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Environmental Quality Management

Wojciech Adamski, Evan Parks

WATER QUALITY MANAGEMENT

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1. INTRODUCTION

Water is one of the most important substances in the environment and necessary for life on Earth. Water also strongly influences climate and has been a limiting resource in the development of civilizations.

Every individual requires water, although it is unrealistic for each person to have their own water source. This is because water reservoirs often have an immense volume and contain pollution from point and non-point sources. Such pollution, which can even stem from natural sources, can be difficult or impossible to remove from within the water body. Thus, water taken from reservoirs must undergo treatment prior to human consumption. Water treatment technology is constantly developing and depends on the kind and intensity of pollution present as well as the amount of water and the quality required by the population. Water treatment technology is specially adapted to the water source and quality; however, the design must be easily modified to adapt to seasonal variations as well as the threat of sudden anthropogenic pollution. Therefore, it is important to accurately predict the composition of intake water.

The goal of this book is to provide the reader with the necessary tools to recognize and evaluate the factors governing the migration and transformation of pollution in the hydrosphere that strongly influence the quality of water bodies. These tools include mathematical modeling to predict variable water quality in rivers, reservoirs, and aquifers.

2. ANALYTICAL METHODS FOR PREDICTING WATER QUALITY

Formulas for modeling water quality are based on kinetics, stoichiometry as well as on mass balances and known physical relationships. When developing models to describe ecosystems, simplifications must be made. Simplifications are necessary due to the overall complexity of ecosystems and the lack of precise information about ecosystem processes, their limiting factors and the interactions between these factors.

However, if the models become too simplified, the predicted values can have a large discrepancy from actual results.

Mathematical modeling in environmental engineering requires the following four steps:

- identifying the relevant and dominating mechanisms in the physical, chemical and biological processes,
- describing the relationships between system processes using mathematical formulas which can take the form of algebraic equations, differential equations or a system of such equations,
- solving analytical or numerical equations or a system of equations,
- verifying the modeled values with results from experiments; in the case when the values do not correspond to the experimental results, it is necessary to adjust or build a new model.

2.1. Stoichiometry and kinetics of reactions in the aquatic environment

Water quality predictions are based in part on the stoichiometry and kinetics of reactions in the aquatic environment. Stoichiometry is related to the conservation of mass and is quantified by the number of moles transported into the system and the number of moles produced in the system. The rate of the reaction can be defined by how quickly the mass of substrate decreases and is transformed into products through the specified stoichiometric relationships.

In the natural environment, reactions can be categorized into two groups: homogeneous and heterogeneous.

Homogeneous reactions occur within only one phase. In the ecosystem, this can be within water, air, or soil. It should be pointed out that the same homogeneous reactions can occur within different phases, but in this case the reactions have different kinetics depending on the phase. Homogeneous reactions may be reversible or irreversible. They can also occur as elementary reactions, several reactions in parallel or as a sequence of reactions (complex reactions) [7, 10, 12].

Heterogenic reactions occur at the interface between phases. Some examples include ion exchange, chemical sorption on the surface of a solid and reactions that are initiated and driven by the presence of catalysts. Heterogenic reactions are more complicated than homogeneous reactions due to the large variation and interaction of possible species [7, 9, 10, 11, 12].

2.1.1. Kinetics and reaction order

The reaction rate (r) is used to describe the disappearance or formation of substances in time. For homogeneous reactions, the units describing the reaction rate are the number or moles or mass of a substance per unit volume multiplied by unit time ($g/m^3 \cdot h$). Unlike homogeneous reactions, the reaction rate of heterogeneous reactions is described by the units number of moles or mass of a substance per unit of surface area multiplied by unit time ($g/m^2 \cdot h$).

When describing the reaction rate in terms of substrates, a negative sign is used to denote their disappearance.

At a constant temperature, the reaction rate is dependent on the concentration of substrate. For reactions of the following type:

$$\mathrm{aA + bB \rightarrow cC + dD} \qquad (2.1)$$

the reaction rate is generally defined as

$$\mathrm{r = k[A]^{\alpha}[B]^{\beta}} \qquad (2.2)$$

in which

k – reaction rate constant,

[A], [B] – molar or mass concentration of substrates,

α, β – experimental reaction coefficients defining the reaction order for the respective reagents.

In general, the reaction order is given by the sum of the experimental reaction coefficients ($\alpha + \beta$.).

Exponents α i β in most cases take the value of 0, 1, or 2; however, they may also take decimal values. Reactions whose rates are defined according to equation (2.2) have the reaction order of α corresponding to substrate A and order β corresponding to substrate B.

Special attention should be given to the fact that the units of the reaction rate constant (k) depend on the order of the reaction. For homogeneous zero order reactions, the reaction rate constant has the units of number of moles or mass of substrate per unit volume multiplied by unit time ($g/m^3 \cdot h$). The reaction rate constant takes the units reciprocal of time (h^{-1}) and volume per mole or mass multiplied by unit time ($m^3/mol\cdot h$) for first and second order reactions, respectively.

When defining the reaction rate, it is important to distinguish between the general reaction rate (r) and the reaction rate corresponding to specific substrates or products. In the case when the stoichiometric coefficients for two substrates are different, the reaction rate expressed for one substrate will differ from the reaction rate of the second substrate. Thus, to avoid confusion, the general reaction rate is defined using the stoichiometric coefficients and the reaction rates corresponding to specific substrates. For the reaction described in equation (2.1), the general reaction rate and the reaction rates corresponding to the substrates and products are defined as

$$r = \frac{r_A}{a} = \frac{r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d} \qquad (2.3)$$

Equation (2.3) shows that the general reaction rate as well as the reaction rate for each substrate or product divided by its stoichiometric coefficient must be equal.

2.1.2. Types of reactions and their reaction rates

The majority of reactions in environmental engineering are irreversible, reversible, saturation-type and autocatalytic. Irreversible reactions are mostly elementary reactions and thus occur in one step as shown in (2.4).

$$aA + bB \rightarrow P \qquad (2.4)$$

The reaction rate of elementary, irreversible reactions are determined by the stoichiometric relationships and the reaction rates corresponding to specific substrates or products as described in section 2.1.1.

Irreversible reactions are characterized as complex and described by a sequence of reactions as in (2.5).

$$aA \xrightarrow{(1)} bB \xrightarrow{(2)} cC \qquad (2.5)$$

For purposes of analysis, the reaction sequence is treated as single elementary reactions as shown in (2.6) and (2.7).

$$aA \xrightarrow{(1)} bB \qquad (2.6)$$

$$bB \xrightarrow{(2)} cC \qquad (2.7)$$

For complex reactions (2.5) the reaction rate is defined as follows:

$$r_1 = \frac{r_A}{a} = \frac{r_{B_1}}{b} \tag{2.8}$$

$$r_2 = \frac{r_{B_2}}{b} = \frac{r_C}{c} \tag{2.9}$$

Thus, the reaction rates corresponding to substrates A and B and product C are given by

$$r_A = ar_1 \tag{2.10}$$

$$r_B = r_{B_1} + r_{B_2} = b\,(r_1 + r_2) \tag{2.11}$$

$$r_C = cr_2 \tag{2.12}$$

If both reactions are first order then

$$r_A = ak_1[A] \tag{2.13}$$

$$r_B = b\,(k_1[A] + k_2[B]) \tag{2.14}$$

$$r_C = ck_2[B] \tag{2.15}$$

The procedure (2.5–2.15) can be used to determine the reaction rate for irreversible, multi-step reactions.

Reversible reactions can be described by the general form:

$$aA \underset{(2)}{\overset{(1)}{\leftrightarrow}} bB \tag{2.16}$$

The rate of species formation in reversible reactions (2.16) can be considered to be the result of two independent reactions (2.17) and (2.18):

$$aA \xrightarrow{(1)} bB \tag{2.17}$$

$$bB \xrightarrow{(2)} aA \tag{2.18}$$

Thus, it is possible to use the same procedure for determining the reaction rate of reversible reactions as for irreversible, multi-step reactions:

$$r_1 = \frac{r_{A_1}}{a} = \frac{r_{B_1}}{b} \tag{2.19}$$

$$r_2 = \frac{r_{B_2}}{b} = \frac{r_{A_2}}{a} \tag{2.20}$$

The reaction rate in terms of A and B is described as

$$r_A = r_{A_1} + r_{A_2} = a(r_1 + r_2) \tag{2.21}$$

$$r_B = r_{B_1} + r_{B_2} = b(r_1 + r_2) \tag{2.22}$$

In the case when both reactions are first order:

$$r_A = ak_1[A] + ak_2[B] \tag{2.23}$$

$$r_B = bk_1[A] + bk_2[B] \tag{2.24}$$

It is important to note that for reversible reactions the stoichiometric coefficients are always positive and their value depends on the overall direction of the reaction.

Saturation type reactions have a maximum reaction rate, i.e. above a certain substrate concentration the reaction rate does not increase. When the reaction described in (2.6) is a saturated type reaction, the function of its reaction rate is given by

$$r = \frac{k\,[A]}{K + [A]} \tag{2.25}$$

It is important to note that the constant of half saturation (K) has the units of concentration and the reaction rate constant (k) has the units number of moles or mass per unit volume multiplied by time. In the case that K<<[A], the function of the reaction rate for saturation type reactions can be described as a zero order reaction $(r = k)$. When A<<[K], the reaction can be considered first order $(r = k[A])$. Figure 2.1 shows the rate of a saturation reaction as a function of the substrate concentration.

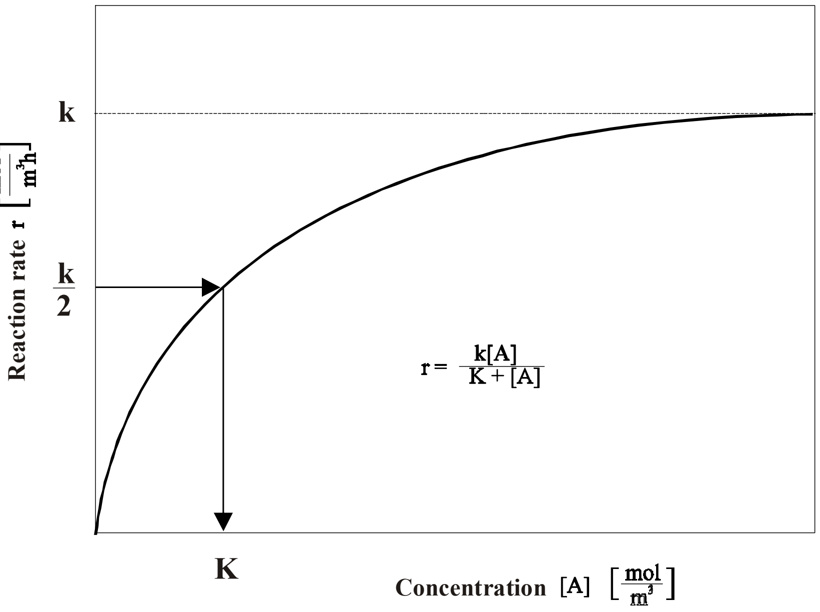


Fig. 2.1. Dependence of reaction rate on substrate concentration for a saturation type reaction.

Often, the reaction rate function for saturation type reactions is much more complicated than shown in (2.25). Two kinds of equations are used for describing saturation type reactions in the environment:

$$r = \frac{k[A][B]}{K + [A]} \tag{2.26}$$

and

$$r = k\left(\frac{[A]}{K_1 + [A]}\right)\left(\frac{[B]}{K_2 + [B]}\right) \tag{2.27}$$

Many reactions occur in which the rate of reaction is a function of the concentration of products. An example of this is the reproduction of bacteria in a system with the speed of population growth proportional to the number of bacteria currently in the system. The increase in the bacteria population is an example of an autocatalytic reaction that can be zero, first or second order or also a saturation type reaction [13].

In the ecosystem, it is common to encounter partly autocatalytic reactions in which the reaction rate is a function of the substrate and product concentrations.

The reaction rate for first order autocatalytic reactions having the form (2.6) is defined as

$$r = k\,[B] \tag{2.28}$$

$$r_A = ak\,[B] \tag{2.29}$$

$$r_B = bk\,[B] \tag{2.30}$$

If the reaction is a second order partly autocatalytic reaction, the reaction rate is defined as

$$r = k\,[A][B] \tag{2.31}$$

$$r_A = ak\,[A][B] \tag{2.32}$$

$$r_B = bk\,[A][B] \tag{2.33}$$

2.1.3. Reaction rate constant dependence on temperature

The reaction rate is most often strongly dependant on the temperature of the system. This dependence of the reaction rate constant on temperature is described by the modified form of the van’t Hoff-Arrhenius equation:

$$k_T = Ae^{-E/RT} \tag{2.34}$$

where

k_T – reaction rate constant at temperature T, units depending on the order of the reaction,

A – van't Hoff-Arrhenius coefficient, units are the same as the reaction rate constant,
E – activation energy [J/mol],
R – ideal gas constant [8.314 J/mol·K],
T – temperature [K].

Since the van't Hoff-Arrhenius coefficient (A) is difficult to determine, the following empirical relationship describing the ratio of reaction rate coefficients at different temperatures is often used:

$$\frac{k_{T_1}}{k_{T_2}} = \exp\left[\left(\frac{E}{RT_1T_2}\right)(T_1 - T_2)\right] \tag{2.35}$$

In aquatic systems in the environment, the temperature generally ranges from 0° to 35°C. In this range, the term $\exp(E/RT_1T_2)$ can be assumed to be the constant θ and thus equation (2.35) is simplified to equation (2.36)

$$k_{T_1} = k_{T_2}\ \theta^{(T_1 - T_2)} \tag{2.36}$$

in which the parameter θ is described as a temperature constant [3] and takes values from 1.016 to 1.038 for systems in the hydrosphere.

2.2. Methods of interpreting experimental results

The goal of laboratory scale experiments and pilot studies is to estimate the value of parameters used to determine reaction rates, their corresponding reaction orders, and also for modeling changes appearing in the natural environment and unit processes in water treatment.

There are many methods used to determine the reaction order. This text explains two methods commonly used: integral and differential [11].

