
Review of the use of Péclet numbers to determine the relative importance of advection and diffusion in low permeability environments

Marijke Huysmans · Alain Dassargues

Abstract In low permeability environments, transport by advection is often neglected based on a Péclet number criterion. Such a criterion usually states that if the Péclet number (Pe) is much smaller than 1, diffusion dominates over advection and transport may be modeled considering diffusion only. Unfortunately, up to 10 different Péclet number definitions exist and for a particular case these different definitions lead to very diverse Péclet number values, differing several orders of magnitude from each other. In this paper, the different Péclet number definitions are therefore evaluated on their ability to determine the relative importance of transport by advection and by diffusion in low permeability environments. This is done by comparing the results of the analytical solution for pure diffusion with the analytical solution for diffusion, advection and dispersion for a large number of different input parameter values. The relation between the different Péclet numbers and the difference between the calculated concentration considering diffusion only and the calculated concentration considering both diffusion and advection is studied. These calculations show that some Péclet number definitions are not well suited to decide whether advection may be neglected in low permeability media.

Résumé Dans les milieux à faible perméabilité, le transport par advection est souvent négligeable lorsqu'on se base sur le critère du nombre de Péclet. Un tel critère suggère habituellement que pour un nombre de Péclet beaucoup plus petit que 1, la diffusion domine sur l'advection et que le transport peut être modélisé par diffusion seulement. Malheureusement, il existe jusqu'à environ dix définitions du nombre de Péclet et pour un cas spécifique, ces différentes définitions mènent à des valeurs du nombre de Péclet très différentes, et qui varient entre elles de plusieurs ordres de grandeur. Dans cet article, les différentes définitions du nombre de Péclet sont évaluées en fonction de leur habileté à déterminer l'importance relative du transport par advection et par diffusion dans les milieux à faible perméabilité. Ceci est fait en comparant les résultats de la solution analytique pour la diffusion pure à la solution analytique pour la diffusion, l'advection et la dispersion, et ce, pour un grand nombre de valeurs différentes comme paramètre d'entrée. La relation entre les différents nombres de Péclet et la différence entre la concentration calculée en considérant la diffusion seulement et la concentration calculée considérant simultanément la diffusion et l'advection est étudiée. Ces calculs prouvent que certaines définitions de nombre de Péclet ne sont pas appropriées afin de décider si l'advection peut être négligée dans les milieux à faible perméabilité.

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Resumen Frecuentemente se descuida el transporte por advección en ambientes de baja permeabilidad sobre la base del criterio del número de Péclet. Dicho criterio usualmente sostiene que si el número de Péclet (Pe) es mucho menor a 1, la difusión domina sobre la advección y es posible modelar el transporte considerando la difusión únicamente. Desafortunadamente existen 10 definiciones diferentes del número de Péclet y para un caso en particular estas diferentes definiciones conducen a valores de número de Péclet muy diversos los cuales difieren entre sí en varias magnitudes. Por lo tanto, en este artículo se evalúan las diferentes definiciones en base a su habilidad para determinar la importancia relativa del transporte por advección y difusión en ambientes de baja permeabilidad. Esto se lleva a cabo mediante la comparación de los resultados de la solución analítica para difusión pura con los de la solución analítica por difusión, advección y dispersión para un número amplio de diferentes valores como

parámetro. Se ha estudiado la relación entre los diferentes números de Péclet y las diferencias entre la concentración calculada considerando difusión únicamente y considerando tanto difusión como advección. Estos cálculos muestran que algunas de las definiciones de los números de Péclet no son muy apropiadas para decidir si se puede descuidar la advección en medios de baja permeabilidad.

Keywords Solute transport · Analytical solutions · Low permeability units · Diffusion

Introduction

In a large number of studies it is necessary to model the groundwater flow and the transport of solutes in low permeability porous media. Groundwater flow in these low permeability environments appears to influence the evolution of certain hydrologic, geologic and geochemical systems, may affect the accumulation of petroleum and ores and probably has a role in the structural evolution of parts of the crust. Such environments are also important in the context of waste disposal (Neuzil 1986). Important examples are the modeling of the hydrogeology of low permeability formations surrounding nuclear waste disposal sites and landfills.

In general, transport in porous media is simulated by simultaneously considering advection, mechanical dispersion and diffusion. At low flow velocities, transport may be diffusion dominated, whereas at high velocities, transport may be advection dominated. For either case, a transport model that neglects relatively insignificant terms would be easier to implement than one that simultaneously considers all transport mechanisms, particularly if the model is three-dimensional and/or includes simultaneous consideration of multiple and reactive chemical species or parameter optimization routines (Garges and Baehr 1998). Therefore, in case of a low permeability medium, it is worth checking whether advection should be considered. If not, transport may be simulated considering diffusion only. In that case, the head and permeability distribution are not required for transport simulation and the computation time can be significantly reduced. Additionally, neglecting advection leads to a reduction of the numerical difficulties, since the need to treat simultaneously hyperbolic terms (associated with advection) and parabolic terms (associated with dispersion/diffusion) represents an important problem for numerical transport simulation methods (Zheng and Bennet 2002).

A criterion based on a Péclet number is often used to decide whether transport by advection should be considered. A Péclet number is a dimensionless number that can relate the effectiveness of mass transport by advection to the effectiveness of mass transport by either dispersion or diffusion (Fetter 1999). Usually, diffusion is considered as the dominant transport mechanism for Péclet numbers smaller than 1. Unfortunately, up to 10 different definitions of the Péclet number can easily be found in literature and for a given particular case these different definitions

lead to very diverse Péclet number values. Consequently, deciding to neglect advection based only on a Péclet number value smaller than 1 seems not justified for every existing Péclet number definition.

In this study, the different Péclet number definitions are therefore examined and evaluated on their ability to determine the relative importance of transport by advection and transport by diffusion in low permeability environments.

