentration. The total volume of the water in the mine is V_m and the flow rate at the discharge point(s) is Q with a total potential duration of the tracer test t. Furthermore, we assume a complete homogeneous mixing of the tracer with the mine water. This assumption is very optimistic but it has proven to be a good starting point. Furthermore, the concentration factor, f_c, which depends on the sampling equipment, must be known. If the tracer is directly measured in the discharging water, this factor is 1, if the water is filtered through a filter (e.g. MeFisTo System) then it depends on the ratio of the water pumped through the filter systems q to the discharged water. The expected recovery rate shall be r_r and the sampling interval t_s.

Then the following physically-based equation can be used to estimate the necessary tracer amount:

$$m = \frac{(V_m + Q \times t) \times c_{min}}{r_r \times f_c} \tag{71}$$

$$f_c = \begin{cases} 1 & \text{: direct tracer measurement in discharging water} \\ q \times t_s \times r_r & \text{: aliquot pumping of discharged water} \end{cases} \tag{72}$$

So far, this conservative approximation was successful in all of the tracer tests that we have conducted in fully flooded mines.

10.3.5 Tracer Test Plan

When applying for a permit from the responsible water authorities, a tracer test plan should be made available. This plan should list in detail the injection and sampling sites at which temporal distributions shall be sampled and by whom. At the same time, the test plan has to define why the tracer test is being carried out and should predict, if possible, the anticipated results that will be obtained. Normally, the test plan also contains details on the costs of the complete tracer test, including its evaluation. The success of an application and the tracer test itself depends fundamentally on whether the test plan is complete or not.

During sampling, the local or national recommendations for sampling ground water monitoring wells or surface waters have to be considered. Because national and international standards are changing regularly, even locally, the researcher planning to conduct a tracer test is well advised to get into contact with all of the local authorities that are responsible for permitting the tracer test.

According to Käß (1998) and other relevant guidelines (Schwarz et al. 2002), a tracer test plan should at least contain the following details:

- district and place name,
- description of the injection sites,
- person in charge of the tracer test with phone numbers,
- customer with full address,
- experimental purpose,
- injection time (start of tracer test),
- type of tracer,

- water quantities to flush the injection site and the tracer, and
- a list of the sampling sites and sampling intervals.

Furthermore, the following details are meaningful:

- work schedule for continuous sampling,
- necessary measurements on site,
- work schedule for analytical laboratory, and
- emergency plan.

10.4 Approval Procedure

10.4.1 Legal Regulations

Since the legal regulations for permitting tracer tests differ from country to country, you must contact the local authorities before designing a tracer test. In some countries, tracer tests need a formal, sometimes lengthy approval procedure, while in other countries, a telephone call with the water or mining authorities might be sufficient. A typical procedure for applying a permit for a tracer test is described here for Germany, according to Pascaly (1997).

The responsible authorities act under the principle of § 1 of the Federal Water Budget Law ("Wasserhaushaltsgesetz" WHG), which demands that the waters have to be managed for the welfare of the general public and in accordance with the welfare of individuals. Avoidable impairments of ecological function must be avoided. Additionally, in water conservation areas, the water protection ordinance has to be considered.

According to § 2 (1) WHG, the use of waters requires official permission, and the injection of a substance represents a use in the sense of § 3 (1) № 5 WHG. § 3 (2) regulates measures that can cause harmful and significant changes in the physical, chemical, or biological water parameters, be they permanent or temporary.

The official, revocable permission is granted by the authority in accordance with § 7 (1) WHG. This permission allows using waters (including ground water) for a certain purpose in a specific way predetermined by its manner and degree. In accordance with § 4 (1), the permission can be made conditionally, to prevent or compensate for adverse effects to others.

The responsible authorities are determined by legal state regulations. In Saxony, for example, the State Environment Agencies (Staatliche Umweltfachämter) or the lower water authority are responsible for granting the permission. The authority checks the tracer test plan for consistency with the legal specification that harmful changes and impairments be avoided, and ensures that it complies with the regulations or – if applicable – the existing water protection ordinance. Their concern extends beyond toxicological effects to humans and the environment, including other possible chemical (e.g. solution contents, taste), physical (e.g. colour, temperature), or biological changes to the water.

10.4.2 Necessary Details within the Application

As a basis for its permission, the water authority needs an application with a detailed description of the tracer test plan. The reasons for the test, the tests boundary conditions, and the type of tracers to be used, including their environmental compatibility (Arbeitskreis "Human- und ökotoxikologische Bewertung von Markierungsmitteln in Gewässern" 1997; Behrens et al. 2001), should all be documented. To allow the permitting authorities to understand the procedures of the tracer test and give them a means to assess possible environmental risks, be sure to present the following details: the amount of tracer (including its potential dilution), the volume of flushing water, the amount of water to be removed (for flushing reasons or analyses), the duration of the test, and the potential degradation rates of the tracer. Involving the authority as early as possible will allow you to understand any special concerns that they might have so that these can be addressed in your plan. Furthermore, the responsible special authority is frequently asked to give their recommendation to the permitting authority, documenting the necessity of the tests.

10.5 Execution

10.5.1 Injection Time and Injection Type

It is critical that the samples not be contaminated with even trace amounts of the tracer. This is more challenging than you might think. People who are conducting the injection should not collect the samples or carry out the later analyses in the laboratory. If this is not possible, the individuals should carefully clean themselves and completely change their clothes. Furthermore, if there are several sampling points in the test, the probes used for temperature or electrical conductivity measurements must be carefully cleaned with distilled water after each use. Cleaning them only at the new site risks cross-contamination. Unfortunately, the cover photograph of the Field (2003) publication does not show good practice in tracer injection, because the equipment of the person injecting the tracer is being contaminated with the tracer, and will possibly carry off the Na-fluorescein tracer to the next sampling site.

