Environmental Geology (1994) 24: 144–149

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Migration of lignosulfonates in a karstic–fractured–porous aquifer: History and prognosis for a Zn-Pb mine, Pomorzany, southern Poland

Received: 7 March 1994 / Accepted: 30 March 1994

Abstract Lignosulfonate lyes, which had been deposited by a paper factory for about 50 years into Quaternary sediments and accumulated in a quasistagnant depression, became mobile when a depression cone caused by mine activity in a deeper aquifer reached the erosion window close to the disposal site. Their transport parameters in the karstic–fractured–porous carbonate aquifer are shown to be mainly governed by diffusion between the mobile water in karstic channels and fractures and the stagnant water in matrix, although the hydraulic conductivity is shown to depend mainly on the karstic system. The main transport velocity is, with a sufficient accuracy, related to the hydraulic conductivity by a simple model in which matrix porosity is the governing rock parameter. The dispersivity, although also governed by matrix diffusion, depends strongly on several parameters that are difficult to determine.

Key words Lignosulfonate migration · Zn-Pb mining · Poland

Introduction

Since the early works of Foster (1975), Grisak and others (1980), Neretnieks (1980), and Bibby (1981), solute transport in fractured rocks of dual porosity has drawn a lot of attention. As a result, a number of stochastic and deterministic models have been developed, the most advanced ones taking into account both the arrangement of the fracture network and the diffusion effects (e.g., Sudicky and McLaren 1992). However, the fracture network parameters are either unknown or known with an insufficient accuracy, and, therefore, simple approximate models are also useful. In this paper such models are employed in a detailed interpretation of a case study, briefly presented by Adamczyk and others (1988), and Zuber and Motyka (1994), which is related to the migration of lignosulfonates through a karstic–fractured–porous carbonate formation.

Hydrogeology of Pomorzany Mine region

The area of investigation is shown in Fig. 1 and the geological cross section in Fig. 2. The impermeable bedrock is represented in the south by Permian conglomerates. In the north, the Devonian and Carboniferous are not well known. They are represented by local occurrences of limestones and dolomites with a hydraulic conductivity (K) of about 1×10^{-6} m/s. The main waterbody is contained in the karstic–fractured–porous Triassic dolomites and limestones (Motyka 1988). This complex is overlain by impermeable Keuper clays with several erosion windows at the bottom of the Quaternary paleo-river valley. Well permeable Quaternary sediments ($K = 2.5 \times 10^{-4}$ m/s) are recharged directly by precipitation and by horizontal flow from Jurassic limestone elevations ($K = 1.6 \times 10^{-5}$ m/s). Under natural conditions, the Quaternary aquifer was also recharged by flows from the Triassic aquifer, where a higher water pressure existed. The natural drainage was by Biata (White) Przemsza river. An intensive draining started in 1973 when a mine corridor that led from the Permian conglomerates crossed the Pomorzany fault and entered the carbonate Triassic formations. A large drawdown cone developed very quickly in these formations and soon caused local drops in the water level of the Quaternary aquifer at the windows, which next joined and formed a single large decrease of the water table, which reached the river and the disposal site. The mine drains about 3 m^3/s of water, nearly two thirds is of good quality and tapped, whereas the remaining fraction is polluted and discharged into the river.