Péclet number definitions

A variety of Péclet number definitions can be found in literature. The main difference between them lies in the underlying assumptions about solute transport. Different simplifications of the general solute transport equation result in different Péclet number definitions. In this section, an overview of the available Péclet number definitions is given (Table 1). Nine different definitions are presented. They are grouped according to the solute transport equation they are based on.

In the general form of the solute transport equation, a distinction is made between the effective porosity n_e , which is the porosity available for fluid flow or advection (Fetter 2001), and the diffusion accessible porosity n , which is the fraction of the total water filled porosity that is available for diffusive transport (Horseman et al. 1996). The diffusion accessible porosity is not always equal to the total porosity but may be smaller since research on compact clays suggests that only a fraction of the total water-filled porosity is available for diffusive transport. This is caused by size-exclusion effects, i.e. some pores are narrower than the ion size, and by the permanent structural negative charge on the clay surface, which can cause negatively charged ions to be excluded from the narrower interparticle spaces of the clay (Horseman et al. 1996). The effective porosity and the diffusion accessible porosity are not necessarily the same since no advection or dispersion of a pollutant can take place in a body of immobile water, although these immobile water bodies can exchange a pollutant with the water surrounding them by molecular diffusion (Bear and Verruijt 1994). The diffusion accessible porosity may therefore be larger than the effective porosity since the former also includes a

Table 1 Péclet number definitions

Péclet number	Porosity	Dispersion/diffusion coefficient	Characteristic length
Pe_1	$n=n_e$	D_h	L
Pe_2	$n=n_e$	D_h	$V_e T$
Pe_3	$n=n_e$	D_h	Δm
Pe_4	$n=n_e$	D_e	d
Pe_5	$n=n_e$	D_e	R
Pe_6	$n=n_e$	D_d	d
Pe_7	$n=n_e$	D_d	b
Pe_8	$n=n_e$	D_d	\sqrt{k}
Pe_9	$n \neq n_e$	D_e	L
Pe_{10}	$n \neq n_e$	$D_e + \frac{n_e}{n} D$	L

fraction of the immobile water porosity. Consequently, one porosity may be required for advection velocity calculation while another may be needed for evaluating the rate of mass accumulation. However, rather than invoking two porosity terms, the convention in advective-dispersive transport analysis has been to use a single lumped value of porosity (Zheng and Bennett 2002).

The three-dimensional advection-dispersion-diffusion equation in its general form with a distinction between effective and diffusion accessible porosity is written as follows (de Marsily 1986):

$$n \frac{\partial C}{\partial t} = \text{div}(n \cdot D_e \cdot \text{grad } C + n_e \cdot D \cdot \text{grad } C - n_e \cdot v_e \cdot C) \quad (1)$$

where n is the diffusion accessible porosity (-), C is the solute concentration (kg/m^3), n_e is the effective porosity (-) and V_e is the effective advection velocity (m/s). D_e is the effective diffusion coefficient (m^2/s), which is related to the molecular diffusion coefficient that occurs in Fick's first law:

$$F = -D_d \frac{\partial C}{\partial x} \quad (2)$$

where F is the mass flux of solute per unit area per unit time ($\text{kg}/\text{m}^2/\text{s}$), D_d is the molecular diffusion coefficient (m^2/s) and C is the solute concentration. In porous media, diffusion cannot proceed as fast as it can in water because the ions must follow longer pathways as they travel around mineral grains. To account for this, an effective diffusion coefficient, D_e , must be used:

$$D_e = \omega D_d \quad (3)$$

where ω is a coefficient that is related to the tortuosity (-), which is a measure of the effect of the shape of the flow path followed by water molecules in porous media. The dispersion coefficient D (m^2/s) is defined in a similar way as the diffusion coefficient: dispersive flux = $-D \text{ grad } C$. The dispersion coefficient is equal to a property of the medium called dispersivity α (m) times the average linear velocity. In the direction of flow, D_L is the longitudinal dispersion coefficient, which is equal to the longitudinal dispersivity times the average linear velocity while in the directions at right angles to the velocity, D_T is the transverse dispersion coefficient, which is equal to the transverse dispersivity times the average linear velocity (de Marsily 1986).

The solute transport equation is often simplified by assuming that the component of solute transport due to immobile water in the porous medium can be neglected. Consequently, the effective porosity is considered as nearly equivalent to the total porosity and the diffusion accessible porosity. This equation then becomes:

$$\frac{\partial C}{\partial t} = \text{div}(D_h \cdot \text{grad } C - v_e \cdot C) \quad (4)$$

where D_h is the coefficient of hydrodynamic dispersion (m^2/s) which is defined as

$$D_h = D + D_e \quad (5)$$

The general form of the Péclet number corresponding to this equation is defined as the ratio of the coefficients of the advective and dispersive term of the equation multiplied by a length L (m), characteristic for the scale of the problem at hand:

$$Pe = \frac{v_e L}{D_h} \quad (6)$$

A first variation of this Péclet number is an often used Péclet number definition:

$$Pe_1 = \frac{V_e L}{D_L} = \frac{V_D L}{n_e D_L} \quad (7)$$

where V_e is the effective groundwater velocity, L is a reference length e.g. the distance from the contaminant source (m), D_L is the longitudinal hydrodynamic dispersion coefficient (m^2/s), V_D is the Darcy velocity (m/s) and n_e is the effective porosity for advection (Fetter 1999; Sauty 1980). This Péclet number occurs in the dimensionless form of the analytical solutions (Ogata and Banks 1961) of the advection-dispersion equation for aquifers.