Independently of the tracer chosen, all containers carrying the tracer have to be flushed out repeatedly to make sure that the tracer is fully injected into the mine- or ground water. In the case of a solid tracer, this also ensures that all of the tracer reaches the water body to be examined. To avoid contamination in the field, it is recommended that fluorescent tracers be pre-diluted in the laboratory.

If necessary, several tens to hundreds of litres of water should be poured into the injection point, especially when the injection site is dry. For tracer injections in the unsaturated zone, one has to ensure that the tracer reaches the ground water. Without additional water, the tracer would remain in the pore space of the unsaturated zone. Of course, this is not an issue if the tracer test is being carried out to examine the unsaturated zone.

When evaluating tracer tests, it is assumed that the injection has the form of a Dirac function:

$$\delta(t) = \begin{cases} 0, & t \neq 0 \\ \infty, & t = 0 \end{cases}$$
$$\int_{t_1}^{t_2} dt\delta(t) = 1 \qquad (73)$$

Therefore, you should completely inject the tracer as quickly as possible. In the past, it was recommended that you inject the tracer slowly, but this is not advisable because it "smudges" the tracer cloud, could feign a non-existing dispersion, and make the results of the tracer test considerably harder to evaluate.

In contrast, Kimball et al. (2002) and Kimball et al. (2007) conducted tracer tests in mine water impacted surface streams in Colorado/USA, Utah/USA, and Tuscony/Itay where they injected soluble salt tracers at a constant rate and calculated the dilution of the tracer. This allowed them to locate mine water inflows, characterise flows below the streambed, and find where stream water was leaking into fractures.

10.5.2 Sampling

Correct sampling is essential when conducting all hydrogeological investigations. Good instructions are given by the Saxonian Agency for Environment and Geology (Sächsisches Landesamt für Umwelt und Geologie 1997) and Ficklin et al. (1999). The following instructions focus on specific aspects of sampling that are applicable to tracer tests. These recommendations are mainly the result of working together with students, mining-engineers, and personnel not normally involved in regular sampling for such tracer tests, and hopefully, will allow you to learn from their mistakes.

It is important that you correctly label all of the sampling containers, record everything, and follow the sampling protocols exactly. All details of the sample have to be written down in the protocol as well as on the sample containers (usually bottles). It is particularly important to denote irregularities (e.g. extreme water levels, insufficient amounts of sample, tracer spilled); mishaps can happen to anybody, and can typically be dealt with, as long as they are properly recorded and accounted for.

Another issue are the containers used for water samples. They must be appropriately selected for each parameter that will be measured in the laboratory. PVC or glass bottles are a good selection for the main ions and the trace elements. TOC samples must be collected in glass bottles and TIC samples must be collected in PVC bottles sealed with aluminium foil. New containers have to be rinsed out three times with the water to be sampled before they are filled. Prior to being reused, all containers have to be washed with hot water and phosphate-free lab-grade soap, rinsed with deionised water thereafter and washed again with dilute acid (e.g. 10% nitric acid). After acid washing, the containers have to be finally rinsed with deionised water.

As indicated above, the sampling has to follow the tracer test plan. In agreement with the customer and the authorities, the test plan can be changed, provided that unforeseen events require this (e.g. appearance of the tracers in till-now unsampled springs, shafts, or drippers; no more tracer analytically detectable; incomplete breakthrough).

A well drawn up sampling plan considers the travel time between the withdrawal points as well as possible difficulties that might develop (e.g. breakdown of equipment, weather conditions). As a rule, sampling intervals are short at the beginning and increase during the tracer test. Without knowledge of the hydrogeological conditions, no rule of thumb can be given. However, it is better to take too many than too few samples. If a numerical model was carried out before the tracer test, the sampling intervals can be deduced from the results of the modelling. Furthermore, the EHTD software code provides tools to calculate the initial sample collection time and the approximate sampling intervals as part of an optimised sampling scheme (Field 2003), based on the predicted tracer mass as well as the aquifer's hydraulic and geometric parameters (Fig. 80).

All staff should be instructed to record the actual sampling times and not simply use the ones in the sampling plan. Many things can cause you to sample earlier or later than projected in the original plan, but a "well-meaning" correction can cause a major problem!

The necessary size of the sampling containers must be discussed with the analytical laboratory. In the case of fluorescent tracers, brown glass bottles are recommended, since fluorescent dyes can be decomposed by light (Käß 1964). For tracer tests with bacteria, phages, spores, or microspheres, a careful selection of the appropriate laboratory is imperative, as those tracers are not easily detectable.

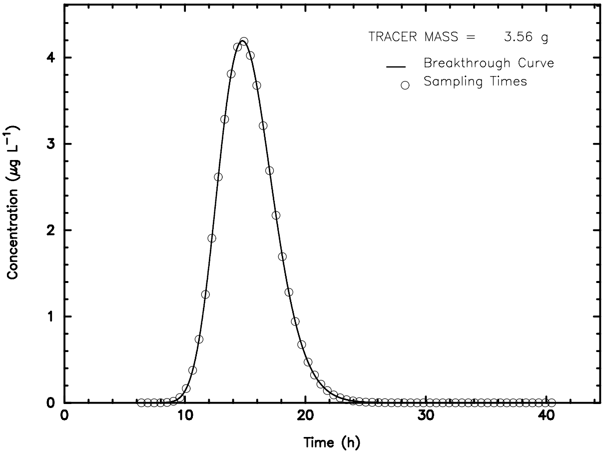

Fig. 80. Sample output of the Efficient Hydrologic Tracer-Test Design (EHTD) software code for a tracer test at the Dyers Spring (data from Field 2003). The circles indicate the optimised sampling intervals.