The most straight forward integral method for determining the reaction order is to measure the amount of remaining substrate at different time intervals of the reaction. This data should be presented in integral form and then solved to obtain the reaction rate constant. The reaction order can be determined from the integral or graphically by creating a function from experimental data. The graphical method is generally preferred when analyzing experimental data. Typical experiments for determining the reaction rate and order are conducted in a batch reactor.

For an irreversible reaction:

$$A \rightarrow P \tag{2.37}$$

being a zero order the reaction rate is described by the formula

$$r_A = \frac{d[A]}{dt} = -k \tag{2.38}$$

Separating variables (2.38) and integrating from [A_0] to [A] and from t = 0 to t produces:

$$[A] = [A_0] - kt \tag{2.39}$$

The reaction rate constant can be determined graphically from [A] as a function of time (t).

If the reaction in the batch reactor is first order, irreversible and of the type (2.37) then

$$r_A = \frac{d[A]}{dt} = -k\,[A] \tag{2.40}$$

Separating variables and integrating with the boundary conditions [A_0] to [A] and t = 0 to t gives

$$\ln\left[\frac{A}{A_0}\right] = -kt \tag{2.41}$$

The reaction rate constant is equal to the tangent of the angle described by the function - ln [A/A_0] = f(t).

If the reaction is second order, irreversible and of the type (2.37) then

$$r_A = \frac{d[A]}{dt} = -k[A]^2 \tag{2.42}$$

Separating the variables and integrating with the two boundary conditions [A_0] to [A] and t = 0 to t gives

$$\frac{1}{[A]} - \frac{1}{[A_0]} = kt \tag{2.43}$$

The reaction rate constant is determined from the function [1/A] = f(t).

The reaction rate for first order irreversible parallel reactions of the type

$$\begin{tikzcd} & B \\ A \arrow[ur, "(1)"] \arrow[dr, "(2)"'] & \\ & C \end{tikzcd} \qquad (2.44)$$

is defined according to substrates and products as

$$r_A = \frac{d[A]}{dt} = -(k_1 + k_2)[A] \tag{2.45}$$

$$r_B = \frac{d[B]}{dt} = k_1[A] \tag{2.46}$$

$$r_C = \frac{d[C]}{dt} = k_2[A] \tag{2.47}$$

Solving the integral from (2.45) with the boundary conditions [A_0] to [A] and from t = 0 to t gives

$$\ln\left[\frac{A}{A_0}\right] = -(k_1 + k_2)\,t \tag{2.48}$$

Dividing equation (2.46) by (2.47) gives

$$\frac{r_B}{r_C} = \frac{d[B]}{d[C]} = \frac{k_1}{k_2} \tag{2.49}$$

Separating the variables in (2.49) and integrating from $[B_0]$ to [B] and from $[C_0]$ to [C] produces

$$\frac{[B]-[B_0]}{[C]-[C_0]} = \frac{k_1}{k_2} \tag{2.50}$$

The values of k_1 and k_2 are determined by solving the system of equations (2.48) and (2.50).

Integrating the equation of the reaction rate for saturation-type reactions (2.25) using the limits of integration produces:

$$kt = 2.3K \log\frac{[A_0]}{[A]} + ([A_0]-[A]) \tag{2.51}$$

Transforming the previous equation to the following form

$$\frac{2.3}{t}\log\frac{[A_0]}{[A]} = -\frac{1}{K}\frac{([A_0]-[A])}{t} + \frac{k}{K} \tag{2.52}$$

provides a graphical method of determining the reaction rate constant (k) and the half saturation constant (K) by the following relationship:

$$\frac{2.3}{t}\log\frac{[A_0]}{[A]} = f\left(\frac{([A_0]-[A])}{t}\right) \tag{2.53}$$

The reaction order can be determined by the differential method of analyzing experimental data based on the assumption that the reaction rate is proportional to the n^{th} power of concentration:

$$r_A = \frac{d[A]}{dt} = -k[A]^n \tag{2.54}$$

Two different substrate concentrations for two different reaction times are represented by the following equations:

$$\frac{d[A_1]}{dt} = -k[A_1]^n \tag{2.55}$$

$$\frac{d[A_2]}{dt} = -k[A_2]^n \tag{2.56}$$

Taking the log of both sides of the previous two equations and dividing (2.55) by (2.56) reduces k while solving for the reaction order (n):

$$n = \frac{\log\left(-\frac{d[A_1]}{dt}\right) - \log\left(-\frac{d[A_2]}{dt}\right)}{\log[A_1] - \log[A_2]} \qquad (2.57)$$

2.3. Mass balance

The mass balance, based on the conservation of mass, is a quantitative description of all substances which enter, leave and are generated under defined boundary conditions in a system. The overall mass balance is described by the rate of accumulating mass in a system equaling the rate of mass entering the system minus the rate of mass leaving the system and plus the rate of mass generated in the system [6, 8, 11].

Analyzing the mass balance of substance A in a differential volume element ΔV assuming that the reaction rate of the generating substance A in volume element ΔV is r_A and that dispersion and diffusion of substances are negligible allows the mass balance to be written in the following quantitative form:

$$\frac{\delta C_A}{\delta t}\Delta V = (QC_A)|_X + (QC_A)|_Y + (QC_A)|_Z + \\ - (QC_A)|_{X+\Delta X} - (QC_A)|_{Y+\Delta Y} - (QC_A)|_{Z+\Delta Z} + r_A \Delta V \qquad (2.58)$$

in which

C_A – concentration of substance A [g/m^3],

Q – single-direction volumetric flow [m^3/s],

V – element volume [m^3],

r_A – reaction rate for generating substance A [g/m$^3\cdot$s].

Taking into account three-dimensional flow in the x, y, and z directions produces

$$Q_x = V_x \Delta y \Delta z \qquad (2.59)$$
$$Q_y = V_y \Delta x \Delta z \qquad (2.60)$$
$$Q_z = V_z \Delta x \Delta y \qquad (2.61)$$

in which V_x, V_y, V_z are velocities in their respective directions. Approaching the limits Δx, Δy, Δz equation (2.58) can be transformed into the following form:

$$\frac{\delta C_A}{\delta t} = -\left[\frac{\delta V_x C_A}{\delta x} + \frac{\delta V_Y C_A}{\delta y} + \frac{\delta V_Z C_A}{\delta z}\right] + r_A \qquad (2.62)$$

The rate of generating a substance may take a positive or negative value. In the majority of circumstances encountered in the natural environment (e.g. oxidation) the mass of substances is declining and this is reason that r_A often takes a negative value. For example, in nitrification the ammonium (NH_4^+)

concentration decreases while the nitrate concentration increases. Thus, in this case $r_{NH_4^+}$ is negative while $r_{NO_3^-}$ is positive.

2.3.1. Steady and non-steady state conditions

Mass balances are considered to occur either in a steady state or non-steady state. With steady state or equilibrium conditions, the flow of substances into the system is equal to the outflow. Such systems can occur in water, the atmosphere and even in plants and animals. Steady state conditions indicate that there is no substance accumulation in the system, so:

$$\frac{\delta C_A}{\delta t} = 0 \qquad (2.63)$$

Steady state models can be used in the analysis of global phenomena such as the average retention time of water in the atmosphere, the average retention time of carbon in the biosphere, the amount of natural and anthropogenic SO_2 in the atmosphere, constant pollutant loading in lakes, the cycle of phosphorus in water reservoirs as well as the water cycle in the natural environment.

It is much more difficult to model the class of problems in which parts of the set change in time. In this case, conditions are non-steady state and the rate of accumulation varies in time:

$$\frac{\delta C_A}{\delta t} \neq 0 \qquad (2.64)$$

Non-steady state models can be used in analyzing global phenomena such as the amount of time before the world's oil reserves are exhausted by taking into account the worldwide oil demand, the global extraction of groundwater having specified initial and boundary conditions as well as the increase in pollution in lakes from specified pollution inflows [1, 4, 5].

2.3.2. Using mass balance to determine reaction rate and order

Applying mass balance equations to describe most of the processes in the environment requires information about the generation rate of components in the analyzed system. This is of particular importance in the analysis of water and wastewater treatment processes.

Balance equations can be used to determine the reaction order and rate based on experimental results from a batch reactor. The mass balance equation of substrate A undergoing the reaction of the type:

$$A + B \rightarrow C \qquad (2.65)$$

occurs in a batch reactor as follows:

$$\frac{d[A]}{dt}V = Q[A_0] - Q[A] + r_A V \qquad (2.66)$$

Since the process occurs in a batch reactor, the inflow and outflow components of substrate A in equation (2.66) are zero. Thus, the equation simplifies to the following form:

$$\frac{d[A]}{dt} = r_A \qquad (2.67)$$

The selection of an appropriate reaction rate equation is done using trial and error with the assumed functional dependencies.

Assuming the reaction is first order taking the form of equation (2.40), separating the variables and integrating over the appropriate intervals produces equation (2.41). If the assumed first order reaction model was correct, the value of parameter k calculated from equation (2.41) through several experiments with different substrate concentrations would be constant.

Assuming that the analyzed reaction is second order, the equation for determining its reaction rate can take the following form:

$$r_A = -k[A][B] \qquad (2.68)$$

The stoichiometry of the reaction shows that

$$\Delta[A] = \Delta[B] \qquad (2.69)$$

Thus, the concentration of substrate [B] at any time during the experiment is:

$$[B] = [B_0] - [A_0] + [A] \qquad (2.70)$$

Substituting equation (2.70) for (2.68) yields

$$r_A = \frac{d[A]}{dt} = k[A]\{[B_0] - [A_0] + [A]\} \qquad (2.71)$$

After separating the variables and integrating from $[A_0]$ to [A] and from t = 0 to t the following is obtained

$$dt = \frac{-\,d[A]}{k[A]\{[B_0] - [A_0] + [A]\}} \qquad (2.72)$$

$$\int_0^t dt = -\int_{[A_0]}^{[A]} \frac{d[A]}{k[A]^2 + k([B_0] - [A_0])[A]} \qquad (2.73)$$

$$[A] = \frac{[A_0]([B_0] - [A_o])\exp\{-([B_0] - [A_0])kt\}}{[B_0] - [A_0]\exp\{-([B_0] - [A_0])kt\}} \qquad (2.74)$$

Conducting the experiment with equal initial concentrations of substrate $[B_0] = [A_0]$ equation (2.73) simplifies to the form:

$$\int_{0}^{t} dt = -\int_{[A_0]}^{[A]} \frac{d[A]}{k[A]^2} \qquad (2.75)$$

$$[A] = \frac{[A_0]}{1+[A_0]kt} \qquad (2.76)$$

In the case that the value of k found using equation (2.76) for the individual experiments is constant, the analyzed reaction is then second order.

2.4. Other types of balances

Several different types of balances can be used in analyzing water systems. Mass balances are based on the law of conservation of mass. Thermodynamic balances, based on the laws of conservation of energy and momentum, are also important and applied in analyzing water quality. Energy balances based on internal mechanic and electromagnetic energy are applied in analyzing the movement of water in deep lakes and dammed reservoirs. Momentum balances are used in modeling the complex relationships between wind, waves and water movement. The basic setup of these balances is comparable to the mass balance equation [2].

2.5. Example calculations

EXAMPLE 1

This example shows the process of determining the rate constant and the order of reaction for the transformation of $A \rightarrow B$. This can be done using experimental combined with integral or differential methods. Data collected from testing the reaction kinetics in batch reactors is summarized in the following table. The initial concentration in the experiment is $A_0 = 300$ g/m^3.

Experiment time t [h]	2	4	6	8	10	12	14	16	18	20	22
Concentration of substance A after time t [g/m^3]	200	133.7	89.3	59.6	39.8	26.6	17.7	11.8	7.9	5.3	3.5

– INTEGRAL METHOD

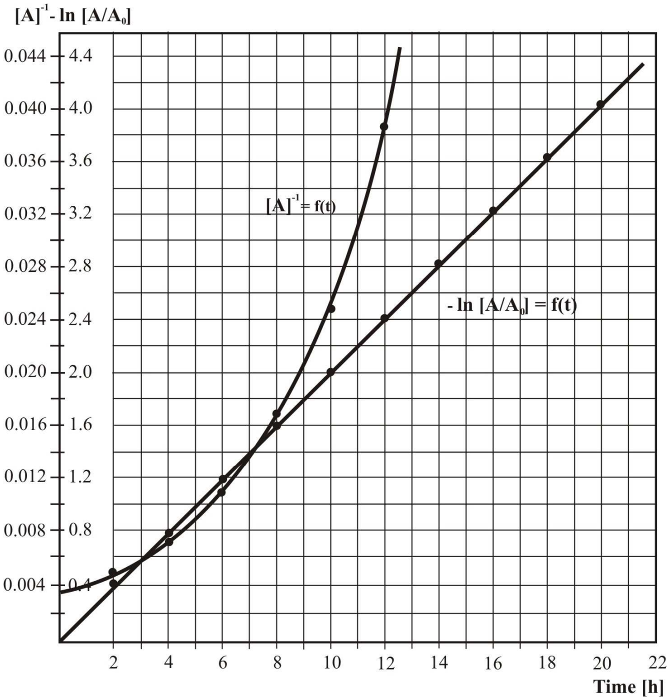
The experimental data was transformed with the goal of obtaining the functional dependence of concentration on time with the assumption that the reaction is first or second order.

Experiment time t [h]	0	2	4	6	8	10	12	14	16	18	20	22
$-\ln [A/A_0]$	0.00	0.405	0.808	1.21	1.616	2.02	2.42	2.83	3.24	3.64	4.04	4.45
$[A]^{-1}$	0.0033	0.005	0.0075	0.0112	0.0168	0.0251	0.0376	0.059	0.0847	0.1266	0.1887	0.2857

The function $-\ln [A/A_0] = f(t)$ is used to verify that the reaction is first order while the function $[A]^{-1} = f(t)$ is used to verify that the reaction is second order.