A similar Peclet number is applied by Remenda et al. (1996) in their study about the use of vertical profiles of $\delta^{18}\text{O}$ to constrain estimates of the hydraulic conductivity in a thick unfractured aquitard. They state that the magnitude of advective transport relative to diffusive transport can be characterized by the following Péclet number:

$$Pe_2 = \frac{V_e^2 T}{D_h} \quad (8)$$

where V_e is the average (effective) linear groundwater velocity, T is the total duration of the process (s) and D_h is the hydrodynamic dispersion coefficient. The denominator can be broken down into $V_e \times V_e T$, where the second term ($V_e T$) represents the distance traveled by the center of mass, making this formulation very similar to Pe_1 . Remenda et al. (1996) assume that if Pe_2 is much smaller than 1, advective transport is negligible, and the process is diffusion dominated.

The third Péclet number definition deduced from the same equation usually has a purpose quite different from the purpose discussed in this paper. This Péclet number is often calculated in relation with possible numerical problems arising in transport calculations. Transport simulation methods using spatial discretization often lead to artificial oscillations and numerical dispersion in the numerical solution. This is especially true when a sharp concentration front must be simulated, that is, when the problem is advection-dominated. The sharpness of the concentration front, or the degree to which the transport problem is dominated by advection, can be measured by the grid Péclet number Pe_3 :

$$Pe_3 = \frac{V_e \Delta m}{D_h} \quad (9)$$

where V_e is the effective groundwater velocity, Δm is the grid spacing (m) and D_h is the coefficient of hydrodynamic dispersion (Zheng and Bennet 2002).

The solute transport equation is sometimes also simplified by neglecting dispersion. The equation is then formulated as:

$$\frac{\partial C}{\partial t} = \text{div}(D_e \cdot \text{grad } C - v_e \cdot C) \quad (10)$$

where C is the volume concentration, D_e is the effective diffusion coefficient, and V_e is the effective advection velocity. The Péclet number corresponding to this equation, defined as the ratio of the coefficients of the advective and dispersive term of the equation multiplied by a characteristic length L , is defined as:

$$Pe = \frac{v_e L}{D_e} \quad (11)$$

The first Péclet number with this general form is the Péclet number presented by Freeze and Cherry (1979):

$$Pe_4 = \frac{V_e d}{D_e} \quad (12)$$

where V_e is the average linear velocity, d is the average particle diameter (m), and D_e is the effective diffusion coefficient of the porous medium.

A similar Péclet number uses the waste container radius as characteristic length:

$$Pe_5 = \frac{V_e R}{D_e} \quad (13)$$

where V_e is the effective groundwater velocity, R is the waste container radius (m) and D_e is the effective diffusion coefficient in porous media. Diffusion is expected to dominate when $Pe_5 < 1$.

The next three Péclet number definitions are very similar to the previous ones but differ in the choice of the diffusion coefficient. The Péclet number, Pe_6 , defined in order to express the ratio of transport by advection to the rate of transport by molecular diffusion in column studies, is a dimensionless parameter defined as $v_x d / D_d$, where d is the average grain diameter and D_d is the coefficient of molecular diffusion in water (Fetter 1999). The coefficient of molecular diffusion in water is used instead of the effective diffusion coefficient in porous media (i.e. the coefficient of molecular diffusion in water multiplied with a factor related to the tortuosity of the porous medium):

$$Pe_6 = \frac{V_e d}{D_d} = \omega Pe_4 \quad (14)$$

where ω is a coefficient related to tortuosity.

The pore or fracture junction Péclet number is defined as the mean advective velocity multiplied with pore/fracture size, divided by the diffusion coefficient:

$$Pe_7 = \frac{V_e b}{D_d} \quad (15)$$

where V_e is the mean velocity in one of the entering channels, b is the channel width (m) and D_d is the mo-

lecular diffusion coefficient. At high velocities and high Péclet number there is little mixing across the dividing stream line, yielding advective control. At small velocities and Péclet numbers diffusion dominates, resulting in complete mixing. The transition between these limits occurs between Péclet numbers of 1.5 and 15 (Wilson et al. 1993).

A similar Péclet number is the dimensionless number defined by de Marsily (1986). To distinguish whether diffusion is prevailing or advection, the following number of Péclet Pe_8 is considered:

$$Pe_8 = \frac{V_D \sqrt{k}}{n_e D_d} = \frac{V_D \sqrt{\left(K \frac{\mu}{\rho g}\right)}}{n_e D_d} \quad (16)$$

where V_D is the Darcy velocity, k is the intrinsic permeability (m^2), n_e is the effective porosity, K is the hydraulic conductivity (m/s), μ is the dynamic viscosity (kg/m/s), ρ is the water density (kg/m³), g is the acceleration of gravity (m/s^2) and D_d is the molecular diffusion coefficient. Contaminant transport is only controlled by diffusion if $Pe_8 < 2$, a combination of diffusion, advection and dispersion if $2 < Pe_8 < 9$ and mainly by advection and dispersion if $Pe_8 > 9$. The factor $k^{-1/2}$ can be related to effective grain size by using the empirical relations developed by Hazen:

$$K = C(d_{10})^2 \quad (17)$$

where K is the hydraulic conductivity, d_{10} is the effective grain size (m) and C is a coefficient dependent on the sorting characteristics of the sediment (Fetter 2001). This definition is therefore very similar to Pe_4 and Pe_6 , which also include the grain size as characteristic length.

If the distinction between effective and diffusion accessible porosity is made in the solute transport equation and if dispersion is neglected, the equation is given by:

$$n \frac{\partial C}{\partial t} = \text{div}(n \cdot D_e \cdot \text{grad } C - n_e \cdot v_e \cdot C)$$

$$\frac{\partial C}{\partial t} = \text{div}\left(D_e \cdot \text{grad } C - \frac{V_D}{n} C\right) \quad (18)$$

where n is the diffusion accessible porosity, C is the volume concentration, D_e is the effective diffusion coefficient, n_e is the effective porosity, V_e is the effective advection velocity and V_D is the Darcy velocity.