As in the case of water samples for chemical analysis, tracer samples have to be transported and stored carefully packed and cooled. Since the concentration of tracers can change over time, samples should be brought back to the laboratory and analysed as quickly as possible.

10.5.3 Tracer Analyses

For good results, you should use a high quality laboratory, ideally one that you have used before and trust. The cheapest laboratory will rarely produce the best results! If necessary, some selected laboratories should be compared with each other by using a ring or round-robin test to find out which one has the best reproducibility. Such tests are conducted by sending a sample of known composition or tracer concentration to different laboratories. The results of the different laboratories can be compared with the expected result and the best laboratory selected.

It is important that a laboratory book with numbered pages be used and maintained, and that a precise protocol is followed for every test. Experience shows that reliable laboratories have properly recorded protocols and laboratory books that are in good order! No confidence should be placed in laboratories with “piece of paper economy” and adhesive notes sticking to the sample containers!

You should consult the appropriate technical literature for the analytical methods for the different tracers. A good reference is Käß (1998).

10.5.4 Documentation and Presentation

The results of a tracer test will be evaluated based on the final documentation. Even small tracer tests can produce several hundreds of datasets, each of which must be recorded and presented. The results of a small test can often be analysed using a spreadsheet, while you should use professional, electronic database tools for larger tests. If several institutions are collaborating in a tracer test, a common database structure is recommended. All researchers involved must be urged to follow the database structure provided by the leading team.

Lists or tables are the simplest means to present the sampling place and time, and obviously the tracer amount. Cartesian coordinates (usually in the system UTM WGS84, because such data are provided by modern satellite navigation systems, i.e. GPS, GLONASS, or GALILEO) have to be included when several injection and sampling places are involved. It is generally advantageous to tie the data together using GIS-applications, allowing the reader to immediately see the relationships between the different injection and sampling points. All modern GIS-applications permit coupling of existing databases with graphical and topographical information.

Presenting the data in time-concentration-diagrams (“breakthrough curves”) provides a quick understanding and appreciation of the results of a tracer test, as Fig. 81 illustrates. The most important characteristics of the tracer test should also be shown in such a figure.

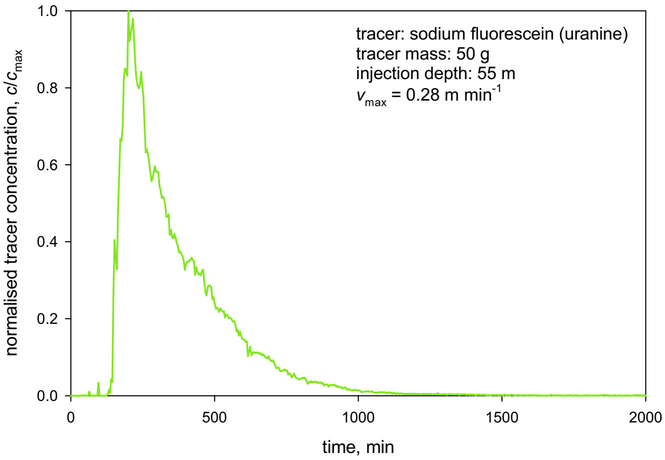

Fig. 81. Normalised breakthrough curve of a characteristic tracer test in the shaft of a flooded underground mine.

10.6 Evaluation and Characteristics of the Tracer Test

10.6.1 Porous Aquifer

Tracer tests in porous aquifers can normally be interpreted easily using existing tools, since there is very extensive experience. Let's start by discussing the governing transport equations for porous aquifers in detail, since the interpretation of nearly all tracer tests (even in mine aquifers) is based on porous aquifer theory. Flow in porous aquifers is determined by Darcy's law (assuming one-dimensional; stationary flow; homogeneous, infinitely extensive aquifer):

$$\frac{Q}{A} = v_{\mathrm{f}} = k_{\mathrm{f}} \times \frac{dh}{dx} \tag{74}$$

with Q flow, $\mathrm{m^3\ s^{-1}}$
A sectioned area through which flow passes, $\mathrm{m^2}$
v_{f} Darcy velocity, $\mathrm{m\ s^{-1}}$
k_{f} hydraulic permeability, $\mathrm{m\ s^{-1}}$
$\frac{dh}{dx} = i$ hydraulic gradient, –

and

$$v_{\mathrm{a}} = k_{\mathrm{f}} \times \frac{i}{n_{\mathrm{e}}} \tag{75}$$

with v_{a} flow velocity, $\mathrm{m\ s^{-1}}$
n_{e} effective porosity, –

Due to the microstructure of the aquifer and its inhomogeneities, a deviation from the ideal flow path is regularly observed. This deviation is expressed by the hydrodynamic dispersion:

$$D_{\mathrm{h}} = D_{\mathrm{m}} + D_{\mathrm{e}} = \alpha \times v_{\mathrm{a}} + D_{\mathrm{e}} \tag{76}$$

with D_{h} hydrodynamic dispersion, $\mathrm{m^2\ s^{-1}}$
D_{m} hydromechanical dispersion, $\mathrm{m^2\ s^{-1}}$
D_{e} effective diffusion coefficient, $\mathrm{m^2\ s^{-1}}$
α Dispersivity (dispersion length), m
v_{a} flow velocity, $\mathrm{m\ s^{-1}}$