Since the function $-\ln [A/A_0] = f(t)$ is a linear dependency, the analyzed reaction is first order and the reaction rate constant is equal to the tangent of the angle of the slope:

$$k = \frac{2.02}{10} = 0.202\ \text{h}^{-1}$$



– DIFFERENTIAL METHOD

The reaction order can be determined using differential methods as shown in equation (2.57). Experimental data are used after 4 and 8 hours to determine the reaction order.

Experiment time t [h]	[A] [g/m^3]	$\left(\frac{[A_{t+1}]-[A_{t-1}]}{4}\right)=\frac{d[A_t]}{dt}$
4	133.7	$\left(\frac{89.3-200}{4}\right)=-27.675$
8	59.6	$\left(\frac{39.8-89.3}{4}\right)=-12.37$

Substituting the values from the table into equation (2.57) yields

$$n=\frac{\log\left(\frac{-d[A_1]}{dt}\right)-\log\left(\frac{-d[A_2]}{dt}\right)}{\log[A_1]-\log[A_2]}=\frac{\log(27.675)-\log(12.37)}{\log(133.7)-\log(59.6)}=\frac{1.442-1.092}{2.126-1.775}=1$$

The reaction is first order.

The reaction rate constant is calculated for two experiment times, i.e. after 4 and 8 hours.

$$\frac{d[A]}{dt}=-k[A]$$

For 4 hours:

$$27.675 = -k \cdot 133.7$$
$$k = 0.207\ h^{-1}$$

For 8 hours:

$$12.37 = -k \cdot 59.6$$
$$k = 0.2075\ h^{-1}$$

This example shows that integral and differential methods of determining the reaction order and the rate constant yield, in principle, the same results.

EXAMPLE 2

This example shows how to determine the rate constant and the reaction order for a synthesis reaction of the type $A+B\rightarrow C$. Two tests were conducted to determine the kinetics of the process.

In the first test the initial substrate concentrations were $[A_0]$ = 10 mol/m^3 and $[B_0]$ = 100 mol/m^3 while in the second test they were $[A_0]$ = 10 mol/m^3 and $[B_0]$ = 10 mol/m^3.

The results of the experiments are presented in the following table.

Experiment time t [d]	0.01	0.05	0.1	0.5	1.0	5	10	15	20	25
Concentration of substance A after time t [mol/m^3] TEST 1	9.51	7.8	6.13	0.96	0.10					
Concentration of substance A after time t [mol/m^3] TEST 2				8.0	6.67	2.86	1.67	1.17	0.91	0.74

The mass balance equation of substrate [A] was solved in the following way. Since the experiments were carried out in a batch reactor, there are no inflow nor outflow terms in the mass balance equation. Thus, assuming that the analyzed reaction is first order in terms of substrate [A], the following equation is valid:

$$\frac{d[A]}{dt} = r_A = -k[A]$$

Separating variables, integrating from $[A_0]$ to [A] and from 0 to t and then rewriting the equation in terms of k yields

$$k = -\ln[A/A_0]\, t^{-1}$$

The values of the rate constant from the previous equation are summarized in the following table.

Experiment time t [d]	0.01	0.05	0.1	0.5	1.0	5	10	15	20	25
TEST 1 k [d^{-1}]	5.024	4.97	4.894	4.687	4.605					
TEST 2 k [d^{-1}]				0.446	0.404	0.25	0.179	0.143	0.120	0.104

Since the values of coefficient k are not the same for both experiments and they also vary with time, the assumed first order reaction model is inappropriate for the analyzed reaction.

It is then assumed that the analyzed reaction is second order and its reaction rate can be described by the following equation:

$$r_A = -k[A]\,[B]$$

For the first test in which $[A_0] = 10$ mol/m^3 and $[B_0] = 100$ mol/m^3, the reaction rate constant k can be determined from the transformed form of equation (2.74):

$$k = \frac{\ln\left\{\dfrac{[A_0]([B_0]-[A_0])+[A][A_0]}{[A][B_0]}\right\}}{([B_0]-[A_0])\,t}$$

For the second test in which $[A_0] = [B_0]$ the reaction rate constant k can be determined from the transformed form of equation (2.76):

$$k = \frac{[A_0]-[A]}{[A][A_0]t}$$

The rate constants determined from the previous equations are shown in the following table.

Experiment time t [d]	0.01	0.05	0.1	0.5	1.0	5	10	15	20	25
TEST 1 k [m^3/mol d]	0.05	0.05	0.05	0.05	0.05					
TEST 2 k [m^3/mol d]				0.05	0.05	0.05	0.05	0.05	0.05	0.05

The analyzed reaction is second order having a reaction rate constant of $k = 0.05\ m^3/mol\cdot d$.

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3. MATHEMATICAL MODELING OF PHYSICAL PROCESSES IN THE HYDROSPHERE

The majority of systems in water resources management have adequate flows. Water systems, i.e. lakes, reservoirs, rivers and estuaries along with technological unit processes for water and wastewater treatment generally differ, but with few exceptions they all have a continuous inflow and outflow. For this reason, the mass balance presented in equation (2.58) is applicable to each system.

Two basic hydraulic models are used in the simulation of phenomena in natural systems: complete mixing and plug flow models. Often, these two models are combined to simulate the phenomena occurring in large, complex systems having spatially differentiated characteristics [4, 9].

3.1. Hydraulic models of natural systems

The aim of modeling water quality is to analyze and predict the reaction of systems in response to the interactions of various factors. One important element in this modeling includes the hydraulic characteristics. In this respect, commonly used models have been developed that describe the hydraulic characteristics of reactors in which chemical and biological processes occur.

Five common reactor models are used to simulate changes in water quality [5, 6, 8].

Batch Reactors (BRs) are characterized by the absence of inflow and outflow. Biochemical oxygen demand (BOD) as well as tests to determine the kinetic reaction coefficients, diffusion coefficients and adsorption equilibrium parameters are all carried out in batch reactors. Batch reactors are often used to model shallow lakes where there is no outflow and the water is completely mixed. This type of reactor is also applied in the biological and chemical treatment of wastewater when the amount of sewage is small and the flow is very irregular.

Completely mixed flow reactors (CMFRs) are often called continuous flow mixed reactors in environmental and chemical engineering. In these reactors, the inflow particles are immediately distributed and mixed throughout the entire reactor volume. The particles that leave the reactor as the outflow have a concentration proportional to their statistical population in the reactor. In other words, the outflow concentration is equal to the concentration in the volume of the reactor.

This type of reactor is applied in modeling the quality of water in lakes and reservoirs having continuous inflow and outflow as well as unit processes in water and wastewater treatment.

Plug flow reactors (PFRs) are characterized by particles flowing through the reactor while maintaining the same order as when they entered the reactor. Furthermore, all parts of the solution remain in the reactor for the time equal to the theoretical retention time. Plug flow reactors are used to simulate flow in rivers and their estuaries as well as to model water and wastewater treatment processes.

Cascades of completely mixed flow reactors are applied to model phenomena that correspond to both completely mixed flow and plug flow systems. If the reactor cascade consists of just one reactor, the rules applying to completely mixed flow reactors are valid. On the other hand, the rules applying to plug flow reactors are valid when the number of completely mixed flow reactors in the cascade is infinite.

Packed bed reactors (PBRs) can have properties similar to completely mixed flow reactors or plug flow reactors. Reactors of this type are filled with a medium that does not change during the process. In water quality management, packed bed reactors are used to analyze the movement of water and contaminants (as well as their transformation) in aquifers. When the volume of the pores of the medium is completely filled with solution, the flow is considered to be saturated. If the volume of the pores is only partly filled with solution, the flow is unsaturated.

3.1.1. Completely mixed flow reactor model

A completely mixed flow reactor, as shown in Figure 3.1, does not have a concentration gradient. Upon entering the reactor the inflow solution is instantaneously and uniformly distributed throughout the volume of the reactor. For this reason, the substance concentration in the reactor outflow is exactly the same as the substance concentration found at any point in the reactor volume.

The overall mass balance of substrate A in the reactor inflow is as follows:

$$\frac{dC_A}{dt}V = QC_{A_0} - QC_A + r_A V \qquad (3.1)$$

in which C_{A_0} and C_A are the concentration of substrate A in the inflow and in the reactor, respectively.

If the substrate flowing through the reactor is unreactive, the generation component of the mass balance (3.1) is zero meaning that $r_A = 0$.

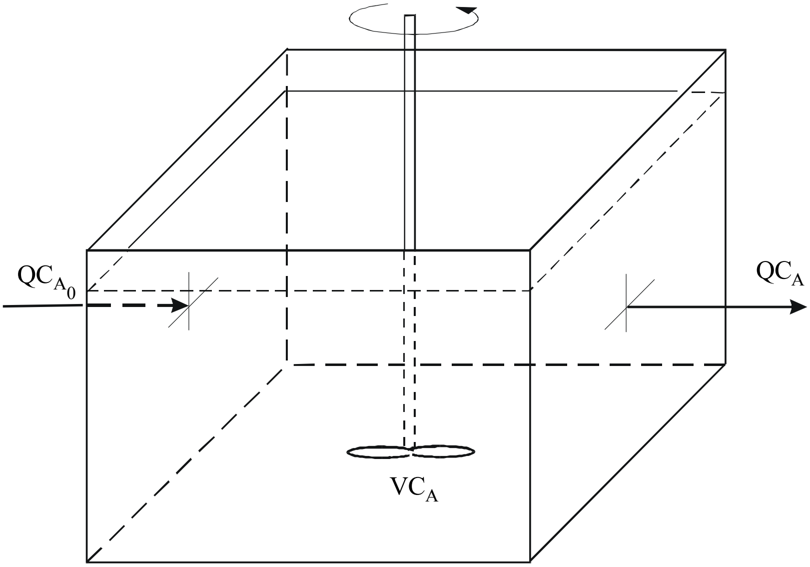

Fig. 3.1. Diagram of a completely mixed flow reactor.

Transforming equation (3.1) and integrating from 0 to C_A and from 0 to t yields

$$\frac{dC_A}{dt} = \frac{Q}{V}\left(C_{A_0} - C_A\right) \tag{3.2}$$

$$\int_0^{C_A} \frac{dC_A}{C_{A_0} - C_A} = \frac{Q}{V}\int_0^t dt \tag{3.3}$$

$$\ln\left(\frac{C_{A_0} - C_A}{C_{A_0}}\right) = -t\left(\frac{Q}{V}\right) \tag{3.4}$$

$$C_A = C_{A_0}\left\{1 - \exp\left[-t\left(\frac{Q}{V}\right)\right]\right\} \tag{3.5}$$

Assuming that the value of $C_{A_0} = 1$, it is possible to plot a function showing the dependence of the relative concentration of substrate A in the reactor in terms of the ratio of process time to the average retention (residence) time (Fig. 3.2).

The average hydraulic retention time T_H, an important parameter in environmental engineering and modeling, is defined as the reactor volume V divided by the reactor flow Q.

The relative concentration of $C_A/C_{A_0} = 0.95$ for the unreactive substrate A is reached after three hydraulic retention times ($t = 3T_H$). In practice, the conditions obtained after three times the average hydraulic retention time are considered satisfactory for approximating steady state conditions ($dC_A/dt = 0$). Thus, new steady state conditions following a sudden change in a completely mixed flow reactor are achieved after three average hydraulic retention times.

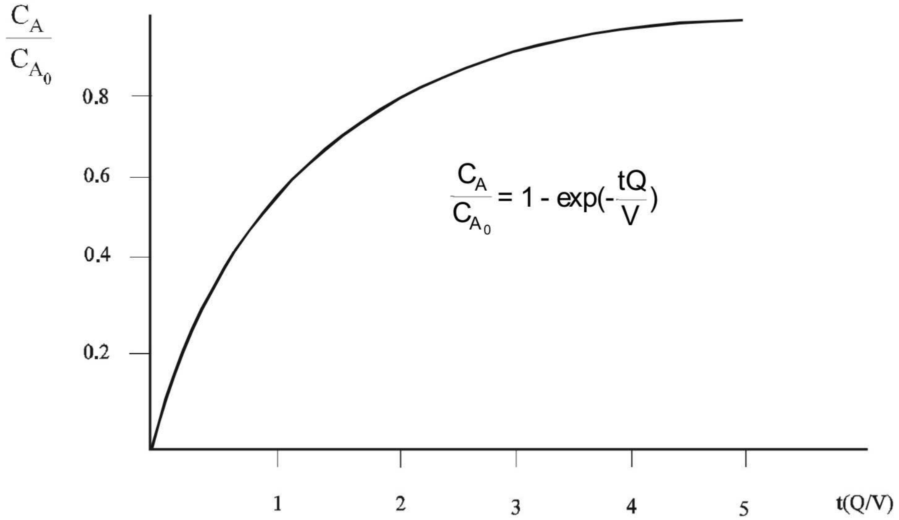

Fig. 3.2. The dependence of the relative concentration of unreactive substrate in a completely mixed flow reactor on the ratio of process time to the average retention time [7].

While equation (3.1) shows the mass balance for an unreactive substance, chemical reactions often occur in reactors adding an additional term in the mass balance. For the case regarding substrate A flowing into a completely mixed flow reactor and undergoing an irreversible, first order reaction of the type (2.37), the mass balance equation can be written in the following form:

$$\frac{dC_A}{dt} = \frac{Q}{V}\left(C_{A_0} - C_A\right) - kC_A \tag{3.6}$$

Separating variables and integrating from 0 to C_A and from 0 to t produces the following equation for determining the concentration of substance A:

$$\int_0^{C_A} \frac{dC_A}{C_{A_0} - C_A\left(1 + kT_H\right)} = \frac{1}{T_H}\int_0^t dt \tag{3.7}$$

$$-\frac{1}{kT_H + 1}\ln\left[\frac{C_{A_0} - \left(1 + kT_H\right)C_A}{C_{A_0}}\right] = \frac{t}{T_H} \tag{3.8}$$

$$C_A = \frac{C_{A_0}\left[1-\exp\left(-\frac{1+kT_H}{T_H}\cdot t\right)\right]}{1+kT_H} \tag{3.9}$$

Since t approaches infinity for steady state conditions, the previous equation can be simplified to the following form:

$$C_A = \frac{C_{A_0}}{1+kT_H} \tag{3.10}$$

Response curves showing the relative concentration of reactive substrate A in the outflow from a completely mixed flow reactor $[C_A/C_{A_0} = f(t/T_H)]$ are given in Figure 3.3 [7]. From the figure, it is evident that a shorter average hydraulic retention time leads to a higher relative concentration of reactive substrate A in the outflow.