The Péclet number definition deduced from this equation includes the Darcy velocity divided by the diffusion accessible porosity instead of the effective advective velocity (i.e. Darcy velocity divided by effective advective porosity). In the SAFIR 2 report of ONDRAF/NIRAS (2002), the Belgian Agency for Radioactive Waste and Enriched Fissile Materials, this Péclet number is applied to evaluate the role of advection and diffusion in a low permeability clay:

$$Pe_9 = \frac{V_D x}{n R D_{app}} = \frac{V_D x}{n D_e} \quad (19)$$

where V_D is the Darcy velocity, x is a distance, n is the diffusion accessible porosity, R is the retardation factor, D_{app} is the apparent diffusion coefficient (m/s^2) and D_e is the effective diffusion coefficient. For $Pe < 1$ diffusion dominates over advection at the distance x from the source (ONDRAF/NIRAS 2002). The same Péclet number definition is used for examining transport phenomena in the Opalinus Clay (Soler 2001). At a spatial scale defined by the reference length L , advection will be dominant over chemical diffusion if $Pe_0 \gg 1$, and chemical diffusion will be dominant if $Pe_0 \ll 1$ (Soler 2001).

It is clear that not all of the choices presented for the Péclet number would ever be applicable to the plume scale problem that is tested in this study. For example, Pe_3 is defined for a purpose quite different from the purpose discussed in this paper, i.e. avoiding numerical problems in transport calculations. Other Péclet number definitions are designed for a scale very different from the plume scale. These Péclet numbers are however included in the calculations to examine the effect of applying an inappropriate Péclet number on the decision to neglect advection in low permeability media.

Method

In order to evaluate these 9 different Péclet number definitions, a large number of transport calculations is carried out. To minimize the computation time, a simple test case geometry is chosen so that an analytical solution can be written. The chosen example is a one-dimensional case with a fixed-concentration boundary. For this simple case,

the analytical solutions of the advection-dispersion-diffusion equation and the diffusion equation in low permeability environments are available.

The most general form of the three-dimensional advection-dispersion-diffusion equation is applied (de Marsily 1986):

$$n \frac{\partial C}{\partial t} = \text{div}(n \cdot D_e \cdot \text{grad } C + n_e \cdot D \cdot \text{grad } C - n_e \cdot v_e \cdot C) \tag{20}$$

where n is the diffusion accessible porosity, C is the volume concentration, D_e is the effective diffusion coefficient, n_e is the effective porosity, D is the dispersion coefficient and V_e is the effective advection velocity. This equation is used since in low permeability environments, the effective porosity can be much smaller than the diffusion accessible porosity and the total porosity, as shown on Fig. 1.

For a one-dimensional flow in homogeneous, isotropic porous media of low permeability, Eq. (20) can be written as follows:

$$n \frac{\partial C}{\partial t} = n \cdot D_e \cdot \frac{\partial^2 C}{\partial x^2} + n_e \cdot D \cdot \frac{\partial^2 C}{\partial x^2} - n_e \cdot V_e \cdot \frac{\partial C}{\partial x} \tag{21}$$

For particular initial and boundary value conditions, an analytical solution to this partial differential equation exists. The boundary condition chosen for this study is the one-dimensional step change in concentration (Fig. 2). The boundary and initial conditions are given by

Fig. 1 Porosity components as a function of grain size (after Castany 1967)

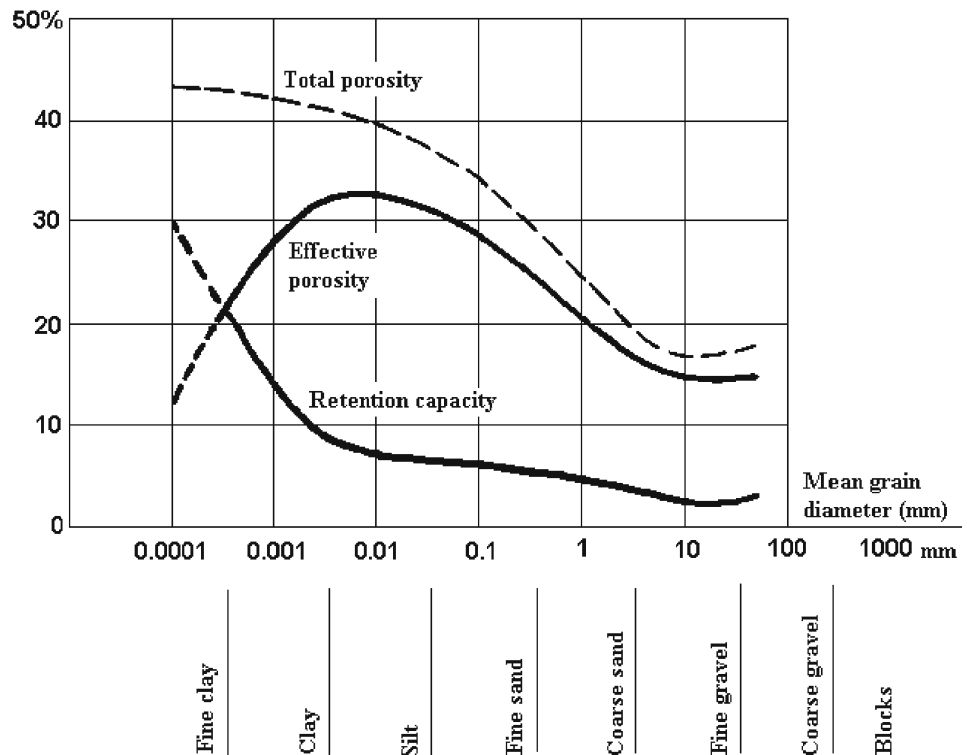




Fig. 2 Boundary conditions for the analytical solution

$$\left. \begin{aligned} C(x, 0) = 0 \quad x \geq 0 \\ C(0, t) = C_0 \quad t \geq 0 \\ C(\infty, t) = 0 \quad t \geq 0 \end{aligned} \right\} \begin{array}{l} \text{Initial condition} \\ \text{Boundary conditions} \end{array} \quad (22)$$