Consequently, the mass transport in a homogeneous, three-dimensional aquifer is described by a combination of advection and dispersion:

$$\frac{\partial c}{\partial t} = D_{\mathrm{L}} \frac{\partial^2 c}{\partial x^2} + D_{\mathrm{T}} \frac{\partial^2 c}{\partial y^2} + D_{\mathrm{V}} \frac{\partial^2 c}{\partial z^2} - v_{\mathrm{a}} \frac{\partial c}{\partial x} \tag{77}$$

with	
c	concentration, g L^{-1}
t	time, s
x, y, z	distance in the x, y, or z direction, m
D_{L}	longitudinal dispersion coefficient, $\mathrm{m}^2\ \mathrm{s}^{-1}$
D_{T}	transversal dispersion coefficient, $\mathrm{m}^2\ \mathrm{s}^{-1}$
D_{V}	vertical dispersion coefficient, $\mathrm{m}^2\ \mathrm{s}^{-1}$
v_{a}	flow velocity, m s^{-1}

As the tracer distribution usually approximates a Gauss normal distribution (Fig. 81) and as the tracer injection is in the form of a Dirac function, the following equation describes the two-dimensional case of the tracer distribution at position x, y and time t:

$$c_{x,y,t} = c_{\max,t} \times \exp\left(-\frac{(x - v_a \times t)^2}{4 \times D_L \times t} - \frac{y^2}{4 \times D_T \times t} \right) \tag{78}$$

In reality, breakthrough curves seldomly conform exactly to a Gauss normal distribution, as can be seen in the Rabenstein/Germany tracer test example (section 10.5.1). Commercial software allows you to interpret the results of your tracer tests and obtain simulated breakthrough curves, which in turn allows you to deduce the appropriate parameter values by parameter approximation.

10.6.2 Fractured Aquifer

The researcher must know that completely different flow conditions exist in porous and fractured aquifers and that ground water flow behaves entirely differently in the two cases. Although the evaluation of breakthrough curves of those two aquifers is similar, breakthrough curves of fractured aquifers are different from those of porous aquifers. One of the most striking differences can be seen in the recovery rate of the tracers. While more than 50% of the tracers are often recovered from porous aquifers, the values from fractured aquifers are usually less than 50%.

Due to the heterogeneity and the anisotropy of fractured aquifers, preferential flow directions are characteristic of fractured aquifers. Consequently, the assumption that there is a homogeneous, virtually porous system is only partially correct. The fact that breakthrough curves usually do not show a Gauss normal distribution confirms that this assumption only has a low degree of truth.

Fractures represent preferential flow paths for water, pollutants, and tracers within a relatively homogeneous rock matrix. If there is no fracture connection between the injection and sampling sites, no tracer can be recovered at the sampling site. To model the flow in fractured aquifers, different model approaches exist (e.g. artificial or random fracture distribution by fracture generators, e.g. Wendland and Himmelsbach 2002). Whichever approach is used, the researcher must know that it is practically impossible to describe fractured aquifers adequately. This always has to be considered in evaluating the results of tracer tests in fractured aquifers.

In a system with several parallel fractures, variable fracture widths and roughnesses can cause almost all of the water to flow though only a few fractures. Normally, this effect, called "channelling", results in a breakthrough curve with multiple peaks, each of which represents a preferential flow path (Fig. 82).

Another effect arises in fractured aquifers when the matrix porosity has a significant value. In such cases, the tracer from the matrix is slowly transported into the fractures, which usually have a high hydraulic conductivity. When this occurs, the breakthrough curves tail out, which indicates that the tracer from the matrix is continuing to interact with the water in the fractures (dual or double porosity aquifers).

Many tracer tests in fractured rocks show a causal relation of the distance between the injection and sampling sites and the flow velocity: the flow velocity frequently increases with increasing distance. There are similar observations in the case of distance and hydraulic dispersion.

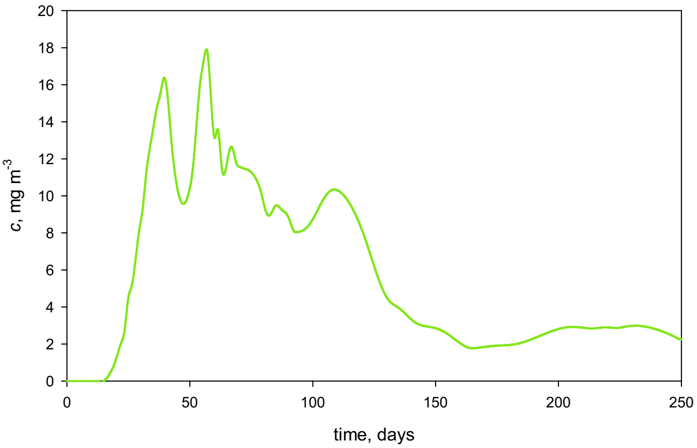

Fig. 82. Breakthrough curve of a tracer test with preferential flow paths (data modified and simplified after Käß 2004).

Often, tracer tests in fractured aquifers turn out to be more difficult than those in karst or porous aquifers since the result of the experiment depends more on a correct choice of injection and sampling sites than in the case of the other two aquifer types. Despite numerous research projects over the last two decades, the number of experiences with tracer tests in fractured aquifers, compared with tracer tests in porous aquifers, is still low. A thorough interpretation of such tracer tests therefore is still difficult, though the single fissure dispersion model (SFDM) generally yields sufficient accuracy (Małoszewski and Zuber 1985; Himmelsbach et al. 1992; Bäumle et al. 2001; Bäumle 2003). At present, research is being conducted in this field in many different countries (e.g. Germany, USA, Slovenia, France, Austria, and United Kingdom).