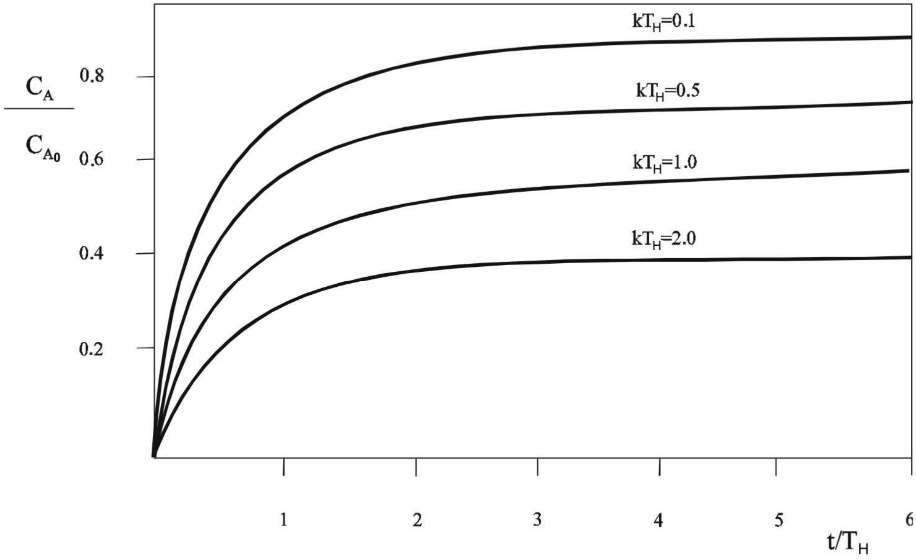

Fig. 3.3. Dependency of the relative concentration of reactive substances in a completely mixed flow reactor on the ratio of reaction time to the average hydraulic retention time [7].

3.1.2. Modeling plug flow reactors

In ideal plug flow reactors, the constituents are assumed to be completely mixed in the transverse direction (perpendicular to flow) and completely unmixed in the longitudinal direction (parallel to flow). Although these ideal conditions for plug flow reactors are unrealistic, they do provide a very good approximation in modeling actual phenomena.

Since mixing in the plug flow reactor does not occur longitudinally, the average hydraulic retention time (T_H) is equal to the real time of retention. For the unreactive substance A, the outflow concentration (C_A) is equal to the inflow concentration (C_{A_0}); however, compared to the inflow concentration the outflow concentration is shifted by the time $T_H = V/Q$.

The volume element (ΔV) of a plug flow reactor used in mass balances is defined as the cross sectional area of the flow (F) multiplied by the element length (Δx) (Fig. 3.4).

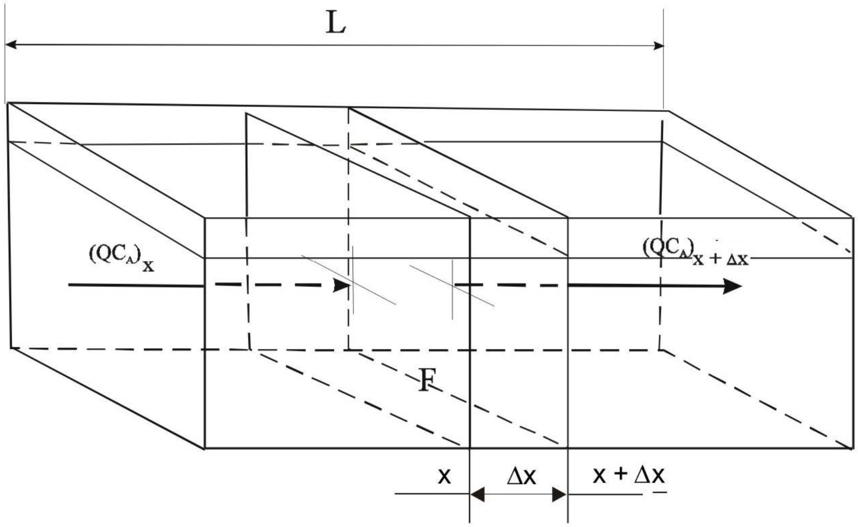

Fig. 3.4. Diagram of a plug flow reactor.

The following equation shows the mass balance of substance A for an irreversible reaction of the type (2.37):

$$\frac{\delta C_A}{\delta t}\Delta V = \left(QC_A\right)\big|_x - \left(QC_A\right)\big|_{x+\Delta x} + r_A\Delta V \tag{3.11}$$

The substance inflow $\left(QC_A\right)\big|_x$ is equivalent to the expression $Q\left(C_A + \frac{\Delta C_A}{\Delta x}\Delta x\right)$.

Introducing this change into the balance equation produces:

$$\frac{\delta C_A}{\delta t}\Delta V = QC_A - Q\left(C_A + \frac{\Delta C_A}{\Delta x}\Delta x\right) + r_A\Delta V \tag{3.12}$$

Using the definition of a differential volume element and dividing the equation by FΔx yields

$$\frac{\delta C_A}{\delta t} = -\frac{Q}{F}\frac{\Delta C_A}{\Delta x} + r_A \qquad (3.13)$$

As Δx approaches zero:

$$\frac{\delta C_A}{\delta t} = -\frac{Q}{F}\frac{\delta C_A}{\delta x} + r_A \qquad (3.14)$$

Since the volumetric flow (Q) is roughly constant, the following transformation can be performed:

$$\frac{Q}{F}\frac{\delta C_A}{\delta x} = \frac{\delta C_A}{\frac{F\delta x}{Q}} = \frac{\delta C_A}{\delta T_H} \qquad (3.15)$$

Using this substitution in equation (3.14) produces

$$\frac{\delta C_A}{\delta t} = -\frac{\delta C_A}{\delta T_H} + r_A \qquad (3.16)$$

Under steady state conditions, meaning that there is no accumulation in the reactor ($\delta C_A/\delta t = 0$), the previous equation takes the following form:

$$\frac{\delta C_A}{\delta T_H} = r_A \qquad (3.17)$$

This equation has the same form as the equation derived from the mass balance to determine the order of reaction (2.67).
It is important to note that although these two equations are similar, equation (2.67) presents the dependence of the accumulation rate dC_A/dt on the reaction rate while equation (3.17) presents the dependence of the longitudinal concentration gradient dC_A/dT_H on the reaction rate.

Under steady state conditions, first order reactions in plug flow reactors can be written in the following form:

$$\frac{\delta C_A}{\delta T_H} = -kC_A \qquad (3.18)$$

The solution of the previous equation gives the concentration in the outflow (effluent) of the reactor as a function of the retention time. Separating variables and integrating from C_{A_0} to C_A and from 0 to T_H produces

$$C_A = C_{A_0}\exp(-kT_H) \qquad (3.19)$$

3.1.3. Reactor comparison

A comparison under steady state conditions between completely mixed flow reactors and plug flow reactors can be made based on the hydraulic retention time (T_H) required to achieve a desired outflow concentration from the reactors. For this reason, the equations previously derived describing completely mixed flow reactors and plug flow reactors have been rewritten in terms of T_H.

For first order reactions in completely mixed flow reactors equation (3.10) can be rewritten as

$$T_H = \frac{1}{k}\left(\frac{C_{A_0}}{C_A} - 1\right) \tag{3.20}$$

For the same reaction but in a plug flow reactor the retention time is

$$T_H = \frac{1}{k}\ln\frac{C_{A_0}}{C_A} \tag{3.21}$$

The steady state mass balance can be rewritten as follows to determine the necessary retention time in a completely mixed flow reactor for obtaining the required outflow concentration of a substance undergoing a second order reaction:

$$0 = QC_{A_0} - QC_A + \left(-kC_A^2\right)V \tag{3.22}$$

$$C_{A_0} - C_A = kC_A^2 T_H \tag{3.23}$$

$$T_H = \frac{C_{A_0} - C_A}{kC_A^2} \tag{3.24}$$

Equation (3.17) can be rewritten in terms of the retention time in a plug flow reactor of a substance undergoing a second order reaction:

$$\frac{dC_A}{dT_H} = -kC_A^2 \tag{3.25}$$

$$\int_{C_{A_0}}^{C_A} \frac{dC_A}{C_A^2} = -k\int_0^{T_H} dT_H \tag{3.26}$$

$$T_H = \frac{C_{A_0} - C_A}{kC_A C_{A_0}} \tag{3.27}$$

The retention time for a substance undergoing a saturation type reaction in a completely mixed flow reactor as determined from the mass balance equation takes the following form:

$$0 = QC_{A_0} - QC_A - \frac{kC_A}{K + C_A}V \tag{3.28}$$

$$C_{A_0} - C_A = \frac{kC_A}{K + C_A} T_H \qquad (3.29)$$

$$T_H = \frac{\left(C_{A_0} - C_A\right)\left(K + C_A\right)}{kC_A} \qquad (3.30)$$

For the same saturation reaction in a plug flow reactor, the retention time in equation (3.17) can be written as

$$\frac{dC_A}{dT_H} = -\frac{kC_A}{K + C_A} \qquad (3.31)$$

$$\int_{C_{A_0}}^{C_A} \frac{K + C_A}{kC_A} dC_A = -\int_0^{T_H} dT_H \qquad (3.32)$$

$$T_H = \frac{1}{k}\left[K \ln\frac{C_{A_0}}{C_A} + C_{A_0} - C_A\right] \qquad (3.33)$$

For a first order reaction, the ratio of the retention time in a completely mixed flow reactor (T_{H_w}) to the retention time in a plug flow reactor (T_{H_T}) for obtaining the same outflow concentration can be written as

$$\frac{T_{H_w}}{T_{H_T}} = \frac{\frac{C_{A_0}}{C_A} - 1}{\ln\frac{C_{A_0}}{C_A}} \qquad (3.34)$$

The same ratio for a second order reaction can be written as

$$\frac{T_{H_w}}{T_{H_T}} = \frac{C_{A_0}}{C_A} \qquad (3.35)$$

For a saturation reaction, the relationship between the retention times of a completely mixed flow reactor and a plug flow reactor is described by

$$\frac{T_{H_w}}{T_{H_T}} = \frac{\left(1 - \frac{C_A}{C_{A_0}}\right)\left(\frac{K}{C_{A_0}} - \frac{C_A}{C_{A_0}}\right)}{\frac{C_A}{C_{A_0}}\left[\frac{K}{C_{A_0}} \ln\frac{C_{A_0}}{C_A} + 1 - \frac{C_A}{C_{A_0}}\right]} \qquad (3.36)$$

In comparing reactors for saturation reactions, the initial substance concentration (C_{A_0}) and the half saturation constant (K) must be known.

For the purposes of this analysis, $C_{A_0} = 10\ g/m^3$, $K = 1.0\ g/m^3$.

A comparative analysis of retention times for first order, second order and saturation reactions for different relative effluent concentrations from the reactors are presented in Table 3.1

Table 3.1. A comparison of the relative retention times in completely mixed flow reactors and plug flow reactors for first order, second order and saturation reactions depending on the reactor outflow concentration [7].

C_A/C_{A_0}	T_{H_w}/T_{H_T}		
	First order reaction	Second order reaction	Saturation reaction
0.1	3.90	10.00	1.59
0.2	2.48	5.00	1.25
0.3	1.94	3.33	1.14
0.4	1.63	2.50	1.08
0.5	1.44	2.00	1.05
0.6	1.30	1.67	1.03
0.7	1.20	1.43	1.02
0.8	1.12	1.25	1.01
0.9	1.05	1.11	1.00

This analysis shows that for all three reaction types, first order, second order and saturation, the most effective reactor is the plug flow reactor. This is due to the fact that the average reaction rate in the plug flow reactor is greater than in the completely mixed flow reactor. The largest reaction rate occurs at the beginning of the plug flow reactor where the maximum substrate concentration (C_{A_0}) is located while the smallest reaction rate occurs at the end of the plug flow reactor where the substrate concentration (C_A) is the lowest.

In completely mixed flow reactors the substrate concentration is identical at all points in the reactor as well as equal to the reactor outflow (C_A). Thus, in order to obtain the same effluent concentration from both types of reactors for the same reaction, the reaction rate in the completely mixed flow reactor must be equal to the lowest reaction rate in the plug flow reactor.

Using several completely mixed flow reactors in a cascade increases the efficiency of the entire system. Under steady state conditions ($dC_A/dt = 0$) and with a first order reaction, a cascade composed of n completely mixed flow reactors having identical dimensions is described by the following relationship:

$$\frac{C_A}{C_{A_0}} = \frac{1}{(1 + kT_H)^n} \tag{3.37}$$

The retention time in a single completely mixed flow reactor, part of a cascade of n reactors, is described by

$$T_H = \frac{1}{k}\left[\left(\frac{C_{A_0}}{C_A}\right)^{1/n} - 1\right] \tag{3.38}$$

while the total retention time in the cascade of n reactors is given by

$$T_{H_C} = \frac{n}{k}\left[\left(\frac{C_{A_0}}{C_A}\right)^{1/n} - 1\right] \tag{3.39}$$

The hydraulic retention time in a single completely mixed flow reactor for achieving 90% removal of substance A is

$$T_H = \frac{9}{k} \tag{3.40}$$

The same removal of substance A from a cascade of three completely mixed flow reactors is obtained after the following retention time:

$$T_H = \frac{3.46}{k} \tag{3.41}$$

The hydraulic retention time in a plug flow reactor (3.21) required to achieve 90% removal of substance A is given by

$$T_H = \frac{2.3}{k} \tag{3.42}$$

Using a cascade of reactors can be advantageous. For example, applying three completely mixed flow reactors in a cascade achieves the same effluent concentration as a single reactor while using 2.6 times less total volume. The total volume of the cascade of three completely mixed flow reactors is only 1.5 times greater than the volume of the plug flow reactor, which achieves a 90% reduction in concentration. This is in contrast to a single completely mixed flow reactor requiring a 3.9 times greater volume to achieve the same results [3, 7].

