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Basic flow and mass transport considerations in the exploitation and protection of groundwater resources

GROUNDWATER RESOURCES Occurrence of Groundwater

Fueled by solar radiation, water, in all its phases, moves through the atmosphere, the land and the oceans of the earth in a continuous *hydrologic cycle*. Promoted by gravity, it flows over the land as surface-water and through the soils and deeper geologic formations as groundwater. Water-bearing geologic media are classified based on their ability to transmit water: *aquifers* are called the hydraulically most conductive ones (confined, unconfined, leaky, or perched); *aquitards* and *aquicludes* are leaky systems of low permeability.

Scope of this work

Groundwater is a valuable resource, supplying ~20% of the water for agriculture, industry and municipalities worldwide, and the main source of drinking water in most of Europe, 40% in the USA and 70% in China; it is also important for the ecology. Its exploitation is controlled by the low flow rates in the vast subsurface water reservoirs, and the long residence times. This major water resource is threatened increasingly by intense use and by contamination. Careful management is required to check the intense use, while prevention and remediation are necessary to ensure good groundwater quality. Basis for the study of groundwater are geology, hydrology, hydraulics and geochemistry, all contributing towards a competent analysis of complex groundwater problems. This chapter presents tools for a first study of flow and of mass transport in aquifers.

Elements of Porous Media (PM) Physics

A PM consists of solids (minerals) and voids; the minerals form a skeleton that is surrounded by mostly interconnected empty spaces, the pores. Among the geologic materials are unconsolidated soils, rocks, clays and fractured rocks. The voids fraction of the total PM volume is called the porosity; its value ranges between 0 and 1 (0 and 100 %). Generally, the porosity depends on grain size, shape and on the way the grains are packed. The grain size distribution of unconsolidated PM (*sieve curve*) is determined by passing the material through standard-size sieves. The wider the sieve curve is the tighter the packing and the lower the porosity. In groundwater dynamics, it is necessary to distinguish the total, geometric porosity n from the kinematic porosity n_k , which is the volume fraction of a PM that is available for circulation. The physical makeup of the PM determines its ability to transmit fluids; relevant parameter is the hydraulic conductivity that we define in the next section. Meaningful parameter values are referenced to samples of finite size (Representative Elemental Volume – continuum approach).

GROUNDWATER HYDRAULICS

Basic Groundwater Flow Concepts and the law of Darcy

The differential balances for mass and for momentum describe groundwater flow, supplemented by equations of state for the fluid and the PM. Darcy's law expresses the energy dissipation, introducing the hydraulic conductivity $K = k \rho g / \mu$, which depends on the PM and on the fluid properties; k is the PM's intrinsic permeability. K is determined better via field *pumping* and *slug tests* than in the laboratory. After

generalising Darcy's law (vector form and anisotropic PM) as $q = -K \text{grad } h$, it is used to explain flow nets.

Fundamental Equations of Groundwater Flow (following de Marsily, 1986)

Introducing into the law of mass conservation of fluids mechanics, the law of Darcy and the equations of state for the fluid, for the solid grains and for the skeleton of the PM, with appropriate simplifications, we obtain the general groundwater flow equation where $S_s = \rho g n (\beta + \alpha/n)$ is the specific storage coefficient [L^{-1}], α the compressibility of the porous matrix (see Table 1) and $\beta = 5 \cdot 10^{-10} \text{ m}^2/\text{N}$ that of the water. For its solution, we must specify initial and boundary conditions (Dirichlet and/or Neumann). Discussion of 2-D models (*profile & areal*); the notion of transmissivity. Treatment of unconfined aquifers in areal models with the Dupuit approximation; introduction of the specific yield.

Determination of formation parameters (transmissivity & storativity) of a confined aquifer through evaluation of pumping test data with an analytical solution of transient radial flow, with an illustrative example (Cooper-Jacob solution).

GROUNDWATER CONTAMINATION Contaminants in groundwater and their sources

Groundwater contamination is closely linked to waste disposal (residuals), deriving from energy industrial, mining, agricultural, and military production activities. Sources of contamination are distinguished as concentrated and diffuse. Septic tanks and injection wells are concentrated sources designed to release contaminants. However, contaminant releases occur also accidentally from storage sites; in addition, contaminants may leak or be spilled during transport, or may reach aquifers inadvertently via abandoned wells. The contaminants comprise organic and inorganic chemicals. The organics can dissolve in groundwater, be present as non-aqueous phase liquids, or as vapour in the vadose zone, and sorb onto the solid matrix. Prime organic contaminants are petroleum hydrocarbons such as the fuel components benzene, toluene, ethyl-benzene and xylene (BTEX), chlorinated solvents such as trichloroethylene (TCE) and perchloroethylene (PCE), polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs) and most pesticides. Main inorganic pollutants include metals, radionuclides and certain pesticides.