10.6.3 Karst Aquifer

Tracer tests in karst areas have a long tradition reaching back to Roman times (Käß 1998) and they are a critical tool in understanding the hydrogeological conditions of karst terrains. Nearly all of the potential tracers have been used in karst tracer tests investigations, and were positively tested in several multi-tracer approaches in Slovenia (Gospodarič and Habič 1976; Kranjc 1997). Other, more recent applications are described in the proceedings of the International Symposia on Water Tracing (e.g. Hötzl and Werner 1992).

Karst is named after its typical appearance in the Kraš Region of the Slovene Dinarides (Bates and Jackson 1987). Predominant features of karst areas are dolines, sinkholes, caves, ponors, karren, roofless caves, or poljes. Most of those features were described in the fundamental work of Cvijić (1893). Karst aquifers occur in all water-soluble rock formations, namely limestone, dolostone, gypsum, anhydrite, and even quartzite. The dissolution of the forenamed rocks by the acids in the ground water forms cavities, through which ground water can flow (Šušteršič 1996). In the underground, the diameters of those structures range from several micrometers to several decametres, mostly offering an excellent hydraulic connection for water flowing within that conduit network. As many karst researchers and karst aquifer tracer tests showed, this network of channels gives rise to different flow paths (Brown and Ford 1971); tracer tests proved that water uses different pathways with different effective velocities, reaching maximum velocities of 10–585 m h^{-1} (Gospodarič and Habič 1976; Hölting and Coldewey 2005). Recently, the triple-porosity-model has become more and more prominent in carbonate aquifer research (Worthington 1999) and future tracer tests will have to consider that approach.

As has been seen before, karst aquifers are characterised by high to extremely high flow velocities via discrete flow paths. Modelling of karst aquifers, which is thought to be extremely complicated, has to a special degree been possible in the Tübingen and Göttingen working groups. They developed the computer code CAVE (Clemens et al. 1999; Liedl and Sauter 2000), which has also been used to model water rock interactions in flooded underground mines (Spiessl et al. 2002).

Karst tracer tests are evaluated in the same way as described before, though they often demonstrate multi-peak breakthrough curves and comparatively long tails. These are due to different flow paths through the karst conduits, and are usually interpreted by applying the multi-dispersion-model (MDM; Małoszewski et al. 1992).

10.6.4 Mine Aquifer (Underground Mines)

Underground mines are very similar to karst aquifers (Sammarco 1995; Burbey et al. 2000) and like them, can be viewed as triple-porosity-aquifers with one-, two-, and three-dimensional porosity elements. The one-dimensional elements would be the main adits, shafts, and workings; the two-dimensional elements are the fractures, faults, and bedding planes; and the three-dimensional element is the rock matrix. If a mine is worked in a karst aquifer, the karst conduits would have to be counted as one-dimensional elements as well. Yet, the author knows of no publication that applies the triple-porosity model *sensu strictu* to mine water research.

The triple porosity model clearly shows how important all three porosities are (e.g. Worthington 1999). Comparing the hydraulic conductivities in a flooded underground mine with the nature of the first-flush scenario clearly proves that the most important factor for mine aquifers is still "conduit" porosity. Of course, the long tail of the first flush is due to natural attenuation and the comparatively lower hydraulic conductivities of the minor porosities (fractures, matrix, and panels). Yet, from an environmental point of view, the large volumes are of greater importance in determing the characteristics of the first flush and that of tracer tests.

Due to the similarities of mine aquifers and karst aquifers, the first quantitative tracer tests in deep flooded underground mines used the techniques established for those types of aquifers (Wolkersdorfer 1996). Liebisch and Remus (1966) also concluded that the methods applied in karst tracer tests could be used in mines, and used Na-fluorescein for a tracer test in the Mansfeld/Germany mining area. Despite the similarities, some major differences can be listed (most of which are not valid for prehistoric and medieval mines):

- channels (e.g. adits, shafts, workings) in modern mines are usually not curvilinear and typically meet at right angles,
- diameters usually do not change for a longer distance,

- the water level changes are comparatively small, and
- mine voids are not subject to dissolution.

In detail, mine aquifers comprise a combination of karst aquifers, porous aquifers, and fractured aquifers (see section 7.1). All the larger openings that were used for man or material haulage can be viewed as karst aquifers. Typically, the openings and the effective velocities are large, the storage capacity is small, and the water flow is non-Darcian. Shafts, boreholes, and old abandoned mine workings above the mine water table can be considered epikarstic. Between that zone and the mine water table comes the vadose zone and finally, below the mine water table, the phreatic zone is exposed. As the Straßberg/Harz mine water tracer test shows, those three zones in a mine act very similarly to the real karst features.

A fractured aquifer exists in most mines, especially those near the surface. That fracture network is usually a prominent region of infiltration and has been intensively studied by those investigating the feasibility of underground radioactive waste disposal (e.g. Galloway and Erickson 1985; Abelin and Birgersson 1985; Sawada et al. 2000). Sometimes, this fractured zone is the source of catastrophic mine water inrushes and consequently it has also been studied to prevent inundation (e.g. Singh and Atkins 1985; Singh et al. 1986; Grapes and Connelly 1998; Waterhouse et al. 2003). Though the importance of the fracture network for working or non-flooded mines is obvious, the role of fractures within the flooded part of a mine has not yet been studied in detail. From a hydraulic point of view, their role should not be over-estimated, as most transport occurs in the flooded voids. Yet, the tracer test in the abandoned Königshütte/Harz mining field proved that fractures above the ground water level can be hydraulically well connected during high precipitation periods. An additional fracture network can be found in the immediate vicinity of the mine workings due to the loosening of the rock during mining. Depending on the mining technology, this fracture network can reach several centimetres to several meters into the rock matrix (see section 4.2). Though not important to the overall water flow, it is important to the diffusive transport of the metals into the mine water (see section 4.2).