3.2. Disturbed flow models

The majority of natural hydraulic systems differ significantly from the idealized conditions of completely mixed flow reactors and plug flow reactors. Deviations from these idealized models include dispersion caused by longitudinal and transverse turbulence and molecular diffusion. Other factors causing discrepancies between the idealized models and real situations include the presence of a ‘dead’ volume in which there is little or no flow, the presence of a ‘short circuit’ that occurs mostly in systems using the completely mixed flow reactor model and the density stratification of liquid in tanks and reservoirs. These types of variations from the idealized models nearly always occur and are especially evident at the confluence of water bodies such as for estuaries and the intersection of rivers.

Small differences in the flux density between different points may be the result of differences in temperature causing independent mass flux. Also, dead volume often occurring in the bottom of reactors below the inflow and outflow streams will shorten the effective retention time.

A similar effect occurs from the ‘short circuit’ phenomenon that is caused by the formation of independent streams within the system due to density stratification [3].

3.2.1. Flow with dispersion

Dispersion or hydrodynamic diffusion is often represented as a function of the concentration gradient

$$N_A = -D_h \frac{\delta C_A}{\delta x} \tag{3.43}$$

in which N_A is the mass of substance A flowing through the unit area in direction x [g/m^{2}s] and D_h is the dispersion coefficient in direction x [m^2/s].

When considering the one dimensional dispersion model (Fig. 3.5) it is important to realize that this is a simplification because dispersion is in fact three dimensional.

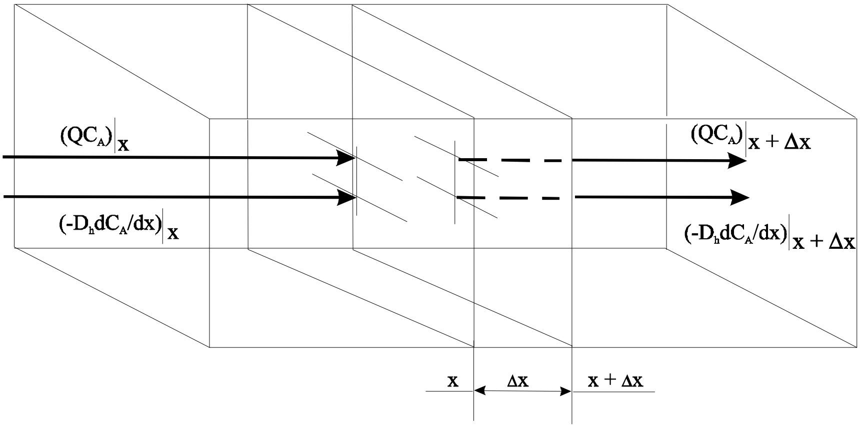

Fig. 3.5. Diagram for analyzing a plug flow reactor with dispersion.

The one dimensional mass balance taking dispersion into account is as follows:

$$\frac{\delta C_A}{\delta t} F\Delta x = \left(V_p F C_A - F D_h \frac{\delta C_A}{\delta x} \right)\Bigg|_x + \\ -\left(V_p F C_A - F D_h \frac{\delta C_A}{\delta x} \right)\Bigg|_{x+\Delta x} + r_A F \Delta x \tag{3.44}$$

In the previous equation, V_p is the average flow rate [m/s]. If Δx approaches zero the previous equation takes the following form:

$$\frac{\delta C_A}{\delta t} = D_h \frac{\delta^2 C_A}{\delta x^2} - V_p \frac{\delta C_A}{\delta x} + r_A \tag{3.45}$$

Since the hydraulic retention time ∂T_H in a plug flow reactor is defined as δx/Vp, equation (3.45) can be rewritten in the following form:

$$\frac{\delta C_A}{\delta t} = D_h \frac{\delta^2 C_A}{\delta x^2} - \frac{\delta C_A}{\delta T_H} + r_A \tag{3.46}$$

For unreactive substances, the equation can be further simplified to the following form:

$$\frac{\delta C_A}{\delta t} = D_h \frac{\delta^2 C_A}{\delta x^2} - \frac{\delta C_A}{\delta T_H} \tag{3.47}$$

For small values of the dispersion coefficient with a unit impulse into the system, a symmetrical concentration output curve is produced and defined by the following equation:

$$C_w = \frac{1}{2\sqrt{\pi\left(\frac{D_h}{V_p L}\right)}} \exp\left[-\frac{\left(1-\frac{t}{T_H}\right)^2}{4\left(\frac{D_h}{V_p L}\right)}\right] \tag{3.48}$$

A unit impulse is defined as the amount of a substance in an element having a width of $\Delta x \rightarrow 0$ and an area equal 1.0.

In equation (3.48) C_w is the dimensionless concentration of the substance in the effluent relative to the unit impulse inflow concentration, L is the characteristic length defined as the distance between the entrance to the system and the measurement point, t is the time from the impulse entry to the system to the time of measurement and T_H is the average hydraulic retention time [2, 7].

For cases in which the dispersion is large, equation (3.47) can be used and rewritten by applying the appropriate initial and boundary conditions:

$$C_w = \frac{1}{2\sqrt{\pi\left(\frac{t}{T_H}\right)\left(\frac{D_h}{V_p L}\right)}} \exp\left[-\frac{\left(1-\frac{t}{T_H}\right)^2}{4\left(\frac{t}{T_H}\right)\left(\frac{D_h}{V_p L}\right)}\right] \tag{3.49}$$

Estimating dispersion is difficult and in practical situations when solving the balance equation the degree of dispersion is considered to be small when

$$\frac{D_h}{V_p \cdot L} < 0.025 \tag{3.50}$$

and dispersion is considered to be large when

$$\frac{D_h}{V_p \cdot L} > 0.2 \tag{3.51}$$

Estimating the value of the dispersion coefficient (D_h) in natural water systems is done through complicated and expensive experiments. Empirical formulas in literature give a rough approximation with the majority of the formulas giving the dispersion coefficient as a function of the Reynold’s number (Re) [9]:

$$D_h = 10^{-6} Re^{0.875} \quad [m^2/s] \tag{3.52}$$

Typical open channel flow is characterized by a Reynold’s number in the range of $10^4 - 10^5$ with the corresponding values of the dispersion coefficient being between $D_h = 0.00316$ m^2/s and $D_h = 0.0237$ m^2/s.

3.2.2. Flow with a reaction and dispersion

The solution of equation (3.46) under steady state conditions and with the first order reaction of substrate A is given by the Wehner-Wilhelm equation [9].

$$\frac{C_A}{C_{A_0}} = \frac{4a\exp\left(\frac{V_p \cdot L}{2D_h}\right)}{(1+a)^2\exp\left(\frac{aV_p \cdot L}{2D_h}\right) - (1-a)^2\exp\left(-\frac{aV_p \cdot L}{2D_h}\right)} \tag{3.53}$$

in which

$$a = \left[1 + 4kT_H\left(\frac{D_h}{V_p \cdot L}\right)\right]^{1/2} \tag{3.54}$$

The analysis of equation (3.53) shows that in systems with a first order reaction for flows with minimal dispersion $D_h/V_p.L \rightarrow 0$ approaching the ideal conditions of the plug flow reactor, low values of the relative outflow concentration are obtained relative to the high values of the product of k and T_H (kT_H). An increase in the degree of dispersion in a completely mixed flow reactor $D_h/V_p \cdot L \rightarrow \infty$ for the particular product of kT_H increases the relative outflow concentration. Values of the relative outflow concentration (C_A/C_{A_0}) as a function of several selected degrees of dispersion $D_h/V_p \cdot L$ and products kT_H are presented in Table 3.2.
The majority of natural systems including biological processes are characterized by very low values of kT_H, much smaller than one. This greatly reduces the possibilities of applying the Wehner-Wilhelm equation.

3.2.3. Multiparameter models

Taking into account factors causing deviations from the ideal flow models in addition to dispersion and diffusion requires the application of multiparameter models. Most multiparameter models are based on different configurations of completely mixed flow reactors and plug flow reactors.

Table 3.2. Relative outflow concentration dependent on the degree of dispersion and the product of the reaction rate coefficient and the retention time [7].

kT_H	C_A/C_{A_0}			
	Degree of dispersion			
	$D_h/V_p \cdot L \to 0$	$D_h/V_p \cdot L = 0{,}1$	$D_h/V_p \cdot L = 1{,}0$	$D_h/V_p \cdot L \to \infty$
0.5	0.60	0.62	0.65	0.80
1.0	0.37	0.42	0.47	0.53
1.5	0.22	0.29	0.35	0.40
2.0	0.14	0.19	0.28	0.34
3.0	0.05	0.09	0.20	0.25
3.5	0.03	0.07	0.16	0.22
4.0	0.02	0.04	0.14	0.20

For simulating a dead volume located in a plug flow reactor, plug flow reactor with dispersion and plug flow with dispersion and a reaction, a part of the flow is taken out of the plug flow reactor and bypassed through a completely mixed flow reactor and later returned to the plug flow reactor. The dead volume in a completely mixed flow reactor can be simulated in a similar way by using a bypass through a second completely mixed flow reactor having a much longer retention time [7].

Systems consisting of a series of plug flow and completely mixed flow reactors in various configurations can be used to simulate the effects of local turbulence and mixing in the system. For example, plug flow reactors with recirculation can simulate the effects of secondary induced currents of back-mixing (reverse jet).

In the case that the system includes recirculation (α) and the reaction order is greater than zero, the initial reaction rate is less than in the system without recirculation because the new inflow concentration $C^*_{A_0}$ is less than C_{A_0}.

$$C^*_{A_0} = \frac{C_{A_0} + C_A}{1+\alpha} \tag{3.55}$$

The relative effluent concentration from a plug flow reactor with a first order reaction as described in equation (3.19) can be modified as follows to account for recirculation:

$$\frac{C_A}{C^*_{A_0}} = \exp\left(-kT^*_H\right) \tag{3.56}$$

in which T_H^* is the retention time in a system with recirculation described by the following equation:

$$T_H^* = \frac{T_H}{1+\alpha} \qquad (3.57)$$

Thus, the relative outflow concentration from the system with a first order reaction having the degree of recirculation α is described by

$$\frac{C_A}{C_{A_0}} = \frac{\exp\left[-\frac{kT_H}{1+\alpha}\right]}{1+\alpha\left[1-\exp\left(-\frac{kT_H}{1+\alpha}\right)\right]} \qquad (3.58)$$

The previous analysis shows that increasing the degree of recirculation α reduces the reactor efficiency.

3.3. Systems with heterogeneous reactions

This chapter has thus far discussed only homogenous reactions, i.e. reactions occurring in only one phase in which the reaction potential was the same at all points.

Most of the main reactions in the natural environment occur in well defined locations. Examples of heterogeneous reactions include the oxygen uptake by benthic organisms and the sorption of dissolved organic compounds on active surfaces. Heterogeneous reactions can also be first order, second order or saturation reactions. Reaction rates are expressed in units of reacted mass per unit area and unit time compared to unit volume as is the case for homogeneous reactions.

Mechanisms for transporting reagent to the reaction location play an important role and are factors controlling and limiting the character of heterogeneous reactions [1].

There are two general variants in heterogeneous reactions. The first is when the reaction rate is less than the transport rate meaning the reaction rate is the limiting factor while the second occurs when the rate of transport is less than the reaction rate for which the transport rate is the limiting factor. In the first case, there is an increase in the reagent concentration at the phase separation border and a decrease in the concentration gradient. In the second case, the concentration decreases in the boundary layer and thus the concentration gradient increases. In the example of oxygen uptake by benthic organisms, both types of heterogeneous reactions are present and the limiting factors include not only the rate of oxygen transport to the water – benthos interface, but also the diffusion rate of oxygen through the air – water interface.

In the example of adsorption of organic compounds on the surface of porous medium, the second variant is dominant meaning that the limiting factor is the transport rate of the reagent to the solution – solid (adsorbent) interface. As a result, adsorbents are materials with a dense microporous structure promoting internal diffusion. The internal diffusion is a function of molecular diffusion and average pore size with average molecular diffusion values for typical adsorption systems on the order of $10^{-8} – 10^{-9}$ m^2/s. Actual adsorption is always slower than fundamental adsorption or the localization of particle sorption sites which occurs essentially instantaneously.

Inhibition occurs frequently in heterogeneous reactions with three kinds of inhibition most commonly encountered in the natural environment.

– Competitive inhibition occurs when the inhibitor molecules locate in the active sites preventing the reacting particles from locating there.

– Noncompetitive inhibition occurs when the inhibitor molecules are absorbed in positions blocking the reacting particles from reaching the active sites.

– The third type of inhibition occurs when adsorbed inhibitor particles alter the structure of active sites making them inaccessible to the reacting particles.

Many heterogeneous reactions are in fact catalytic reactions and the irreversible inhibition of the system (elimination of the reaction from the system) can be caused by catalyst poisoning.

Some reactions such as *de facto* heterogeneous can be analyzed as homogenous systems. Reactions of this type are referred to as pseudo homogeneous [5].

3.4. Example calculations

EXAMPLE 1

The process of removing dissolved organic carbon (DOC) from water is carried out in a completely mixed flow reactor. The reaction for removing DOC is a saturation reaction with a reaction rate described by the equation (2.25):

$$r_{DOC} = -\frac{k\,[DOC]}{K + [DOC]}$$

The reaction rate constant k = 0,3 $g/m^3 \cdot s$, the half saturation constant K = 5 g/m^3 and volumetric flow Q = 0.5 m^3/s are used to determine the necessary reactor volume for reducing the initial concentration value of $[DOC_0] = 20\ g/m^3$ to $[DOC] = 2\ g/m^3$.