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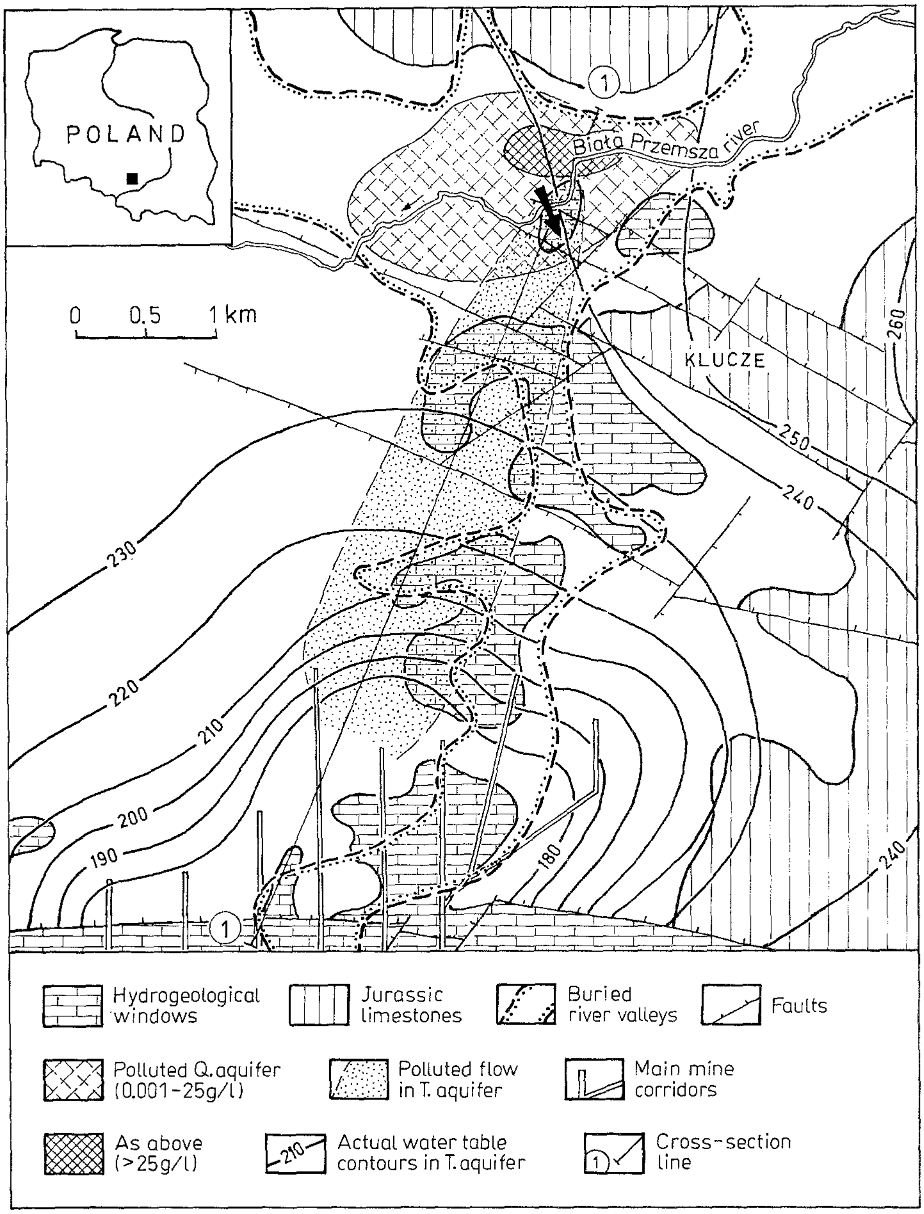

Fig. 1 Simplified hydrogeological map

Pollution of groundwater by lignosulfonates

In the period 1930–1979 a paper factory in Klucze deposited about 450,000 tons of lignosulfonate lyes to the Quaternary sands (Fig. 1). The pollutant migrated through the unsaturated zone to the water table and sank in the aquifer, filling in a paleo-river depression at the bottom. In the 1950s, the lignosulfonates appeared in the river, changing its color to black by reacting with Fe ions. In the 1960s, 15 boreholes were drilled in order to determine the extent of the pollutant in the Quaternary aquifer. The polluted area was about 2 km^2, and the thickness of the polluted waterbody was about 25 m. The highest pollutant concentration found at the bottom was 33 g/l, and it was regularly decreasing to 1 mg/l, which was assumed to be the boundary value. In October 1977 an unexpected explosion of methane occurred in the northern corridor and lignosulfonates appeared in water drained by that corridor. The following environmental tracer data were observed for water and gas samples taken in that corridor and from a borehole drilled at the center of the disposal site: for water in the mine, $\delta^{18}O = -9.9‰$, $\delta D = -70‰$, $\delta^{13}C = -11.2‰$, $^{14}C = 58$ pmc[a], $^{3}H = 92$ TU[b]; for CO_2 in the mine $\delta^{13}C = -18.2‰$; for CH_4 in the mine, $\delta^{13}C = -51‰$, $^{14}C = 101$ pmc; for CO_2 in the borehole, $\delta^{13}C = -8.7‰$, $^{14}C = 76$ pmc; and for CH_4 in teh borehole, $\delta D = -321‰$, $\delta^{13}C = -69‰$, $^{14}C = 89$ pmc, $^{3}H = 356$ TU (Grabczak and others 1978). These data showed that the gases were of modern age and generated from lignosulfonates by facterial activity. The total mass of lignosulfonates that has reached the mine is estimated to be about 9 tons, i.e., about 0.002% of the deposited mass and about 0.03% of the mass estimated to be still present at the end of the deposition.