The solution to Eq. (21) for these conditions is the following (adapted from Ogata and Banks 1961; Fetter 1999):

$$C = \frac{C_0}{2} \left[\operatorname{erfc} \left(\frac{L - \left(\frac{n_e}{n} V_e\right)t}{2\sqrt{\left(D_e + \frac{n_e}{n} D\right)t}} \right) + \exp \left(\frac{\left(\frac{n_e}{n} V_e\right)L}{\left(D_e + \frac{n_e}{n} D\right)} \right) \operatorname{erfc} \left(\frac{L + \left(\frac{n_e}{n} V_e\right)t}{2\sqrt{\left(D_e + \frac{n_e}{n} D\right)t}} \right) \right] \quad (23)$$

This equation may be expressed in a dimensionless form as (adapted from Ogata and Banks 1961; Fetter 1999):

$$C_R(t_R, Pe_{10}) = 0.5 \left\{ \operatorname{erfc} \left[\left(\frac{Pe_{10}}{4t_R} \right)^{1/2} \cdot (1 - t_R) \right] + \exp(Pe_{10}) \operatorname{erfc} \left[\left(\frac{Pe_{10}}{4t_R} \right)^{1/2} \cdot (1 + t_R) \right] \right\} \quad (24)$$

where

$$t_R = \frac{n_e V_e t}{L}, \quad C_R = \frac{C}{C_0} \quad \text{and} \quad Pe_{10} = \frac{\left(\frac{n_e}{n} V_e\right)L}{\left(D_e + \frac{n_e}{n} D\right)} = \frac{\left(\frac{V_D}{n}\right)L}{\left(D_e + \frac{n_e}{n} D\right)} \quad (25)$$

and erfc is the complementary error function.

It is important to notice that the factor V_D/n arising in the nominator of the Péclet number Pe_{10} , occurs in the dimensionless form of the solution of the advection-dispersion-diffusion equation in low permeability environments. The Darcy velocity is divided by the diffusion accessible porosity and not by the effective porosity like in the Péclet number Pe_1 . This last appears in the dimensionless form of the solution of the advection-dispersion-diffusion equation in aquifers. The calculations of the following section show that this may be an important difference since the effective porosity for advection can be much smaller than the diffusion accessible porosity in low permeability environments.

The general equations describing pure diffusion or transport by concentration gradients are Fick's first law (Eq. 2) and Fick's second law. For systems where the concentrations are changing with time, Fick's second law applies. In one dimension this gives:

$$\frac{\partial C}{\partial t} = D_d \frac{\partial^2 C}{\partial x^2} \quad (26)$$

For the considered geometry and boundary conditions, the solution of the diffusion equation is:

$$C(x, t) = C_0 \operatorname{erfc} \left[\frac{x}{2(D_e t)^{0.5}} \right] \quad (27)$$

Using these analytical solutions, the ability of the different Péclet number definitions to determine the importance of transport by advection relative to transport by diffusion in low permeability environments is assessed. The concentration versus time caused by advection and diffusion and the concentration versus time caused by pure diffusion are calculated. A time average of the difference between $[C/C_0]_{\text{diffusion}}$, advection and dispersion and $[C/C_0]_{\text{diffusion}}$ is calculated for all the different parameter combinations. Next, the 10 different Péclet numbers are calculated for all the different parameter combinations. After that, the relation between the time averaged difference between $[C/C_0]_{\text{diffusion}}$, advection and dispersion and $[C/C_0]_{\text{diffusion}}$ and the 10 different Péclet numbers is studied and evaluated.

The input parameter values are presented in Table 2. The first variable is the distance to the source. It varies

Table 2 Input parameter values

Parameter description	Parameter	Minimum	Maximum
Distance to the source	L (m)	0	50
Effective diffusion coefficient	D_e (m ² /year)	$2 \cdot 10^{-4}$	$3.5 \cdot 10^{-3}$
Time	T (year)	10^4	$5 \cdot 10^8$
Hydraulic conductivity	K (m/s)	10^{-12}	10^{-10}
Hydraulic head gradient	grad h (-)	0.02	0.02
Effective porosity	n_e (-)	0.001	0.1
Diffusion accessible porosity	n (-)	0.2	0.4
Longitudinal dispersivity	α_L (m)	0.01	10
Pore size	b (m)	10^{-6}	10^{-6}
Average grain size	d (m)	$12 \cdot 10^{-6}$	$12 \cdot 10^{-6}$
Factor related to tortuosity	ω (-)	0.1	0.1
Grid spacing	Δm (m)	1	1
Waste container radius	R (m)	1	1