The mass balance equation for the analysing the reactor takes the following form:

$$\frac{d[DOC]}{dt} V_r = Q[DOC_0] - Q[DOC] + \left(-\frac{k\,[DOC]}{K + [DOC]} \right) V_r$$

For steady state conditions the mass balance equation simplifies to the following form:

$$Q[DOC_0] - Q[DOC] = \frac{k\,[DOC]}{K + [DOC]} V_r$$

Thus, the required reactor volume is determined from the following equation:

$$V_r = \frac{Q([DOC_0] - [DOC])}{k\,[DOC]} (K + [DOC])$$

and its value is

$$V_r = \frac{0.5\,(20 - 2)}{0.3 \cdot 2} (5 + 2) = 105\ m^3$$

EXAMPLE 2

Using the input data from example 1, determine the necessary volume of the plug flow reactor in which a saturation reaction occurs yielding a reduction from the initial DOC value of 20 g/m^3 to 2 g/m^3.

The applicable mass balance equation of a plug flow reactor (3.16):

$$\frac{\partial[\mathrm{DOC}]}{\partial t}=-\frac{\partial[\mathrm{DOC}]}{\partial T_H}+\left(-\frac{k\,[\mathrm{DOC}]}{K+[\mathrm{DOC}]}\right)$$

Under steady state conditions this equation simplifies to the following form:

$$\frac{d[\mathrm{DOC}]}{dT_H}=-\frac{k\,[\mathrm{DOC}]}{K+[\mathrm{DOC}]}$$

Separating variables and integrating from [DOC_0] to [DOC] and from 0 to T_H yields an equation for the required hydraulic retention time (3.33).
Substituting $T_H = V_r/Q$ gives

$$V_r=\frac{Q}{k}\left[K\ln\frac{[\mathrm{DOC}_0]}{[\mathrm{DOC}]}+[\mathrm{DOC}_0]-[\mathrm{DOC}]\right]$$

Thus, the required volume of the plug flow reactor is

$$V_r=\frac{0.5}{0.3}\left[5\ln\frac{20}{2}+20-2\right]=49.2\ \mathrm{m}^3$$

EXAMPLE 3

A saturated reaction occurs in a cascade of three completely mixed flow reactors of the same volume. Using the input data from examples 1 and 2, determine the outflow concentration from the cascade of reactors when the total sum of reactor volume is equal to the volume of a plug flow reactor whose dissolved organic carbon outflow concentration is [DOC] = 2 g/m^3. The mass balance for the first reactor under steady state conditions takes the following form:

$$Q[\mathrm{DOC}_1]+\frac{k\,[\mathrm{DOC}_1]}{K+[\mathrm{DOC}_1]}V_{r_1}=Q[\mathrm{DOC}_0]$$

Thus, the outflow concentration from the first reactor is described by the following formula:

$$[\mathrm{DOC}_1]=\sqrt{0.25\left(K+kT_{H1}-[\mathrm{DOC}_0]\right)^2+K\,[\mathrm{DOC}_0]}-0.5\left(K+kT_{H1}-[\mathrm{DOC}_0]\right)$$

The value of the hydraulic retention time for a single reactor is

$$T_{H_1}=\frac{49.2}{3}/\,0.5=32.8\ \mathrm{s}$$

The outflow concentration from the first reactor is

$$[\mathrm{DOC}_1]=\sqrt{0.25\left(5+0.3\cdot 32.8-20\right)^2+5\cdot 20}-0.5\left(5+0.3\cdot 32.8-20\right)=12.9\ \mathrm{g/m^3}$$

The outflow concentration from the second reactor is

$$[\mathrm{DOC}_2]=\sqrt{0.25\left(\mathrm{K}+\mathrm{kT}_{\mathrm{H1}}-[\mathrm{DOC}_1]\right)^2+\mathrm{K}\,[\mathrm{DOC}_1]}-0.5\left(\mathrm{K}+\mathrm{kT}_{\mathrm{H1}}-[\mathrm{DOC}_1]\right)$$

$$[\mathrm{DOC}_2]=\sqrt{0.25\,(5+0.3\cdot 32.8-12.9)^2+5\cdot 12.9}-0.5\,(5+0.3\cdot 32.8-12.9)=7.12\ \mathrm{g/m^3}$$

The outflow concentration from the third reactor is

$$[\mathrm{DOC}_3]=\sqrt{0.25\left(\mathrm{K}+\mathrm{kT}_{\mathrm{H1}}-[\mathrm{DOC}_2]\right)^2+\mathrm{K}\,[\mathrm{DOC}_2]}-0.5\left(\mathrm{K}+\mathrm{kT}_{\mathrm{H1}}-[\mathrm{DOC}_2]\right)$$

$$[\mathrm{DOC}_3]=\sqrt{0.25\,(5+0.3\cdot 32.8-7.12)^2+5\cdot 7.12}-0.5\,(5+0.3\cdot 32.8-7.12)=3.24\ \mathrm{g/m^3}$$

Notably, the outflow concentration from a single completely mixed flow reactor with a volume equal to the sum of the three reactors in the cascade (retention time $T_H = 49.2/0.5 = 98.4$ s) is as follows:

$$[\mathrm{DOC}]=\sqrt{0.25\,(5+0.3\cdot 98.4-20)^2+5\cdot 20}-0.5\,(5+0.3\cdot 98.4-20)=5.1\ \mathrm{g/m^3}$$

EXAMPLE 4

The reaction type $A \rightarrow B$ occurs under steady state conditions in a single series of completely mixed flow reactor having a volume of $V_{r_W} = 500\ \mathrm{m}^3$ and plug flow reactor with a volume of $V_{r_T} = 200\ \mathrm{m}^3$.

Compare the results of the following two sequences:

- plug flow reactor – completely mixed flow reactor,
- completely mixed flow reactor – plug flow reactor.

Conduct this comparison for a first order reaction:

$$r_A = -\,10^{-4}\,[A] \quad [\mathrm{g/m^3 \cdot s}]$$

and for a second order reaction:

$$r_A = -\,10^{-4}\,[A]^2 \quad [\mathrm{g/m^3 \cdot s}]$$

The initial concentration is $[A_0] = 25\ \mathrm{g/m^3}$ with a volumetric flow rate of $Q = 0.05\ \mathrm{m^3/s}$.

The outflow concentration for a first order reaction occurring in a plug flow reactor is given by equation (3.19):

$$[A]=[A_0]\exp(-kT_H)$$

The outflow concentration for a first order reaction occurring in a completely mixed flow reactor is given by equation (3.10):

$$[A]=\frac{[A_0]}{1+kT_H}$$

Thus, the results of the process in the first sequence of reactors are as follows:

$$[A]_T = 25 \exp\left(-10^{-4}\frac{200}{0.05}\right)=16.76\ \mathrm{g/m^3}$$

$$[A]_W = \frac{16.76}{1+10^{-4}\cdot\frac{500}{0.05}}=8.38\ \mathrm{g/m^3}$$

The results of the process in the second sequence of reactors are as follows:

$$[A]_W = \frac{25}{1+10^{-4}\cdot\frac{500}{0.05}}=12.5\ \mathrm{g/m^3}$$

$$[A]_T = 12.5 \exp\left(-10^{-4}\frac{200}{0.05}\right)=8.38\ \mathrm{g/m^3}$$

The reactor sequence does not have an influence on the process for the first order reaction, which achieved a reduction of 66.5% from the initial concentration.

The outflow concentration for a second order reaction occurring in a plug flow reactor can be determined by transforming equation (3.27):

$$[A]=\frac{[A_0]}{1+kT_H[A_0]}$$

and the outflow concentration for a second order reaction occurring in a completely mixed flow reactor can be determined by transforming equation (3.24):

$$[A]=\frac{\sqrt{4kT_H[A_0]+1}\ -1}{2kT_H}$$

The first reactor sequence for the second order reaction produces the following result:

$$[A]_T = \frac{25}{1+10^{-4}\,\frac{200}{0.05}\cdot 25}=2.27\ \mathrm{g/m^3}$$

$$[A]_W = \frac{\sqrt{4 \cdot 10^{-4} \frac{500}{0.05} \cdot 2.27 + 1} - 1}{2 \cdot 10^{-4} \cdot \frac{500}{0.05}} = 1.09\ g/m^3$$

The result of the second reactor sequence with the second order reaction is as follows:

$$[A]_W = \frac{\sqrt{4 \cdot 10^{-4} \frac{500}{0.05} \cdot 25 + 1} - 1}{2 \cdot 10^{-4} \cdot \frac{500}{0.05}} = 4.52\ g/m^3$$

$$[A]_T = \frac{4.52}{1 + 10^{-4} \frac{200}{0.05} \cdot 4.52} = 1.61\ g/m^3$$

For the second order reaction, the system with a plug flow reactor followed by a completely mixed flow reactor achieves a 95.64% reduction from the initial concentration while the system consisting of a completely mixed flow reactor followed by a plug flow reactor achieved a 93.56% reduction.

EXAMPLE 5

The process of BOD_5 value decreasing is conducted in three completely mixed flow reactors connected in series. The inflow of BOD_5 to the first reactor is 50 gO_2/m^3 ($[BOD_5]_d$) and BOD_5 removal occurs according to a first order reaction with a rate constant of $k = 10\ d^{-1}$. Oxygen diffuses from the air to the solution at the following prescribed rate:

$$r_{O_2} = k_R \left([O_2]_s - [O_2]\right)$$

in which $k_R = 50\ d^{-1}$, $[O_2]_s = 8\ g/m^3$ – saturation oxygen concentration, $[O_2]$ – oxygen concentration in the solution.

Determine the BOD_5 in the effluent from the reactor cascade as well as the oxygen concentration in each reactor assuming that the hydraulic retention time in each reactor is $T_H = 12\ h = 0.5\ d$ and concentration of oxygen in the inflow to the first reactor is $[O_2]_d = 5\ g/m^3$.

The oxygen balance equation for the first reactor has the following form:

$$\frac{d\,[O_2]_1}{dt} V_r = Q\,[O_2]_d - Q\,[O_2]_1 + k_R\left([O_2]_s - [O_2]_1\right)V_r - k\,[BOD_5]V_r$$

Under steady state conditions for BOD_5 and using the reactor equation (3.10), the previous equation simplifies to the following form:

$$Q\,[O_2]_1 + k_R\,[O_2]_1 V_r = Q\,[O_2]_d + k_R\,[O_2]_s V_r - k\,\frac{[BOD_5]_d}{1+kT_H} V_r$$

and

$$[O_2]_1\left(\frac{1}{T_H} + k_R\right) = \frac{1}{T_H}[O_2]_d + k_R\,[O_2]_s - k\,\frac{[BOD_5]_d}{1+kT_H}$$

The oxygen concentration in the first reactor is determined by the following equation:

$$[O_2]_1 = \left(\frac{[O_2]_d}{T_H} + k_R[O_2]_s - k\,\frac{[BOD_5]_d}{1+kT_H}\right)\frac{T_H}{1+k_R T_H}$$

and the value of the oxygen concentration in the first reactor is

$$[O_2]_1 = \left(\frac{5}{0.5} + 50\cdot 8 - 10\,\frac{50}{1+10\cdot 0.5}\right)\frac{0.5}{1+50\cdot 0.5} = 6.27\ g/m^3$$

The BOD_5 value in the inflow to the second reactor is

$$[BOD_5]_1 = \frac{[BOD_5]_d}{1+k\,T_H} = \frac{50}{1+10\cdot 0.5} = 8.33\,g/m^3$$

The oxygen concentration in the second reactor is

$$[O_2]_2 = \left(\frac{[O_2]_1}{T_H} + k_R[O_2]_s - k\,\frac{[BOD_5]_1}{1+kT_H}\right)\frac{T_H}{1+k_R T_H}$$

$$[O_2]_2 = \left(\frac{6.27}{0.5} + 50\cdot 8 - 10\cdot\frac{8.33}{1+10\cdot 0.5}\right)\frac{0.5}{1+50\cdot 0.5} = 7.65\ g/m^3$$

The BOD_5 value in the inflow to the third reactor is

$$[BOD_5]_2 = \frac{[BOD_5]_1}{1+k\,T_H} = \frac{8.33}{1+10\cdot 0.5} = 1.39\,g/m^3$$

The oxygen concentration in the third reactor is

$$[O_2]_3 = \left(\frac{[O_2]_2}{T_H} + k_R [O_2]_s - k \frac{[BOD_5]_2}{1 + kT_H} \right) \frac{T_H}{1 + k_R T_H}$$

$$[O_2]_3 = \left(\frac{7.65}{0.5} + 50 \cdot 8 - 10 \cdot \frac{1.39}{1 + 10 \cdot 0.5} \right) \frac{0.5}{1 + 50 \cdot 0.5} = 7.93\ g/m^3$$

The BOD$_5$ value in the outflow from the third reactor is

$$[BOD_5]_3 = \frac{[BOD_5]_2}{1 + k\ T_H} = \frac{1.39}{1 + 10 \cdot 0.5} = 0.23\ g/m^3$$

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4. PREDICTING WATER QUALITY CHANGES IN THE NATURAL ENVIRONMENT

In water quality management, quantitative models play an important role in predicting water quality changes. Large scale human activities and natural changes in the environment, e.g. volcanic eruptions and earthquakes, can adversely impact water quality in ecosystems.

An example of such a model is a global quantitative analysis of the hydrosphere used to estimate changes in water circulation. Specifically, this entails analyzing the amount of atmospheric precipitation and surface runoff to the seas and oceans under conditions of reduced evaporation caused by the clearing of forests and the destruction of arable land [1, 10, 12]. Modeling this problem requires identifying individual reservoirs throughout the system and balancing the flows between the different reservoirs. A chart describing the flow between different reservoirs is given in Figure 4.1.

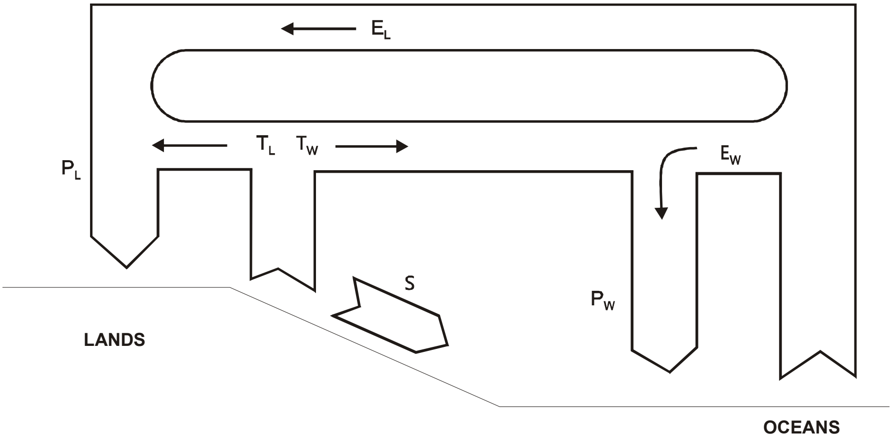

Fig. 4.1. Flowchart showing water circulation in the environment.