The pollutant breakthrough curve is given in Fig. 3. The

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[a] pmc: percent of modern carbon

[b] TU: tritium units

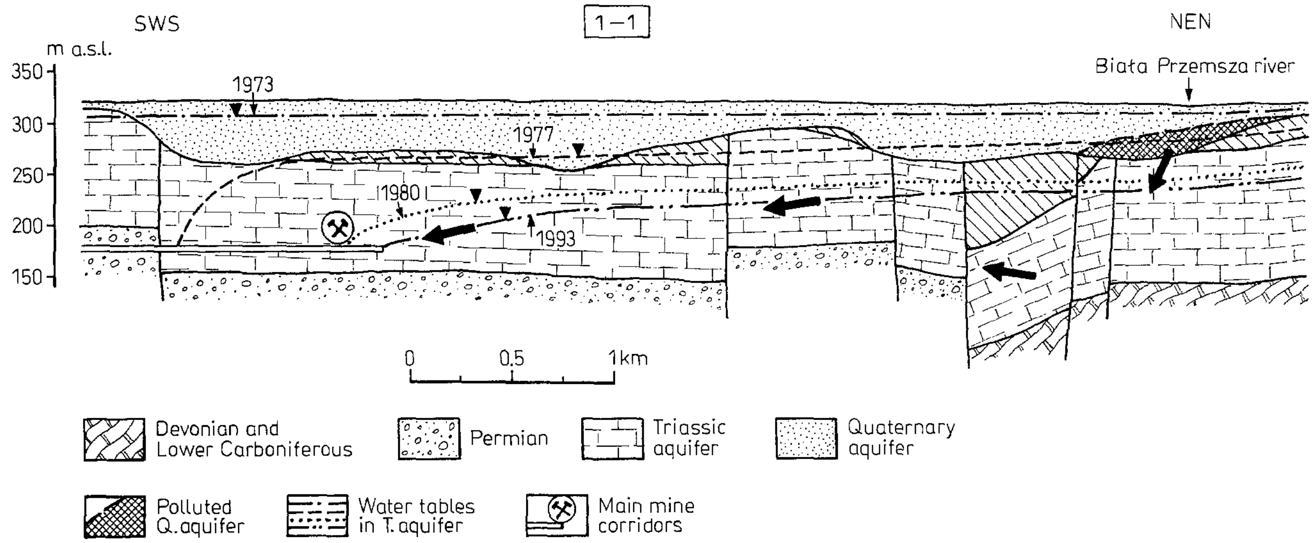
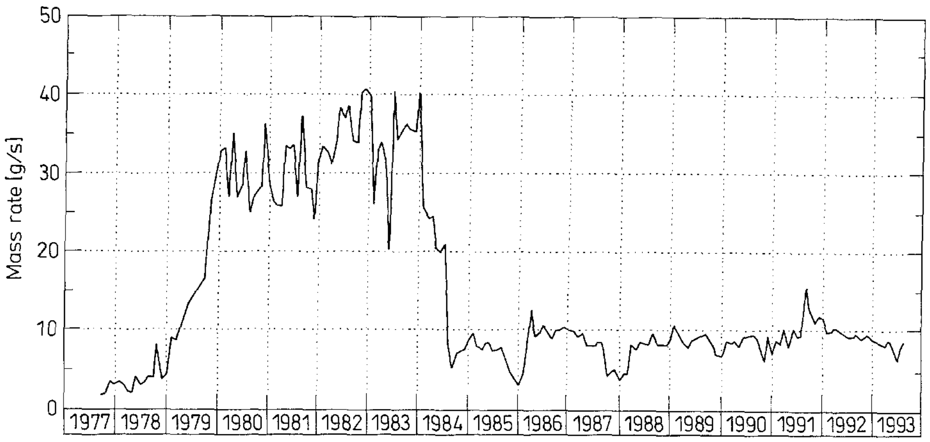


Fig. 2 Simplified geological cross section

Fig. 3 Pollutant breakthrough curve



transport of pollutant to the mine probably started in November 1974, when the drawdown cone in the Triassic formation reached the window close to the disposal site (Fig. 2), as known from piezometric observations. The drop in the concentration in 1984 coincided with a development of a deeper mine level, which overtook a large portion of flow. However, neither the total inflow to the mine decreased nor was the shape of the drawdown cone changed. Therefore, that change must be attributed to the decrease of inflow from the Quaternary sediments caused by a sudden drop of the water table close to the window. After that large change, the concentration of lignosulfonates remained constant for nearly ten years (Fig. 3), whereas the amount of inflowing methane continuously decreased.