from 0 to 50 m since the solute source is assumed to be located in the middle of a 100-m thick clay. The range of effective diffusion coefficient values of clay for several different elements is based on values reported in literature for different types of clay. For example, Boisson et al. (2001) report diffusion coefficients in clay from 10^{-12} to $2 \cdot 10^{-11}$ m²/s, Soler (2001) suggests that diffusion coefficients in the Opalinus Clay range from 10^{-12} m²/s to 10^{-11} m²/s, with an extended range (less probable values) from 10^{-13} to 10^{-10} m²/s and measured diffusion coefficients in the Boom Clay are between $5 \cdot 10^{-11}$ m²/s and $2 \cdot 10^{-10}$ m²/s (ONDRAF/NIRAS 2002). The effective diffusion coefficient for this calculations varies from $6 \cdot 10^{-12}$ m²/s ($2 \cdot 10^{-4}$ m²/year) to 10^{-10} m²/s ($3.5 \cdot 10^{-3}$ m²/year), which corresponds to the range of average values of diffusion coefficients found in literature. The calculations are carried out from 10,000 year till 500,000,000 year since this is considered to be a meaningful time window for the slow transport in low permeability media. The range of hydraulic conductivity values is based on values mentioned in literature for different clays. Hendry and Wassenaar (1999) report hydraulic conductivity values of the order of 10^{-11} m/s and 10^{-12} m/s for a clay-rich till and a massive, plastic clay respectively, Wemaere et al. (2002) measured hydraulic conductivity values of 10^{-10} m/s to 10^{-12} m/s in Boom Clay samples and Keller et al. (1989) present laboratory hydraulic conductivity values of a clayey till between 10^{-11} m/s and $4.5 \cdot 10^{-11}$ m/s. The hydraulic conductivity values for the calculations are therefore between 10^{-12} and 10^{-10} m/s. The hydraulic head gradient is taken as 0.02, which is of the same order as reported hydraulic gradients in low permeability environments of 0.014 (Hendry and Wassenaar 1999) and 0.02 (Mallants et al. 2001). The effective porosity of a clay is rather low. Spitz and Moreno (1996) suggest effective porosities of clay from 0.8% to 6%. For this study, it is assumed that the effective porosity value is situated between 0.1% and 10%. The diffusion accessible porosity as determined in laboratory tests on several clays is usually between 50 and 100% of the total porosity (van der Kamp et al. 1996; Aertsen et al. 2003). Since the total porosity of clay is usually approximately 40% (Fetter 2001; Spitz and Moreno 1996), the diffusion accessible porosity varies between 20% and 40%. The longitudinal dispersivity is estimated to be 0.01 to 10 m, which corresponds to the values suggested by de Marsily (1986) that range from the order of a few centimeters to the order of meters depending on the degree of heterogeneity of the formation. The pore size and average grain size are estimated based on typical cumulative pore size distribution curves (Horseman et al. 1996) and grain size distribution curves (Wemaere et al. 2002) of low permeability clays. The tortuosity factor ω is approximately 0.1 for clays (de Marsily 1986). The grid spacing is considered to be 1 m. The waste container radius is assumed to be 1 m. Within the ranges of these parameters, 54000 combinations of input parameters are drawn based on a uniform distribution of the parameters between the minimum and the maximum value of the parameters.

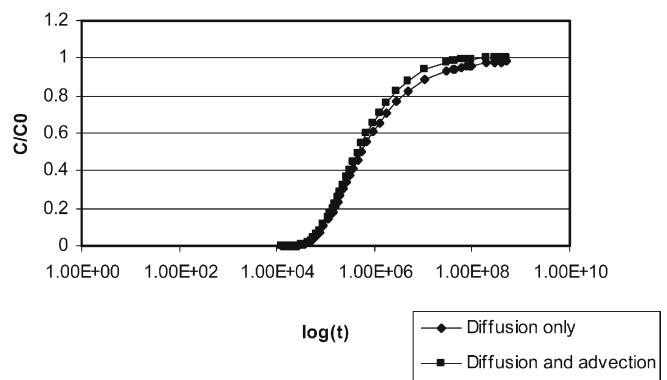


Figure 3 Concentration versus time for $K=10^{-12}$ m/s, grad $h=0.02$, $n_e=0.001$, $n=0.2$, $L=10$ m, $D_e=2.05 \cdot 10^{-4}$ m²/year, $\alpha=0.01$ m; resulting difference=2%

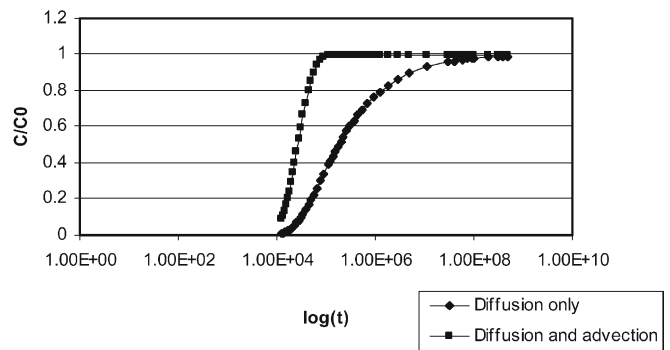


Figure 4 Concentration versus time for $K=10^{-10}$ m/s, grad $h=0.02$, $n_e=0.001$, $L=10$ m, $D_e=6 \cdot 10^{-4}$ m²/year, $\alpha=0.01$ m, resulting difference=30%

For two different parameter combinations out of the 54000 combinations, the calculation results are illustrated in Figs. 3 and 4. In Fig. 3, a situation is shown where the solution considering advection and diffusion and the solution considering pure diffusion are quite similar. Neglecting transport by advection is, in this case, probably justified. The averaged difference between $[C/C_0]_{\text{diffusion, advection and dispersion}}$ and $[C/C_0]_{\text{diffusion}}$ is in this case equal to 2%. In Fig. 4, the situation is completely different. Compared to the situation in Fig. 3, the hydraulic conductivity value is multiplied by 100. In this case, transport by advection is significant and should not be neglected in the transport calculations. In this case the averaged difference between $[C/C_0]_{\text{diffusion, advection and dispersion}}$ and $[C/C_0]_{\text{diffusion}}$ reaches 30%.