Finally, every mine, because of its rock matrix, also consists of a porous aquifer. In addition, backfilled areas or the goaf (collapse zones behind longwall mining operations) can be seen as porous aquifers, with porosities commonly in the range of 0.55 to 0.6 (Paul Younger, pers. comm.).

Though mine aquifers have the characteristics of all of the three known aquifer types, mine water tracer tests usually exhibit patterns that are typical for karst aquifers. Therefore, mine water tracer tests should be evaluated using the methods for evaluating karst tracer tests or, in the future, the triple-porosity-model.

10.6.5 Evaluation of Breakthrough Curves

Breakthrough curves are a first means to evaluate the results of a tracer test (Fig. 81). Such curves plot the concentration c of each tracer against the duration t of the tracer test. From this graph, the following times can be deduced (Fig. 83):

t_0	Start of tracer test
t_{max}	First tracer arrival: maximum distance velocity
t_{dom}	maximum tracer concentration: dominant distance velocity
$t_{\text{med}} = t_{50}$	median tracer concentration: median distance velocity
t_{true}	mean tracer concentration: true/mean distance velocity

where the velocity is calculated as follows:

$$v = \frac{x}{t} \tag{79}$$

The longitudinal dispersion coefficient D_L (Fig. 84) is estimated by using the times at which 16%, 50%, and 84% of the tracers are detected (mean value and twice the standard deviation of a Gauss normal distribution). The equation for this is:

$$D_L = \frac{v^2 \times \left(t_{84} - t_{16}\right)^2}{8 \times t_{50}} \tag{80}$$

As described earlier, the complete dispersivity consists of the three components: lateral, transversal, and vertical dispersivity. In the case of pore or karst aquifers, the predominant dispersivity is the longitudinal one. According to different authors, the transversal dispersivity is between 1/10th and 1/5th (Käß 2004) or 1–2 orders of magnitude smaller (Kinzelbach and Rausch 1995) than the longitudinal dispersivity, whereas $D_T \approx 0.1 \times D_L$ has been found to be a suitable mean approximation:

$$D_T \approx (0.01\text{–}0.2) \times D_L \tag{81}$$

By using computer codes or spreadsheet calculations, these equations can easily be used to calculate the characteristic tracer test parameters. You can download the simple MS Windows code, TRACI98 (also known as TRACI95), from the Borntraeger web page (Käß 1998, 2004), or the more

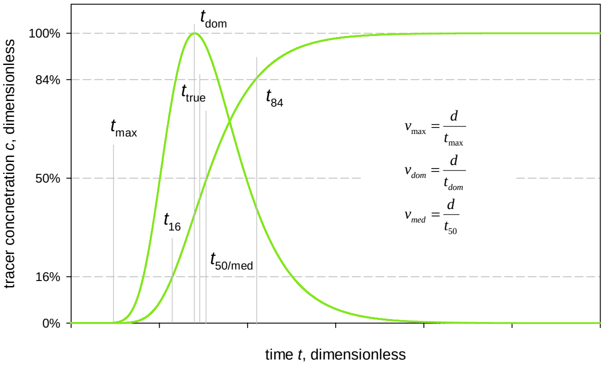

Fig. 83. Velocities that can be derived from a breakthrough curve. t_{16} and t_{84} are needed to calculate the longitudinal dispersion coefficient D_L; t_{true} is exactly in the middle of t_{dom} and t_{med}.

sophisticated programme, QTRACER, from the U.S. Environmental Protection Agency's web page (Field 2002).

10.7 Quality Control and Data Storage

10.7.1 Quality Assurance – Quality Control

Accurate and reliable results and documentation of data acquisition during field and laboratory work are essential when conducting treatment or remediation measures, which, in some cases, might take several decades. Sampling and analyses cost a lot of money and consume a lot of time during a project (Kellner et al. 1998). Very often, the responsible project leader has to rely on external experts and does not personally collect or oversee the analysis of the samples. Furthermore, while laboratories or staff may change during a project, data quality must be ensured at all time. Therefore, quality assurance (QA) and quality control (QC) must be emphasised to exclude variation of the analytical results due to false sampling or inappropriate analytical procedures. This may require a data quality objective (DQO) process (U.S. Environmental Protection Agency 1994), the experience of the project leader, existing QA/QC plans, or decisions made by groups of experts. In the USA, the Environmental Protection Agencies (EPA) employs quality assurance managers, quality assurance officers, or quality assurance representatives, who you can contact for help in setting up QA/QC plans. Furthermore, established procedures are available (U.S. Environmental Protection Agency 1994; EPA QA/R-xx and QA/G-xx series documents).

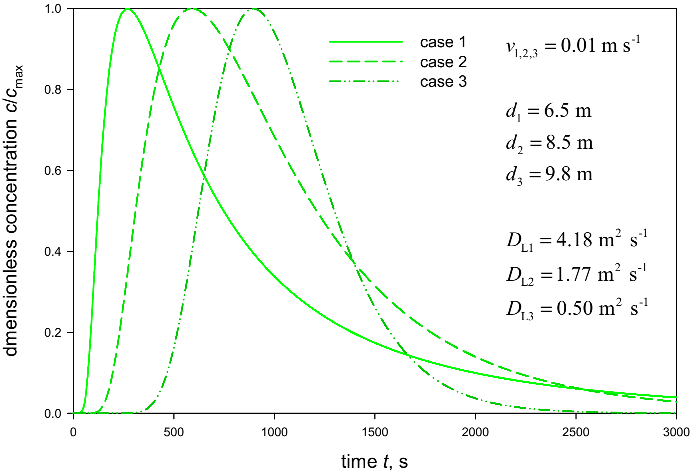

Fig. 84. Graphical representation of different longitudinal dispersion coefficients D_L. v: mean velocity, d: dispersivity.