Rock parameters

The geometric mean of the hydraulic conductivity obtained from 236 pumping tests, which yielded the log-normal distribution, is $K = \left(6.5 \begin{array}{l} +0.8 \\ -0.7 \end{array}\right) \times 10^{-5}$ m/s. The hydraulic conductivity of the rock matrix was measured in the laboratory on 133 samples. The mean value for the whole profile is 8.3×10^{-9} m/s (about 1.8×10^{-8} m/s for dolomites and about 4.1×10^{-10} m/s for limestones), which means that the hydraulic conductivity of the porous matrix is negligible in comparison with that of the bulk rock and that the water stored in the matrix can be regarded as stagnant.

The mean matrix porosity measured in the laboratory on vacuum-dried samples is: 0.109 for dolomites (199 samples) and 0.0176 for limestones (54 samples). The mean value for the whole profile is $n_p = (0.8 \times 0.109) + (0.2 \times 0.0176) = 0.09 \pm 0.01$.

The fracture parameters were directly measured in the Pomorzany mine on seven exposed rock surfaces, $F = 136$ m^2. The total length of fractures was $\Sigma_i l_i = 370.6$ m (where l_i is the length of the ith fracture observed on the exposed surface), which yielded the fracture density of 2.7 m^{-1} ($G = \Sigma_i l_i / F$). The fracture porosity was calculated as $\Sigma_i l_i b_i /$

$F = 0.000716$. The mean fracture apertures were obtained in several ways: the arithmetic mean, $b_a = \Sigma_i (2b)_i / N = 0.373$ mm (where N is the number of fractures); the geometric mean $b_g = (\Pi_i b_i)^{1/N} = 0.257$ mm; the weighted arithmetic mean, $b_{wa} = \Sigma_i l_i b_i / \Sigma_i l_i = 0.263$ mm; the weighted geometric mean, $b_{wg} = (\Pi_i l_i b_i)^{1/N} / (\Sigma_i l_i / N) = 0.109$ mm; the weighted arithmetic mean of the squared aperture, $[(b^2)_{aw}]^{1/2} = [\Sigma_i l_i b_i^2 / \Sigma_i l_i]^{1/2} = 0.363$ mm; and the arithmetic mean of the cubed aperture, equal to the effective aperture as defined by Wilk and others (1984), $b_e = [\Sigma_i l_i b_i^3 / \Sigma_i l_i]^{1/3} = 0.521$ mm.

If the representative fracture aperture and the fracture porosity are known, the hydraulic conductivity can be estimated from the well-known formula:

$$K = \rho g b^2 n_f / (12 \mu \tau_f^2) = 6.28 \times 10^5 b^2 n_f / \tau_f^2 \qquad (1)$$

where ρ and μ are the fluid density and viscosity, respectively; g is the acceleration due to gravity; b is the fracture aperture; τ_f is the tortuosity factor for the fractures (e.g., Małoszewski and Zuber 1985); and the numerical factor given in the final term is calculated for fresh water at 10°C.

The following values of K were obtained for some of the b values given above: $K(b_{wa}) = 1.4 \times 10^{-5}$ m/s; $K(b_{wg}) = 0.24 \times 10^{-5}$ m/s; $K[(b^2)_{aw}] = 2.6 \times 10^{-5}$ m/s; and $K(b_e) = 5.4 \times 10^{-5}$ m/s. A detailed discussion of the relation between these values and the results of pumping tests is beyond the scope of the present paper. However, a preliminary analysis of the results obtained in two other regions suggests that if the data from several observation sites are regarded as one class, the $K(b_{wg})$ values compare best with the K values obtained by other methods (Motyka and Zuber 1993). At first glance, those observations are not confirmed by the results given above, but the K value obtained from pumping tests is strongly influenced by paleokarstic channels that are known to exist in the area, whereas the fracture data were obtained on surface areas free of karstic channels. Therefore, the K values from equation 1 are lower than the real value.