Legislation, costs and policy implications, and remediation technology

Achievement of *good quality status* of water bodies is the objective of the European Union's (EU) Water Framework Directive, 2000/60/EC. The USA enacted legislation regulating the disposal of wastes by the 1980's (since amended): Safe Drinking Water Act, 1974; RCRA, 1976; CERCLA, 1980; Hazardous & Solid Waste Amendments, 1984, and SARA (Superfund), 1986. However, cleaning up the proven and suspected contaminated sites in the EU and the USA is estimated to cost in excess of one trillion € over the next 75 years. Faced with such potential costs, many industrialised nations are considering fitness-for-use policies; but leaving pollutants in place has costs too (liability, maintaining and monitoring a site, and reduced property values). Brief presentation of groundwater remediation technologies: (1) containment technologies, (2) technologies using biological and chemical reactions to destroy or transform pollutants and (3) technologies based on separating the contaminants from the geologic media, mobilising and extracting them from the subsurface. Brief discussion of the methods of *pump-and-treat* and of *natural attenuation*. Remediation of contaminated soils depends on the contaminants' volatility, reactivity and solubility and on the soil's makeup, i.e., on its texture (coarse to fine granular, or clayey), heterogeneity, and on saturation level.

Mass transport in groundwater

Fundamental equations

In aquifers, contaminants are transmitted by the water and stored in the solid matrix. For this reason we describe the flow of the dissolved species (solutes) through the PM and the interactions among the PM, the ambient fluid and the contaminants, as indicated in Fig. 9. This description entails (a) the geology, (b) the physical transport and (c) the bio-geo-chemical reactions. Including appropriate process formulations in the law of mass conservation yields the transport equation. In most instances, the flow field is determined separately, on the assumption that the solutes do not affect the flow (*hydro-dynamically passive*). This simplification holds when the solutes are present in trace quantities (*dilute solutions*), so that the density and viscosity of the fluid mixture are close to those of water (not true in sea intrusion in aquifers; simultaneous computation of flow and salt transport). In the following we treat the transport of a single species, for reasons of simplicity.

A solute's mass conservation equation is obtained from the balance of mass flows through the control surface (CS) of a control volume (CV) of the aquifer against the temporal change of mass stored inside the CV (Fig. 10), also considering reactions. The resulting equation for the transport of a single species of concentration C in a saturated PM reads:

$$\frac{\partial(n_k C)}{\partial t} + \text{div } \dot{m} = \sum_i r_i$$

Control volume & control surface

Conventional division of the specific mass flux of a solute, \dot{m} [$M L^{-2} T^{-1}$], in mass flow by advection, i.e. by the bulk flow field, \dot{m}_a , defined at the macroscopic Darcy scale, and in mass flow at sub-macroscopic scales, by dispersion and *diffusion*, \dot{m}_d : $\dot{m} = \dot{m}_a + \dot{m}_d$, where $\dot{m}_a = q C$ and $\dot{m}_d = -D' \text{grad} C$. D' is hydromechanical dispersion coefficient, a symmetric, 2nd-order tensor. Its principal directions of anisotropy are the direction of the specific discharge q and normal to it (D is diagonal along and normal to the streamlines) and its components have the form $q\alpha_i$. In 2D, the components are $q\alpha_L$ and $q\alpha_T$, where α_L and α_T the respective longitudinal and transverse *dispersivities* [L]; experiments show that $\alpha_L \gg \alpha_T$. Customarily, molecular diffusion is added to hydromechanical dispersion and their combination is termed hydrodynamic dispersion; thus $d = - (D' + n_k D^*) \text{grad} C$.

Substituting the mass fluxes into the solute's mass balance and assuming a rigid solid matrix, yields the common form of the solute transport equation in saturated PM:

where $u = q/n_k$ is the linear pore velocity and $D = D' / n_k$. Specifying r_i to include linear reversible sorption (linear isotherm with partitioning coefficient K_d ; *retardation factor* $R=1+\rho_b K_d$) and 1st-order decay (rate λ), the final mass transport equation PM reads:

$$\frac{\partial C}{\partial t} + \text{div} \left(\frac{u}{R} C \right) = \text{div} \left[\frac{(D + D^*)}{R} \text{grad} C \right] - \lambda C$$

As before, we specify boundary conditions (Dirichlet, Neumann, and Cauchy or source) to define transport problems.