While QA measures refer to the whole project and ensure that an effective QC is in force, QC guarantees that the quality of the data and the monitoring process are consistent. Most laboratories have their own QA/QC plans (compare Kellner et al. 1998); therefore, there is usually no need to include the laboratories in the QA/QC plans of the project. Nevertheless, the responsible project co-ordinator must record under which QA/QC procedures the relevant laboratories work and, if uncertain about the results of a certain laboratory, standard samples should be send to the laboratory in question (e.g. DIN EN ISO 8403 [“Qualitätsmanagement”], DIN EN ISO 8402, 1995-08, or other relevant national regulations). Calow (1991) listed potential and common laboratory errors, of which only “chemical and physical interference” is not due to human error:

- incorrect identification of samples,
- contamination,
- improper, or inappropriate sample preparation,
- inaccuracy of sample weights, or volumes,
- improper, or inappropriate sample dissolution/treatment,
- chemical and physical interference,
- improper, or inappropriate instrumentation/inaccurate measurement,
- calculation errors, and
- incorrect data handling/reporting

QA/QC measures can be time consuming and expensive. In general, the higher the degree of confidence has to be, the more the QA/QC measures will cost. However, since false data interpretation could result in wrong decisions, which might then result in unnecessary remediation requirements, such expenditures should be viewed as money well spent. Saving money by ignoring principles of quality assurance and control very often results in long discussions about how and where a sample was collected, and, in the worst case, malfunctioning remediation measures. A thorough QA/AC plan will also be the basis for trusting co-operation with the regulators and project reviewers (Downing and Mills 1998). A QA/QC program must:

- document the procedures and methods of sample collection, preparation and analysis,
- provide assurance about reliability of analyses using replicate samples, cross-laboratory checks and relevant reference standards,
- provide assurance about the precision and accuracy from duplicate samples,
- provide assurance about the accuracy from using recognised reference standards,
- provide reliable information regarding the interpretation of data about the behaviour of the mine water during time (longevity of mine water discharge), and
- provide a chain of custody of samples

Field sampling is the first step where mistakes can be made; mistakes made at this stage cannot be corrected or often even identified during any of the later stages. Sampling and monitoring procedures must always be precisely described in your field or laboratory books, which books must have properly bound sheets (adhesive binding should be avoided), numbered pages, and no missing pages (the removal of single sheets is against proper QC methods). Only field or laboratory observations and numbers should be written within the book. If a calculation is conducted, it should clearly be noted as SC ("side calculation") or, in Germany, NR ("Nebenrechnung"). Nothing is allowed to be erased or made unrecognizable; errors should be crossed out with a single line so that the wrong number can still be read. This guarantees that the potential reason for the faulty data can be reconstructed (e.g. 7.45 instead of 7.54; or 27 °C instead of 27 °F). In addition to the measured parameters, "soft" parameters have to be written down, too. These include observations that seem to be abnormal, e.g. animal interference, unusually high or low turbidity, ice covers, or any other observation that might be of interest to co-workers. In the future, electronic field books (e.g. PDAs) connected to GPS/GLONASS/GALILEO-systems will replace traditional data recording (e.g.

Ackman 2003). A QA/QC plan should ensure that this type of data storage is also covered.

Sampling points and samples must be numbered precisely throughout the whole project. It is advisable that all researchers and authorities involved agree to use the same numbering system, even though such systems seem to be complicated (e.g. Mueller et al. 1997). Each sample must be labelled with the name of the project, sampling site, sampling date, responsible research institution, and the person who took the sample. Sample numbers containing a three-letter project code, the date, and the sampling site provide a means to exclude mistakes during sample preparation (e.g. FDR-1202-MP1: Project code-short date-sampling point). Optionally, the laboratory can provide bottles pre-labelled with barcodes. In those cases, the associated barcode number has to be recorded in the field book or PDA.

A well-based QA/QC protocol will also lay out the proper analytical methods and equipment for the catchment study. Project errors often arise from using the wrong equipment or calibration methods. Chemicals or standard solutions used for equipment calibration or during analytical procedures must be fresh; you should regularly check the lifetime of the chemicals. From time to time, blanks should be included in the analytical process to check for contamination or overlapping. Field personnel should measure standard solutions from time to time during the day to ensure that their equipment is still working properly.

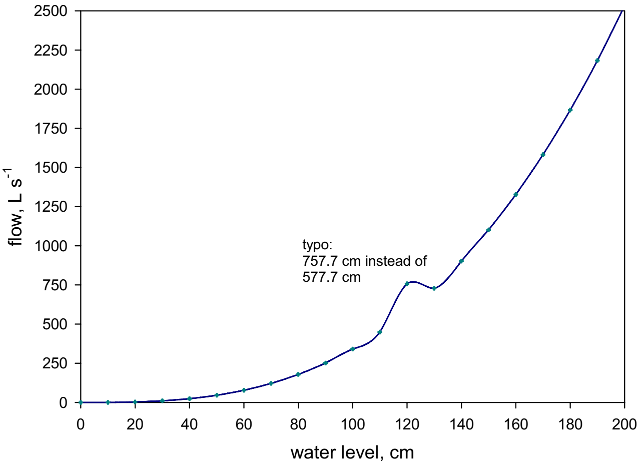

Fig. 85. Example of a scatter plot that would have revealed a typo in a flow/water level calibration table. The table with the wrong data was used for more than six years by a huge German remediation agency without anybody recognising the typo at the 120 cm water level.