The karstic porosity (n_k) estimated from observations in a large number of boreholes and on the exposed rock surfaces in the Pomorzany and Olkusz mines is about 0.004. Therefore, the mobile water porosity (effective porosity) is $n_e = n_f + n_k \cong 0.005$.

If the presence of fissures is neglected and the karstic channels are assumed to form a network of equal-diameter capillaries, the hydraulic conductivity observed in pumping tests yields the diameter (d) of about 0.5 mm, for $K = 0.785 \times 10^5 d^2 n_k$ adapted from Saffman (1959). Therefore, although the karstic system strongly influences the hydraulic conductivity, its chimneys with cross-sectional areas of several square meters and horizontal openings of about 0.25–0.5 m^2 (Motyka 1988) are undoubtedly discontinuous for the horizontal flow.

The specific yield obtained in the laboratory as described by Prill (1961) is: 0.028 for dolomites (134 samples), 0.00063 for limestones (48 samples), and 0.022 for the whole profile. This specific yield is mainly related to the presence of large karstified pores, which in dolomites are up to about 1 mm in diameter, whereas the pores in some limestone samples were too small to be penetrated by Hg. The coefficient of storativity obtained from pumping tests and the decline of water table in Triassic formations caused by mine draining is only 0.019 ± 0.004 (Wilk and Motyka 1980), which confirms that the fracture and karstic porosities do not contribute significantly to the specific yield.

Relations between rock and transport parameters

Due to molecular diffusion between the mobile water in fractures and stagnant or quasistagnant water in the matrix, the velocity of a conservative solute in a densely fractured rock (say, a few fractures per squar meter) is related to the flow velocity in fractures by (e.g., Małoszewski and Zuber 1985):

$$\begin{aligned} R_p &= v_w / v_t = t_t / t_w = (V_p + V_f) / V_f \\ &= (n_p + n_f) / n_f - n_p \cong (n_p + n_f) / n_f \qquad (2) \end{aligned}$$

where (R_p) is the retardation factor caused by matrix diffusion; v_w and v_t are the mean water and solute velocities, respectively; t_t and t_w are the mean travel times of solute and water, respectively; V_p adn V_f are the volumes of water in the porous matrix and fractures, respectively; and n_p and n_f are the matrix and fissure porosities, respectively. In equation 2 the fracture porosity is identified with the effective porosity in which the water flow takes place. In that case the retardation factor is about 125. For karstic rocks, the fracture porosity in equaton 2 should be replaced by n_e. In that case the retardation factor is $(0.091 + 0.005)/0.005 \cong 20$, which means that a conservative solute moves in the investigated formation with a transport velocity about 20 times lower than the flow velocity estimated by conventional methods.

If the water velocity taken from equation 2 is put into the simplified form of Darcy's law, one gets (Zuber 1985; Zuber and Motyka 1994):

$$K = n_e v_w / i = (n_p + n_e) v_t / i \cong n_p v_t / i = n_p (x / t_t) / i \qquad (3)$$

where K is the hydraulic conductivity; and i is the hydraulic gradient. The simplified form of equation 3 results from a common inequality of porosities, which is well satisfied for the investigated rocks, i.e., $n_e \ll n_p$.

From equation 3 it is obvious that if the matrix porosity and the conservative solute velocity (or travel time) are known, the hydraulic conductivity at a large scale can be found without any knowledge of the fracture network parameters, and under favorable conditions without any knowledge of the parameters of the karstic channels. A low spread of the pollutant breakthrough curve and the symmetrical shape of its rising part seen in Fig. 3 suggest that either the matrix diffusion did not take place, or the diffusion was the governing process and the scale was sufficiently large to produce the breakthrough curve to be distributed around the mean solute travel time (Małoszewski and Zuber 1985). For the first assumption, the transport is supposed to take place in the fractures and karstic channels, and the mean travel time of pollutant (tracer age) of 1800 ± 100 days, taken as a difference between an estimated date of the start of flow and the mid-point of the rising part of the breakthrough curve, is supposed to be equal to the mean flow time. Then, $K = n_e v_w / i = n_e x / t_w i$ $= (0.005 \pm 0.001)(3700 \pm 200)/(1800 \pm 100)(0.014 \pm 0.005)86400 = (0.68 \pm 0.30) \times 10^{-5}$ m/s, which is about ten times lower than the results of pumping tests and simply unacceptable. For the second assumption, the matrix is supposed to dominate the solute transport. Then, $K \cong n_p(x/t_t)/i = (15 \pm 6) \times 10^{-5}$ m/s, only about two times larger than the value found from pumping tests, which means that the transport is dominated by matrix porosity. The discrepancy by a factor of about two does not seem to be eseential. Theoretically, there are two possible sources of that discrepancy: the decay of the pollutant (Małoszewski and Zuber 1984), and no access to the smallest micropores for its large molecules. In both cases the pollutant is unable to occupy the whole volume of matrix pores, and then the use of matrix porosity in equation 3 yields too large K values. However, the decay took place mainly in the quasistagnant conditions that existed initially at the disposal site. As mentioned, during the active flow of fresh water, the decay is most probably strongly reduced, and, therefore, its hypothetical influence on the mean transport velocity can be neglected.