Results and discussion

Figures 5 and 6 show the relations between each Péclet number and the time averaged difference between C/C_0 due to diffusion, advection and dispersion and C/C_0 due to diffusion only. As expected, the average difference,

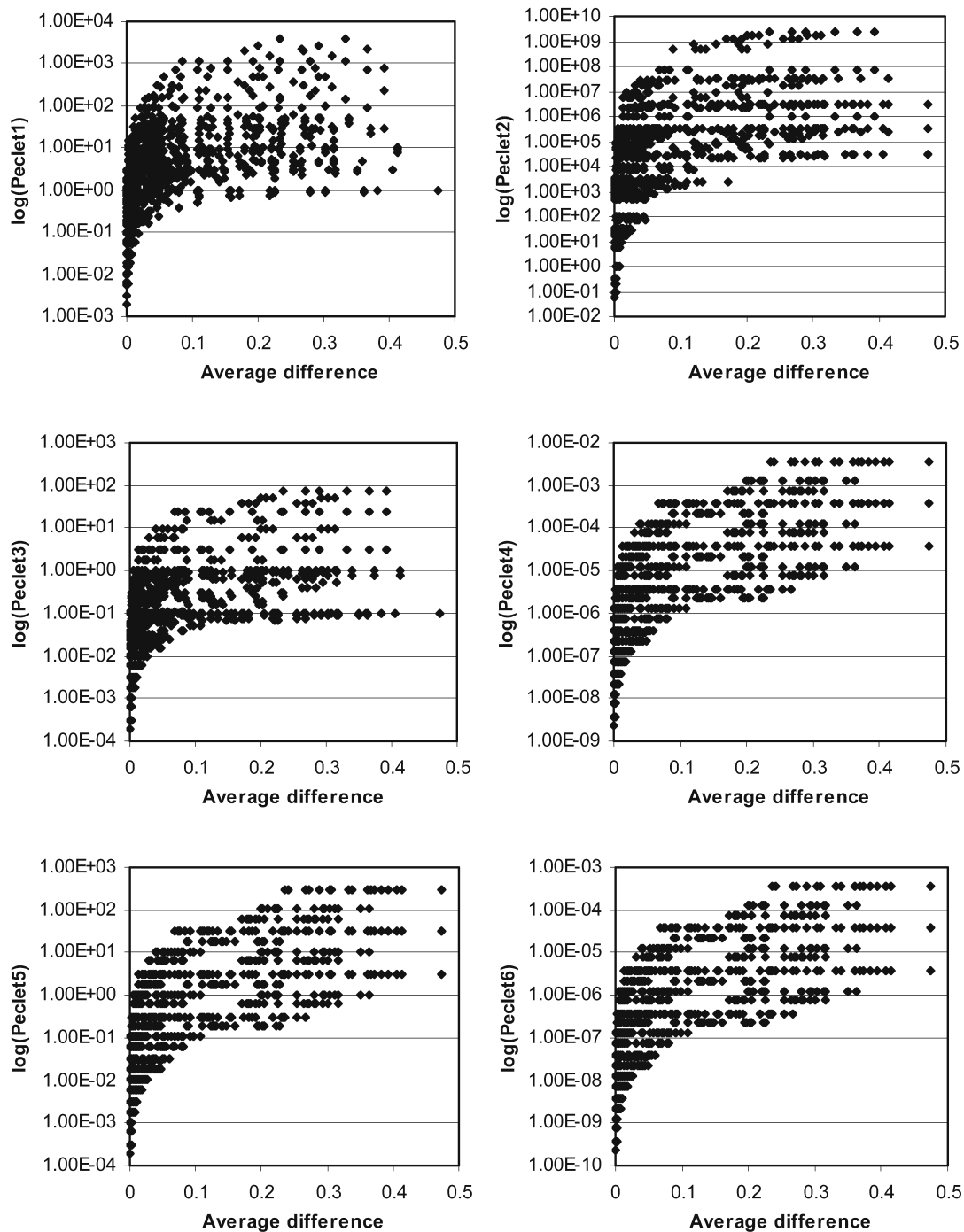


Figure 5 Relation between Péclet numbers 1 to 6 and the averaged difference between C/C_0 due to diffusion, advection and dispersion and C/C_0 due to diffusion only.

giving a measure of the error made by neglecting advection, increases with increasing Péclet numbers for all Péclet number definitions. It is however clear that not every Péclet number has the same efficiency in describing the conditions for which advection may be neglected.

Compared to Péclet numbers 9 and 10, Péclet numbers 1 to 8 all show a more scattered relation between the Péclet number and the difference between C/C_0 due to both diffusion and advection and C/C_0 due to diffusion

only. For Pe_1 to Pe_8 , one value of the Péclet number corresponds with a large number of different average concentration difference values and the relation is thus not well defined. The application of these Péclet numbers as a criterion for neglecting advection in low permeability environments may therefore be problematic. This is illustrated with the example of Pe_1 . This criterion works well for small Péclet numbers, i.e. if this Péclet number is much smaller than one for the problem at hand, advection