A first quality control check is often very easy and can separate "real" outliers, which are mostly typos instead of wrong data. Finding such "simple" errors in data bases of companies that received a lot of money for their work is really annoying, considering how easily such errors could be avoided! One prominent Eastern German remediation agency used a spreadsheet for calculating the flow of a stream and for six years, no-one wondered about extreme flow situations at special water heights in this stream. Those extreme flow situations were due to just one typo in their calibration table! A quick scatter plot would have quickly eliminated this source of errors at its first appearance (Fig. 85).

Quality control thus includes a quick review of current and recent data. When the data has been inconsistent, it is important to ask why. Many errors can be avoided if every person involved in the data gathering and storage chain just followed this simple step. Such simple comparisons do not require a scientific background since they just identify errors or outliers. You should use scatter plots, bar plots, or time series to identify outliers (Fig. 85). Furthermore, at every step, it is important that the data can be traced back through time in a "chain of custody," answering the following questions:

- When, where, and by whom has the sample been taken?
- How, where, and how long has the sample been stored?
- How has the sample been treated and analysed?
- Who handled the sample where and at which time?
- Where have the potential left-overs been stored?

Finally, "it is rather unfortunate that QA/QC reporting is somewhat boring and not readily appreciated by many; however, it is a necessary part of data analysis" (Downing and Mills 1998).

10.7.2 Data Storage and Management

Before a project begins, the project leader has to make sure that a proper data base and data retrieval system is set up and used by all persons, companies, and laboratories working on the project. Many tools are available to assist the project leader in this work, but the data structure and the type of data that shall be stored must be compiled by him, his colleagues, or a working group. For large projects, professional support is available. In Germany, Pangaea, hosted by the Alfred-Wegner-Institute in Bremerhaven, can be used for the management and the storage of geo-projects. They guarantee the persistent storage of the data and they also provide support in setting up the sampling scheme as well as the data structure. In the case of a large and long-lasting project, data storage can be a major task in the project and money should be allocated for this task.

Data storage and retrieval must be given special consideration, because storage systems change quickly and the half-life of an electronic storage technology is in the range of several years, compared to paper storage with half-lives of many decades to centuries. This fact is true for hardware as well as for software. First, widely available computer systems used 9″ disks, which can rarely be read with modern computer systems today, and software produced 10 years ago might have produced data sets that do not produce more than hieroglyphs nowadays. Yet, data storage is not all. Data without a consistent description of the data – if possible in metadata sets – is essential if the data shall be stored for a long time.

Though professional archiving technologies are available that guarantee regular upgrade of the datasets, they are rarely used in mine water research. A discussion of such technologies is far beyond the scope of this book, and as it is very costly, SMEs or authorities are not usually connected to such systems. Therefore, if long life storage is to be achieved, printed reports, tables, and illustrations are the first choice of data storage; from the view of persistency, Hethitian clay tablets and Egyptian hieroglyphs cannot be beaten, yet their storage and handling is rather strenuous and not the means to be used nowadays. Also, ASCII tables should be produced and stored on floppy-discs or CD-ROMs at the end of each project, because such systems are widely used compared to other systems, which guarantees a longer half-life than other electronic storage systems (e.g. streamer tapes, video-cassettes, hard disks). Furthermore, if speaking about proper data storage, a spreadsheet is not a database! It can be used to make quick calculations or draft graphs, but cannot substitute for a real database system – though the reality of consultant work seems to favor it.

Data security (data backup, data encryption) is also important. Many small companies or scientists do not backup their data on a regular basis, because they often think “what shall happen?”. The fact is that all data storage systems can fail to work at any time, no matter what data storage system is used (even Egyptian steles have been reshaped and recycled). Therefore, data backup is an integral part of any mine water and river catchment study and should be included in the QA/QC protocols. Proper data backup has to be conducted daily, with full data backup on a weekly basis. Every month, a copy of a full backup should be securely stored at a place outside the office. All those actions seem to be annoying and time consuming, but from experience, data retrieval after a system crash can take several days and sometimes, data are lost forever, with unforeseeable consequences to the project or the company.

During the writing of a report or after changing a database, it is good practice to add a two or three digit number to the report’s file name (e.g. MINEWATER_01.DOC). This number will then be increased each time the report is stored to the storage system (e.g. MINEWATER_02.DOC). In case a file is corrupted, the previous version can be used instead. At the end of the project, the last file can be renamed (e.g. MINEWATER.DOC) and all the old versions can be deleted (professional desktop publishing systems, such as QuarkXPress™, use a similar system for data security).

Yet, if river catchment projects involve many SMEs, research organizations and authorities, all parties must agree to a common data storage procedure *before* the project starts. Internet or intranet based groupware is commonly used by larger projects. All data should be stored with the corresponding coordinates (keep in mind that GPS/GLONASS/GALILEO data must be recorded with the reference system and the geoid used!), to be usable in GIS-systems. Several countries or authorities provide data storage systems; using such systems allows data exchange between all of the parties involved. Furthermore, since spreadsheets are not databases, data retrieval can be restricted or impossible. In a large project, spreadsheets should only be used for quick reference, and should be organised to provide as much information as possible using as few as possible spreadsheets. A good database system, though its use is more complicated, is always preferred over spreadsheets (although, of course, databases are organised in spreadsheets).