The symbols in Figure 4.1 have the following meanings:

P_L, P_W – amount of precipitation on the land surface and water surface, respectively,

T_L, T_W – transpiration of water from the land surface that falls again as precipitation on the land and ocean surfaces, respectively,

E_L, E_W – evaporation of water from the ocean which falls as precipitation on the land and ocean surfaces, respectively,

S – surface runoff to the oceans.

Using the previously defined parameters, the model seeks to answer the following question: what happens to the precipitation parameter P_L and runoff parameter S when the transpiration parameters T_L and T_W are reduced to a value equivalent to reduction in area that is cultivated and covered by forest (β). A balance model under steady state conditions can be applied to solve this problem.

There are three relationships between the seven defined parameters.
The first balance describes the water in the oceans:

$$P_W + S = E_W + E_L \tag{4.1}$$

The second balance describes the water on the continents with the simplification that groundwater does not respond to changes in the ecosystem:

$$P_L = S + T_W + T_L \tag{4.2}$$

The third balance assumes that the flow of water from the continents to the oceans is equal to the flow of water from the oceans to the surface of the continents.

$$S + T_W = E_L \tag{4.3}$$

Any two of the three described relationships can be derived from the third and two identities result from the definition of the specific parameters:

$$P_L = T_L + E_L \tag{4.4}$$

$$P_W = T_W + E_W \tag{4.5}$$

Equations (4.1) – (4.3) present relationships between the seven parameters. Therefore, in order to solve the problem it is necessary to know the values of at least four of the independent empirical parameters. Literature values [10] are available for the amount of atmospheric precipitation on land and on the oceans as well as for surface runoff. In addition, it can be assumed that evaporation from the oceans is three times greater than evaporation from land since about 75% of the earth's surface is covered by water:

$$3T_L = T_W \tag{4.6}$$

If the reduction in evaporation is evenly distributed on all continents, both T_L and T_W will be reduced by the same extent (β). This assumption would lead to a higher amount of error if transpiration was only analyzed along the coasts of the continents. Thus, it can be assumed that the new situation will not change the intensity of water evaporation from the oceans that returns to the ocean and land as precipitation ($E_W^* = E_W$, $E_L^* = E_L$). The new values T_L^* and T_W^* are given by $(1 - \beta)T_L$ and $(1 - \beta)T_W$, respectively.

Considering this dependence, equations (4.3) and (4.4) take the following form:

$$S^* = E_L^* - T_W^* \tag{4.7}$$

$$P_L^* = T_L^* + E_L^* \tag{4.8}$$

The next transformation leads to the following relationship:

$$S^* = S + \beta T_W \tag{4.9}$$

and

$$P_L^* = P_L - \beta T_L \tag{4.10}$$

From the previous equations it is evident that a decrease in transpiration caused by a reduction of farmland and forest cover increases surface runoff while decreasing the amount of precipitation on the continents.

This is just one example of how human interference in changing the environment can dramatically alter the water balance, often with negative effects. For this reason, this type of analysis should be used when considering investments having a major environmental impact.

This chapter has demonstrated the basic factors in determining water quality in the environment along with the general principals of analytical modeling.

4.1. Migration of pollutants in the environment

The migration of the majority of identified pollutants in the aquatic environment should be analyzed on a global scale. The goal of this analysis is to determine, among others, the extent of the pollutants in the environment from the widespread use of chemicals as well as their ability to migrate. Identifying the most important physical, chemical and biological mechanisms responsible for the migration of contaminants is a prerequisite for modeling their behavior in the aquatic environment.

4.1.1. Interactions in the environment – transport to the phase interface

For the purpose of analysis, the biosphere can be divided into three main phases: water, soil and air.

There are four main transport mechanisms in the evaluation of pollutant migration in the biosphere:

- transport within each phase of the biosphere,
- transport to the phase boundary surface,
- transport through the phase boundary surface,
- transport from the phase boundary surface into body of water.

The natural migration of pollutants in the biosphere occurs through air and water transport. Since this text deals with water quality modeling, emphasis is put on factors affecting the migration of contaminants in surface water and groundwater. It should be noted, however, that factors affecting the migration of pollutants in the atmosphere are similar to those in water.

Once released into the water environment, pollutants are transported in streams, rivers and aquifers. As stated previously, the accumulation of pollutants in a water system is equal to the rate of inflow to the system minus the rate of outflow from the system plus the rate of pollutant mass generation within the system. In the majority of natural water systems, the basic mass transport mechanisms for pollutants undergoing minimal changes are flow (advection), hydrodynamic dispersion and molecular diffusion [2].

The transport of pollutants by advection is dependent on the velocity of water in open and closed channels as well as in porous media. The mass transported through advection can be defined by an equation using vector notation:

$$\vec{N} = \varepsilon \ \vec{V}_{p_x} \cdot F_x \cdot C_A \tag{4.11}$$

in which

ε – system porosity ($\varepsilon = 1{,}0$ for systems without a porous media),

$\vec{V}_{p_x}$ – average velocity of flow in direction x [m/s] through the cross section F_x [m^2],

C_A – pollutant concentration [g/m^3].

As already presented in the chapter discussing non-ideal flow models, pollutant transport by hydrodynamic dispersion can be described for the one dimensional case by the following equation:

$$\vec{N} = \varepsilon \ D_h \cdot F_x \cdot \frac{\delta C_A}{\delta x} \tag{4.12}$$

in which

D_h – coefficient of hydrodynamic dispersion [m^2/s], which can be defined by the following equation:

$$D_h = \vec{V}_{p_x} \cdot k_x^n + D_m \tag{4.13}$$

in which

k_x – hydrodynamic dispersivity [m],

n – empirical constant, equal to approximately 1,

D_m – coefficient of molecular diffusion [m^2/s].

The mass transported by diffusion is defined by the following equation:

$$\vec{N} = \varepsilon \ D_m \cdot F_x \cdot \frac{\delta C_A}{\delta x} \tag{4.14}$$

in which: $\frac{\delta C_A}{\delta x}$ – concentration gradient in direction x [g/m^3·m]

Thus, the total transport by dispersion and diffusion can be described by the following equation:

$$\vec{N} = \varepsilon \left(\vec{V}_{p_x} k_x^n + 2D_m \right) F_x \frac{\delta C_A}{\delta x} \tag{4.15}$$

For very small average flow velocities, transport by hydrodynamic dispersion is, in principal, equal to molecular diffusion; however, situations in which turbulent diffusion and molecular diffusion have the same order of magnitude are extremely rare in natural aquatic environments. In general, the value of hydrodynamic dispersion is several orders of magnitude higher than molecular diffusion. For this reason, molecular diffusion is rarely used in mass transport models [2, 11].

A mathematical mass balance for an unreactive pollutant transported by advection and hydrodynamic dispersion is described as follows:

$$\varepsilon \frac{\delta C_A}{\delta t} F_x \Delta x = \left(\varepsilon \vec{V}_{p_x} F_x C_A - \varepsilon D_h F_x \frac{\delta C_A}{\delta x} \right) \Big|_x + $$

$$- \left(\varepsilon \vec{V}_{p_x} F_x C_A - \varepsilon D_h F_x \frac{\delta C_A}{\delta x} \right) \Big|_{x+\Delta x} \qquad (4.16)$$

Transforming and simplifying the balance equation (4.16) with the assumption that $\Delta x \to 0$ yields

$$\frac{\delta C_A}{\delta t} = D_h \frac{\delta^2 C_A}{\delta x^2} - \vec{V}_{p_x} \frac{\delta C_A}{\delta x} \qquad (4.17)$$

The previous equation is a basic expression used to describe the changes in concentration of unreactive pollutants transported by advection and dispersion. The specific solutions to equation (4.17) depend on the adopted boundary conditions.

The application of this equation will be elaborated in the modeling of pollutant migration in surface water and groundwater.

In the water environment, the factors initiating transport to the air – water interface are

- hydraulically induced turbulence and circulation,
- thermal circulation and circulation caused by wind,
- molecular diffusion.

Transport to the water-soil interface is caused by

- hydraulic circulation, thermal circulation and circulation caused by the wind,
- advection and turbulent dispersion,
- sedimentation,
- filtration.

In the air environment, pollutants such as dust, aerosols, gaseous substances and others are transported to the air – water and air – soil phase boundaries through dry deposition (without precipitation), wet deposition (with precipitation) and as a result of wind erosion.

It is assumed that once the pollutants are deposited, they do not become suspended in the air again.

Soil pollutants are transported to the soil – air interface through advection, capillary rise and molecular diffusion.

Other pollutant transport mechanisms which are encountered in the analysis of ecosystems include evaporation from the surface of plants and various other anthropogenic factors [2].

4.1.1.1. Transfer of mass at the air – water interface

The transport of mass through the air – water phase boundary occurs primarily through evaporation and absorption. Analyzing these mechanisms requires defining fundamental physicochemical relationships for the coefficient of distribution and vapor pressure.

A soluble substance in two nonmiscible phases at a constant temperature will maintain proportionality between the two phases when additional substance is added. This phenomenon is defined as the equilibrium distribution and the concentration ratio in two phases is the partition coefficient (also called the distribution coefficient). The partition coefficient is constant only when the substance dissolved in the phases has the same form and the processes of association and disassociation do not occur. In practice, the partition coefficient is rarely constant. For systems in which the concentrations in both nonmiscible phases are constant, the partition coefficient can be used to calculate the efficiency of the extraction process. All substances, whether solid or in solution, have a tendency to evaporate until the vapor pressure of the substance is equal to the equilibrium vapor pressure at a given temperature. Thus, vapor pressure is a measure of the ability of a substance to evaporate [5].

The transition of a substance into a vapor at a constant temperature is associated with the consumption of a specific amount of energy. This energy, in the form of heat, is mainly used to overcome the attractive forces between the particles of the body. The amount of applied heat is called the enthalpy of vaporization (Δh) or the molar enthalpy of vaporization ($\Delta h/n = \Delta H$) in relation to the number of moles of substance (n). The amount of heat does not cause an increase in the temperature of the system which is why it is referred to as latent heat.

The dependence of vapor pressure on temperature is described by the August equation:

$$\ln p = C - \frac{\Delta H}{RT} \tag{4.18}$$

in which

p – vapor pressure [10^{-1}MPa],

C – constant,

ΔH – molar enthalpy of vaporization [J/mol K],

R – ideal gas constant [J/mol K],

T – temperature [K].

The concept of vapor density, a representation of the concentration of the analyzed substance in the gas phase, is used to analyze specific phenomena occurring at the air – water interface. The vapor density (d) is determined from the ideal gas law:

$$pV = \frac{m}{M} RT \tag{4.19}$$

$$d = \frac{m}{V} = \frac{p \cdot M}{R \cdot T} \tag{4.20}$$

in which

V – volume [m^3],

m – mass of the substance [g],

M – molecular weight of the substance [g/mol],

Vaporization causes the migration of solutions and solids to the atmosphere. The majority of formulas describing vaporization is based on empirical correlations and theoretical principles of energy exchange between bodies. The process of vaporization consists of three steps. In the first step, the substance migrates to the phase boundary surface [16]. The migration to the phase boundary surface is limited by the vapor pressure of the substance at the given temperature. The second step consists of diffusion through the stagnation boundary layer. The last step occurs when the substance is transported from the boundary layer by advection and turbulent dispersion. A simplified vaporization model based on experimental observations can be used in which the mass transfer rate of a substance is roughly proportional to the difference between the saturation concentration and the current concentration of the solution:

$$r_w = k(C - C_s) \tag{4.21}$$

in the previous equation

r_w – rate of mass transport in vaporization process [g/m^2h],

k – mass transfer coefficient in the gas phase [m/h],

C – substance concentration [g/m^3],

C_s – saturation concentration [g/m^3].

The saturation concentration C_s is a function of the atmospheric partial pressure. For the case that the analyzed substance is not present in the air, $C_s = 0$. Vaporization occurs when $C_s < C$.

For the reverse situation when $C_s > C$ absorption occurs.

Assuming the concentration gradient ($C - C_s$) is the dominant factor in the transfer of a substance, the mass balance for a substance in solution at the boundary layer having the surface area F and thickness h takes the following form:

$$\frac{dC}{dt} F \cdot h = r_w \cdot F \tag{4.22}$$

Substituting the previous equation into equation (4.21) produces

$$\frac{dC}{dt} = \frac{k}{h}\left(C - C_s\right) \tag{4.23}$$

Integrating the previous equation gives

$$\frac{C_t - C_s}{C_o - C_s} = \exp\left(-\frac{k\,t}{h}\right) \tag{4.24}$$

in which

C_o – concentration of the substance at time t = 0 [g/m^3],

C_t – concentration of the substance at time t [g/m^3].

In the previous equation, the quotient k/h in literature is often presented as the product $k_L \cdot a$, in which k_L is the mass transfer coefficient in the boundary film of the solution [m/h] and "a" is the ratio of the phase boundary surface area (F) to the volume (V). The volumetric mass transfer coefficient ($k_L \cdot a$) is used in situations in which it is difficult to measure the interface contact surface between the gas and solution phases.

Equation (4.24) is used to estimate the required time for a specified concentration of substance to migrate from a specified volume.

The second type of mass transfer occurring at the water – air phase interface is absorption. Gas is absorbed into the solution by diffusion. The efficiency of diffusion of a gas into solution increases with an increase in system temperature. The second mechanism for transferring a gas into a solution phase is advection resulting from flow or mixing conditions. The process of absorption in a solution may therefore be analyzed as a stationary system in a fixed solution volume or as a system with mixing.