Some analytical solutions of the mass transport equation

The fundamental solution of the 1-D diffusion equation (normal, or Gaussian distribution in space) is used to build analytical solutions of the mass transport equation. The properties of this solution are discussed ($d\sigma_x^2/dt = 2D^* = \text{const.}$, variance $\sigma_x^2 = 2D^*t$; 95% of the mass contained within a spread of $4\sigma_x$ or $\pm 2\sigma_x$, and 99% within $6\sigma_x$ or $\pm 3\sigma_x$).

The fundamental solution is then used as building block in more complex solutions. First is considered the response to an impulse in transport by 1-D advection and dispersion, with or without sorption and with or without decay. The solute's *breakthrough* curve is introduced, and the various transport processes and reactions are presented schematically.

Next, is considered 1-D transport in a semi-infinite aquifer with pore velocity u (also including sorption), when the input is a concentration step (an analytical approximation for the error function is also given). It is shown how the longitudinal (1-D) dispersion coefficient can be estimated from a concentration profile or a breakthrough curve.

Then, solutions for 1-D advection and 2-D and 3-D dispersion are shown for a slug input. These solutions are discussed in some detail; one result of the discussion is that dispersion loses its importance in large scale problems.

Some analytical solutions of the mass transport equation

The transport equation has been used in numerous field-modelling studies, in which the dispersivities of the classical Fickian dispersion model were inferred from tracer observations. But it was noticed that the “fitted” dispersivities increase with the scale of transport (or, with the mean travel distance of the tracer: the *scale* or *time effect*). Field- or *macro-dispersivities* depend on the medium's field-heterogeneity and increase because the fluid's chances of encountering heterogeneities increase with travel (time or distance). Consequently dispersivity may not be considered a *PM-parameter*; since model calibration is based on a snapshot of the plume, model predictions may not be reliable.

To address shortcomings of the established dispersion theory, stochastic theories have been advanced. These accept that a porous medium's hydraulic parameters can be known within certain margins of certainty (by the statistics of their distributions) and estimate mean values and related standard deviations of concentrations in space and time (allowing assessing the reliability of results, or their complement, risk). A key result of the early stochastic work is that the dispersion tensor is time-varying and given by the integral of the covariance of the components of the Lagrangian (mass particle) velocity. Subsequent work linked the time-varying dispersion to the Eulerian velocity field and, via Darcy's law, to the hydraulic conductivity K , the most variable and hence uncertain parameter. Since K passes its randomness onto the flow, and thus onto the macro-dispersivities, the transport must be described on the basis of the K-field's (geo)statistics. The manner in which this can be done is summarised, for $Y = \log K$ normally distributed.

The first-generation stochastic theories of subsurface mass transport, up to ~1990, are outlined. The end-product of these stochastic theories is a transport equation for the *ensemble* concentration $\langle C \rangle$ having the same form as the deterministic one, but different parameters. Advection is by the *mean* flow U and dispersion is scale-dependent, $D_i = UA_i$, with macro-dispersivities A_i (for discrimination from the pore-scale local dispersivities a_i , on the order of 1 cm). The A_i 's vary with the rate of change of the second moment of the plume about its centre of mass.

For 2D transport along the principal axes x and y , with unidirectional flow [macroscopic linear pore velocity $U(x)$], the ensemble transport equation for a non-reactive solute, in the absence of sources/sinks, is a transport equation with space-dependent dispersion coefficients. In the asymptotic regime, the dispersion is Fickian with constant macro-dispersivities (index ∞), $D_{xx} = DL = UA_{L\infty}$ and $D_{yy} = DT_{\infty} = UAT_{\infty}$, thus.

For a statistically isotropic medium, in the asymptotic regime, $A_{L\infty} = \sigma_Y^2 l_Y/\gamma^2$, $A_{T\infty} = A_{L\infty} = \sigma_Y^2 (a_L + 4a_T)/15\gamma^2$ and $\gamma = \exp(\sigma_Y^2/6)$ (assumption $\sigma_Y^2 \ll 1$).

Realising that, in the asymptotic regime, the new transport equations do not differ from the ones developed in section 4.3, it follows that the solution tools applied in the illustrative examples can be used to study schematised, yet real-life problems.

In conclusion, the *multi-scaling fractional* advection-dispersion equation is mentioned as an alternative for highly heterogeneous formations. That equation models non-Fickian dispersion via dispersion terms with fractional derivatives (possibly spatially different). This approach is still in its early stage of development.