If the specific yield is used as the effective porosity for solute transport, $K = (3.2 \pm 1.2) \times 10^{-5}$ m/s, which is only about two times lower than the mean value known from pumping tests. It is evident that for a pollutant with large molecules, and for rock matrix with large pores, the specific yield and the matrix porosity inserted into equation 3 give the K values that bracket the real hydraulic conductivity.

Due to the reasons given earlier, the common dispersion model can be fitted to the pollutant curve to obtain the total (apparent) dispersivity, α_L^*. The dispersivity of about 37 m was obtained by fitting the formula of Banks and Ogata (1961). A number of tracer experiments performed in pumped wells on distances of 10–20 m yielded $\alpha_L^* = 2$–120 m (Kreft and others 1974), with the average values estimated from a larger number of tests to be about 20–40 m (Zuber 1983). However, these large values of the total dispersivity were found later to result to a large degree from matrix diffusion (Małoszewski and Zuber 1985). Therefore, it seems interesting to check how the dispersivity observed at a distance of 3700 m is influenced by matrix diffusion. For a model of parallel fractures of equal spacing and aperture, the diffusion dispersivity (α_L^d) is (adapted from Małoszewski and Zuber 1992):

$$\alpha_L^d = \alpha_L^* - \alpha_L = \frac{5ap^3 v_w}{6(1 + 2ap)^2} \cong \frac{0.1 n_p b^2 v_w}{n_f^3 R_p^2 D_p} \cong \frac{0.1 n_p b^2 v_t}{n_f^3 R_p D_p} \qquad (4)$$

where α_L is the hydrodynamic (intrinsic) dispersivity; $a = n_p(D_p)^{1/2}/b$; $p = (L/2 - b)/(D_p)^{1/2}$; D_p is the coefficient of diffusion in the matrix, and L is the fracture spacing ($L = b/n_f$).

Considering the fracture system only, i.e., $b = 0.109$ mm, $n_f = 0.0007$, and $R_p = 126$, equation 4 yields $5.4 \times 10^{-8}/D_p$ m, which in turn gives $\alpha_L^d = 54$ m for $D_p = 10^{-9}$ m^2/s, and 540 m for $D_p = 10^{-10}$ m^2/s. However, if the influence of karstic system is included, i.e., if $n_f = n_e = 0.005$, $b = 0.216$ mm (calculated from equation 1 for $n_f = n_e$), and $R_p = 19$, the dispersivities are 4 and 40 m, repectively. These examples and equation 4 show that any value of dispersivity can be obtained. However, the dispersivity observed in the Pomorzany mine seems to be governed mainly by matrix diffusion.

Conclusions

Similar to the transport of conservative pollutants, the mean transport velocity of a decaying pollutant with large molecules is also shown to be governed by matrix diffusion, if the matrix of the fractured rock is characterized by large pores. For karstic and fractured rocks, the effective transport porosity for solutes cannot be identified with the common effective porosity for water flow. The transport porosity for solutes is close to the matrix porosity, which is easily measurable on rock samples. When the matrix porosity and solute velocity are known, the hydraulic conductivity can be determined without any knowledge of the fracture system. It is shown that under favorable conditions, i.e., if the karstic systems are discontinuous and the matrix porosity sufficiently high, the same approach can be applied for karstic rocks.

The dispersivity cannot be predicted in a simple way. However, the examples considered seem to suggest that at large scales the dispersivity is also governed mainly by matrix diffusion.