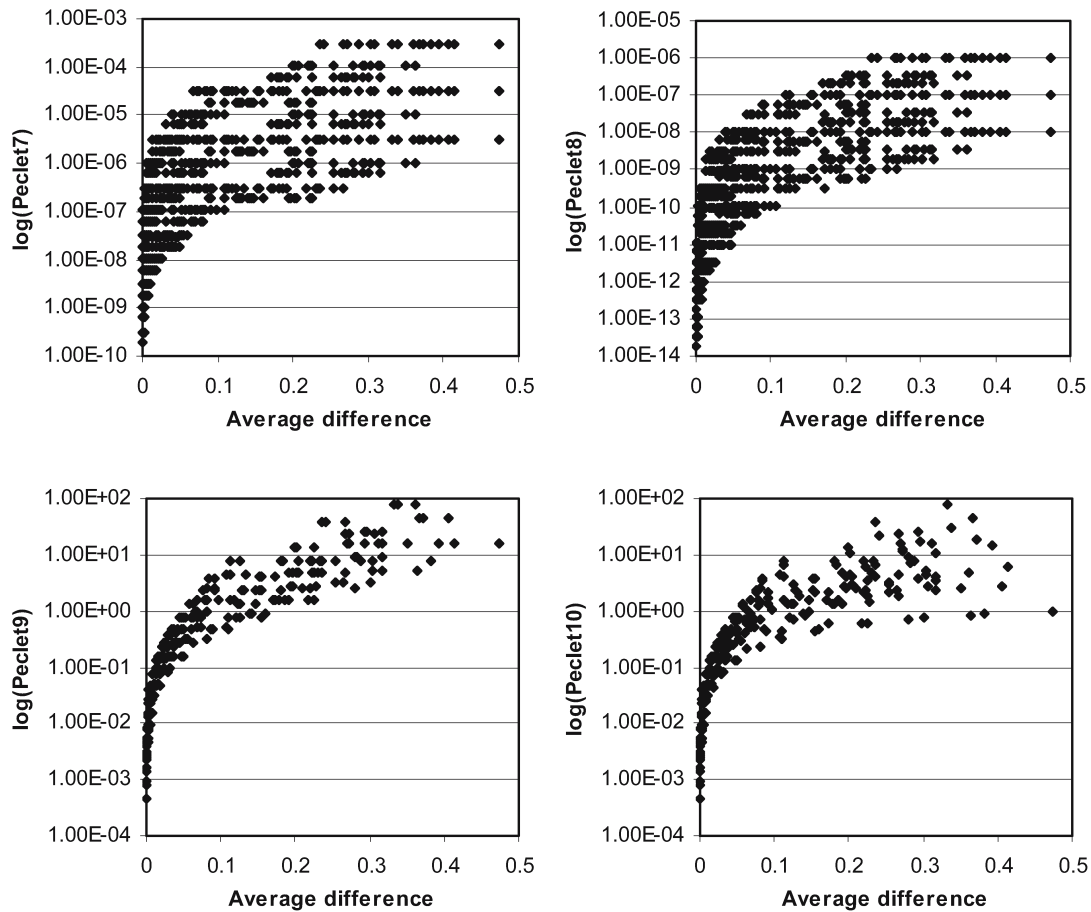


Figure 6 Relation between Péclet numbers 7 to 10 and the averaged difference between C/C_0 due to diffusion, advection and dispersion and C/C_0 due to diffusion only.

may indeed be neglected. The problem is that Pe_1 is often larger than one in situations where advection may in fact be neglected. Péclet number values up to 1000 correspond to situations where the average difference is actually smaller than 0.1 or 10%. Application of this Péclet number as a criterion for neglecting advection in low permeability environments, would therefore result in unnecessarily complicated models for cases where a simple diffusion model would serve.

The large scatter of the relations with the average difference of Pe_1 to Pe_8 is caused by the presence of the advective effective velocity, which is the Darcy velocity divided by the effective advective porosity. The effective advective porosity thus appears in the denominator of these Péclet numbers instead of the diffusion accessible porosity as suggested by the solute transport equation (Eq. 20). Since the effective porosity and the diffusion accessible porosity may be very different in low permeability environments such as clays, the use of the effective porosity instead of the diffusion accessible porosity may lead to very different results. For deciding about neglecting advection in low permeability environments, a Péclet number including the diffusion accessible porosity instead of the effective porosity should therefore be used. In high permeability aquifers, where the effective porosity

and the diffusion accessible porosity are approximately equal, Péclet numbers 1 to 8 are appropriate to determine the relative importance of advection and diffusion.

Another result is that the use of the inappropriate length scale in the Péclet number often results in incorrect decisions about neglecting advection in low permeability environments. Pe_2 , for example, is larger than one in almost all calculated cases. This Péclet number criterion would therefore almost always suggest including advection even if the importance of advection is minor. Pe_4 , Pe_6 , Pe_7 and Pe_8 , on the other hand, are smaller than one for all the calculated cases, although the average concentration difference between $[C/C_0]_{\text{diffusion, advection and dispersion}}$ and $[C/C_0]_{\text{diffusion}}$ may be as big as 40%. Advection may therefore not always be neglected if these Péclet numbers are smaller than one.

The choice of the dispersion or diffusion coefficient has not a large effect on the ability of a Péclet number to determine the importance of advection in low permeability environments. This is shown by the similarity of the results for Pe_9 , which includes the effective diffusion coefficient, and Pe_{10} , which includes both the effective diffusion coefficient and the dispersion coefficient. This small effect of the choice of the dispersion or diffusion coefficient is caused by the proportionality of the dis-

persion coefficient to the effective velocity, which is generally low in low permeability environments. Therefore the dispersion coefficient is relatively small compared to the diffusion coefficient and ignoring the dispersion coefficient does not lead to large differences in calculated Péclet numbers.

The results presented here are obtained for a specific parameter range, but the authors believe that the results are general enough for application on sites with other characteristics where a decision has to be taken about the importance of advection in a low permeability medium. However, the Péclet numbers are evaluated based on their ability to decide about neglecting advection in low permeability environments on a large scale. It is not because some of the Péclet numbers are not well suited for this application, that they may not have an important and justified value in other hydrogeological contexts where Péclet numbers are used.

Conclusion

In this study, ten different Péclet number definitions were evaluated on their ability to determine the relative importance of transport by advection and transport by diffusion in low permeability environments. This is done by comparing the corresponding analytical solutions for a large number of different input parameter values. For 54000 combinations of input parameter values, the relation between the different Péclet numbers and the averaged difference between the calculated concentration considering diffusion only and the calculated concentration considering both diffusion and advection was studied. The main conclusion of this study is that since the effective porosity and the diffusion accessible porosity may be very different in low permeability environments such as clays, the use of the effective porosity instead of the diffusion accessible porosity may lead to very different results. For deciding about neglecting advection in low permeability environments, a Péclet number including the diffusion accessible porosity instead of the effective porosity should therefore be used. The convention in solute transport analysis to use a single lumped value of porosity instead of two different porosity terms is thus not appropriate for low permeability environments.

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