The concentration curve shown in Fig. 3, the flow pattern that has reached a steady state (Fig. 2), and the amount of pollutant still present in the Quaternary sediments suggest that the pollution of mine water may last for a long time.

Acknowledgments The paper has been written within project No. 9 9047 02p/02 supported by the State Committee for Scientific Research (KBN).

References

Adamczyk AF, Motyka J, Wilk Z, Witczak S (1988) Mining drainage of a karstic aquifer and related problems (Olkusz Mining District). In: Karst hydrogeology and karst environment protection. Beijing: Geological Publishing House, Proceedings of the IAH 21st congres, held in Guilin, China, 10–15 October 1988, vol 21, part 2, pp 1097–1104

Banks RB, Ogata A (1961) A solution of the differential equation of longitudinal dispersion in porous media. US Geological Survey Professional Paper 411-A. Washington, DC: US Government Printing Office

Bibby R (1981) Mass transport of solutes in dual-porosity media. Water Resour Res 17(4):1075–1081

Foster SSD (1975) The chalk groundwater anomaly—a possible explanation. J Hydrol 25:159–165

Grabczak J, Różański K, Zuber A (1978) Age of CH_4 and CO_2 in the Pomorzany mine as determined by analyses of ^{14}C and ^{13}C isotopes (in Polish). In: XXXVIII Sesja Naukowa AGH, Vol. I, Wydawnictwa Geologiczne, Warsaw. pp 174–182

Grisak GE, Pickens JF, Cherry JA (1980) Solute transport through fractured media, 2. Column study of fractured till. Water Resour Res 16(4):731–739

Kreft A, Lenda A, Turek B, Zuber A, Czauderna K (1974) Determination of effective porosities by the two-well pulse method. In: Isotope techniques in groundwater hydrology 1974, vol II. Vienna: IAEA.p 295–312

Małoszewski P, Zuber A (1984) Interpretation of artificial and environmental tracers in fissured rocks with a porous matrix. In: Isotope hydrology 1983. Vienna: IAEA. pp. 635–651

Małoszewski P, Zuber A (1985) On the theory of tracer experiments in fissured rocks with a porous matrix. J Hydrol 79:333–358

Małoszewski P, Zuber A (1992) On the calibration and validation of mathematical models for the interpretation of tracer experiments in groundwater. Adv Water Resour 15:47–62

Motyka J (1988) Triassic carbonate sediments of Olkusz-Zawiercie ore-bearing district as an aquifer. Scientific Bulletins of Stanisław Staszic Academy of Mining and Metallurgy No. 1157, Geology No. 36, Kraków (in Polish)

Motyka J, Zuber A (1993) Parameters of fissures and the hydraulic conductivity of rocks. In: Współczesne problemy hydrogeologii. Wrocław: Sudety. pp 421–425 (in Polish)

Neretnieks I (1980) Diffusion in the rock matrix: an important factor in radionuclide retardation? J Geophys Res 85(B8):4379–4397

Prill RC (1961) Comparison of drainage data obtained by centrifuge and column-drainage methods. US Geological Survey Paper 424 D. Washington, DC: US Government Printing Office, pp 399–401

Saffman PG (1959) Dispersion in flow through the network of some capillaries. Chem Eng Sci 11:125–129

Sudicky EA, McLaren RG (1992) The Laplace transform Galerkin technique for large-scale simulation of mass transport in discretely fractured porous formations. Water Resour Res 28(2): 499–514

Wilk Z, Motyka J (1980) Groundwater storativity of karst fissured rocks in the eastern section of the Cracow-Silesian monocline. Ann Soc Geol Pol 50(3/4):447–484 (in Polish)

Wilk Z, Motyka J, Józefko I (1984) Investigations of some hydraulic properties of karst solution openings and fractures. Ann Soc Geol Pol 54(1/2):15–43

Zuber A (1983) Models for tracer flow. In: Tracer Methods in Isotope Hydrology. IAEA-TECDOC-291, Vienna: IAEA. pp 67–112

Zuber A (1985) A review of existing mathematical models for interpretation of tracer data in hydrology. Report No. 1270/AP, Kraków: Institute of Nuclear Physics (IFJ)

Zuber A, Motyka J (1994) Matrix porosity as the most important parameer of fissured rocks for solute transport at large scales. J Hydrol 158:19–46