In stationary system transport by diffusion of a mass N occurs in a direction perpendicular to the phase boundary and is described by the following equation:

$$N = -D_m \frac{\delta C_A}{\delta z} \tag{4.25}$$

in which

D_m – coefficient of molecular diffusion [m^2/s],

$\frac{\delta C_A}{\delta z}$ – concentration gradient of substance A perpendicular to the phase boundary surface [g/m^3·m].

The mass balance for a volume element having the thickness Δz and phase interface surface F with absorption from the air takes the following form:

$$\frac{\delta C_A}{\delta t} F \cdot \Delta z = \left(-D_m F \frac{\delta C_A}{\delta z}\right)\Big|_z - \left(-D_m F \frac{\delta C_A}{\delta z}\right)\Big|_{z+\Delta z} \tag{4.26}$$

Assuming Δz approaches zero, the previous equation can be rewritten as follows:

$$\frac{\delta C_A}{\delta t} = D_m \frac{\delta^2 C_A}{\delta z^2} \tag{4.27}$$

This equation is the basic expression describing the change in gas concentration (C_A) in solution as a function of time and distance resulting from diffusion. Since the surfaces of the majority of water bodies in the natural environment are not fixed, the application of equation (4.27) in describing the adsorption of gasses is limited. For systems in which the absorption mechanisms are advection and diffusion, it is possible to apply the simplified Whitman model [7, 29].

A diagram of the partial pressure and concentration distribution in the phase boundary films of two contacting phases are presented in Figure 4.2.

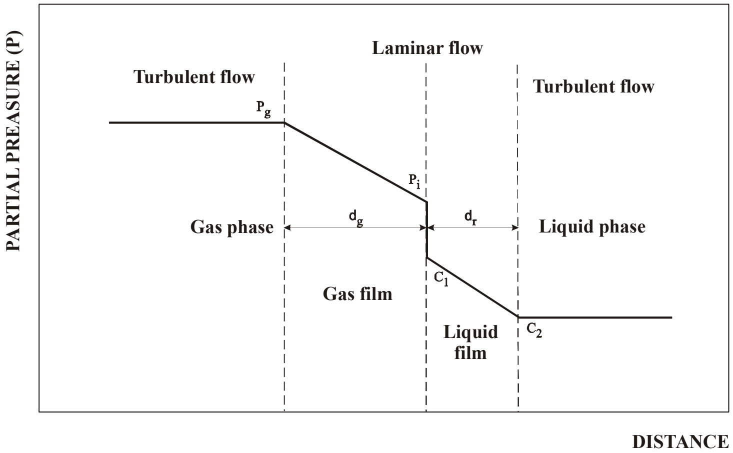

Fig. 4.2. A diagram of the partial pressure and concentration distribution in the phase boundary films according to Whitman [7, 29].

In the Whitman model, it is assumed that the mass transfer of gas takes place in two boundary films, which exist along the phase interface.

Poorly soluble gasses such as O_2, N_2 and CO_2 encounter initial resistance to transport from the boundary film solution while readily soluble gasses such as NH_3 encounter initial resistance from the gas film boundary. In the case of gasses having an intermediate solubility, both films provide resistance to the mass transfer of the gas.

For gasses with a low solubility, the saturation concentration C_s is essentially achieved along the interface surface between phases.

An equation used to estimate the increase in the concentration of a gas in solution has a similar form to equation (4.24), which defines the intensity of vaporization:

$$\frac{C_s - C_t}{C_s - C_0} = \exp\left(-\frac{k\,t}{h}\right) \qquad (4.28)$$

in which

C_s – saturation concentration for a gas in solution [g/m^3],

C_0 and C_t – gas concentration in solution initially and after time t, respectively [g/m^3],

k – mass transfer coefficient in solution [m/h],

h – penetration depth [m],

t – time of absorption [h].

4.1.1.2. Transfer of substances at the water – soil interface

The transfer of substances at the water – soil interface is primarily the result of adsorption and desorption as well as the leaching and dissolution of substances from the solid phase. Other phenomena that may occur at the water – soil interface include chemical precipitation in addition to physical processes such as sedimentation and filtration.

Adsorption is a surface process involving the accumulation of dissolved substances at the interface boundary. Adsorption is usually caused by one of three types of interactions between the dissolved substance (adsorbate) and the surface of the solid (adsorbent): attractive electrical forces, Van der Waals forces and chemical reactions.

The first type of adsorption is called ion exchange adsorption, often referred to as ion exchange. In this process, adsorbate ions concentrate on the surface of adsorbent due to electrostatic attraction to designated locations. At these locations, there is an exchange between the adsorbate ions and the ions at the active sites. The exchange occurs in equivalent quantities meaning that the number of charges joining the adsorbent is equal to the number of charges leaving the adsorbent to the solution. In this respect, the electroneutrality principle remains undisturbed in the solution as well as on the surface of the adsorbent. Higher valence ions are more readily attracted to opposite charge clusters compared to ions with a lower valence. For ions of equal charge, the particle size determines their preference for adsorption with smaller ions having an advantage since they are able to get closer to clusters of active sites.

Adsorption which occurs mainly as a result of intermolecular Van der Waals forces is generally referred to as physical adsorption. Physical adsorption is a reversible process and proceeds with the release of a small amount of heat similar to the heat of condensation.

The process in which the adsorbate chemically interacts with active sites on the adsorbent surface is called chemisorption. Chemical adsorption is generally irreversible or partly reversible, in which case desorption occurs only with great difficulty. The heat of chemisorption achieves significant values similar to the heat of reaction and is favored at high temperatures.

Most of the phenomena involved in adsorption involve a combination of the three types of mentioned interactions between the adsorbate and adsorbent [20]. In analyzing adsorption in soil, the following factors should be considered:

- chemical characteristics of minerals and the organic soil fraction,
- type of adsorption – type of bonding between the adsorbent and adsorbate,
- local factors including temperature and pH.

Adsorption is essentially a process of diffusion and consists of three stages of transport in addition to fundamental adsorption, i.e. the localization of solute on the active sites on the inner sorbent surface. The transport stages include:

- transport from within the solution phase to the direct vicinity of the sorbent surface (the transport mechanisms are advection, hydrodynamic dispersion and molecular diffusion),
- transport through the boundary film (molecular diffusion),
- transport in the internal structure of the sorbent (pore diffusion and surface diffusion).

Each stage of transport can be described mathematically.

The mathematical description of fundamental adsorption is a representation of the quantity of substance adsorbed per unit weight of adsorbent in relation to the concentration remaining in solution in a state of dynamic equilibrium and constant temperature. An expression of this type is called an adsorption isotherm. There are many adsorption models describing the state of dynamic equilibrium with those most widely used are from Freundlich, Langmuir and BET isotherms.

The second common phenomenon occurring at the water – soil interface is **dissolution**. In natural systems, the reaction rate depends not only on the course of the chemical or physical process, but also on rate of transport of reactants to the reaction zone and the rate of removal of reaction products from the reaction zone. When the transport processes are considerably slower than the chemical or physical process, the transport processes will begin to decide the rate of reaction as summarized by [5].

The process of dissolution is described by the Nernst equation, which is derived from the equation of Fick's first law:

$$\frac{dn}{dt} = D_m F\left(\frac{\delta C}{\delta x}\right)_0 \tag{4.29}$$

in which

n – mass of solute [g], passing through the area F [m^2],

D_m – coefficient of molecular diffusion for solute [m^2/h],

$\left(\frac{\delta C}{\delta x}\right)_0$ – concentration gradient at the soil surface [$g/m^3 \cdot m$],

x – distance of transport [m],

t – dissolution time [h].

In terms of measuring the concentration gradient, nonzero values occur within the boundary film having the thickness δ directly adjacent to the sorbent surface. On one side of the layer there is a permanently saturated solution with the concentration C_s while on the other side the solution has the concentration C. The partial derivative $(\delta C/\delta x)_0$ can be replaced by the expression $(C_s – C)/\delta$ and then equation (4.29) takes the following form:

$$\frac{dC}{dt} = \frac{D_m \cdot F}{V\delta}(C_s - C) \tag{4.30}$$

in which V is the volume of solution [m^3].

The thickness of the boundary layer δ depends on the flow conditions and temperature. In general, it is assumed that the boundary layer thickness δ has an order of magnitude of 10^{-5} m [5].

4.2. Transformation of substances in the environment

In balancing the concentrations of substances in the aquatic environment, it is very important to consider transformation mechanisms in surface water and groundwater in addition to substance migration.

A common mechanism for transforming substances in the hydrosphere is the **hydrolysis reaction**. Hydrolysis literally means decomposition under the influence of water. This kind of reaction is a double exchange reaction taking place between water and the dissolved substance leading to the formation of new chemical species. Hydrolysis reactions can be expressed in the general form:

$$AB + H_2O \leftrightarrow AH + BOH \tag{4.31}$$

If the substances are salts, hydrolysis under the influence of water forms acids and bases derived from the salts. In actuality, hydrolysis is a reaction between poorly disassociated water ions and ions of salt well disassociated forming a poorly disassociated weak acid and weak base.

All salts, with few exceptions such as $HgCl_2$, disassociate in water, i.e. completely revert to ionic form. If these ions are derived from strong acids (e.g. Cl^-, NO_3^-, ClO_4^-) and strong bases (e.g. Na^+, K^+, Ba^{2+}) they practically do not react with the ions H^+ or OH^-. Even if molecules of strong acids and strong bases would appear, they would immediately disassociate into ions. For this reason, ions from strong acids and strong bases are not subject to hydrolysis and thus do not affect the pH of the solution. Nearly all salts undergo hydrolysis and the following is an example of hydrolysis for salt of a strong acid and weak base (ammonium chloride):

$$NH_4Cl + H_2O \leftrightarrow NH_4OH + H^+ + Cl^- \tag{4.32}$$

Salts of a weak acid and strong base, e.g. sodium acetate:

$$CH_3COONa + H_2O \leftrightarrow CH_3COOH + Na^+ + OH^- \qquad (4.33)$$

Salts of a weak acid and weak base, e.g. ammonium acetate:

$$CH_3COONH_4 + H_2O \leftrightarrow CH_3COOH + NH_4OH \qquad (4.34)$$

The first two cases show the acidification and alkalization of water, respectively. If the dissociation constants of a weak base and weak acid formed from a salt are equal, adding this salt to the water does not change the pH value. When the dissociation constants are not equal, adding this salt will change the pH value depending on whether the acid or base is stronger [5, 28].

In the case of organic substances, the term hydrolysis has a broader meaning referring to e.g. the inversion of sugars, degradation of proteins and saponification of fats [25]. The following equation shows the hydrolysis of starch under anaerobic conditions:

$$(C_6H_{10}O_5)_n + nH_2O \rightarrow nC_6H_{12}O_6 \qquad (4.35)$$

Surface water and groundwater have natural buffers that help neutralize discharges of alkaline as well as acidic wastewater. The maximum acid load which can be buffered by the receiving water body is a result of the value of the dissociation constant of carbonic acid

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad (4.36)$$

$$K_1 = \frac{\lfloor H^+ \rfloor \lfloor HCO_3^- \rfloor}{[H_2CO_3]} \qquad (4.37)$$

with, for example, $K_1 = 3 \cdot 10^{-7}$ at 18°C. Taking the logarithm of both sides of the equation gives

$$\log K_1 = \log[H^+] + \log[HCO_3^-] - \log[H_2CO_3] \qquad (4.38)$$

Transforming the previous equation, substituting the numerical values for the constant K_1, assuming that the ion HCO_3^- determines the alkalinity and that the acidity is equal to $[CO_2/44]$ gives an equation for determining the pH:

$$pH = 6.52 + \log[\text{alk M}] - \log\left[\frac{CO_2}{44}\right] \qquad (4.39)$$

The addition of x mval of acid, for example HCl, to 1 dm^3 of water reacts with HCO_3^- according to the following equation:

$$Ca(HCO_3)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O + 2CO_2 \qquad (4.40)$$

This leads to a decrease in alkalinity while increasing the CO_2 concentration thus lowering the pH. In this respect, with the addition of acids such as HCl, equation (4.39) can be rewritten in the following form:

$$pH = 6.52 + \log[\text{alk M} - x] - \log\left[\frac{CO_2}{44} + x\right] \qquad (4.41)$$

and for water with a pH = 6.5, which is in the lower range for I class river water cleanness:

$$6.5 = 6.52 + \log[\text{alk M} - x] - \log\left[\frac{CO_2}{44} + x\right] \qquad (4.42)$$

Thus, the value of x is

$$x = 0.5[\text{alk M}] - 0.011[CO_2] \qquad (4.43)$$

Assuming that the maximum concentration of CO_2 in the previous equation does not exceed the insignificantly low value of 10 mg/dm^3, the results show that a volume of 1 dm^3 of receiving water with a pH of 6.5 can buffer an acid load equal to half the alkalinity M [mval].

The discharge of x mval of base, e.g. NaOH to 1 dm^3 of receiving water reacts with CO_2 according to the reaction:

$$CO_2 + NaOH \rightarrow NaHCO_3 \qquad (4.44)$$

and adding x mval of $Ca(OH)_2$ reacts according to the reaction:

$$2CO_2 + Ca(OH)_2 \rightarrow Ca(HCO_3)_2 \qquad (4.45)$$

This causes an increase in alkalinity M at a lower CO_2 concentration and thus an increase in pH.

For water with a pH = 8, which is in the upper range for a class I clean river, it can be written that

$$8.0 = 6.52 + \log[\text{alk M} + x] - \log\left[\frac{CO_2}{44} - x\right] \qquad (4.46)$$

thus

$$x = 0.022[CO_2] - 0.032[\text{alk M}] \qquad (4.47)$$

Since the alkalinity M in the previous equation is generally between 2–4 mval/dm^3, it can be neglected as insignificantly small. With a minimum CO_2 concentration equal to 5 mg/dm^3, 1 dm^3 of receiving water can be assumed to neutralize at most 0.1 mval of added alkalinity.

Photochemical reactions are the second major mechanism of transforming substances in the aquatic environment. Molecules and ions in water temporarily have higher energy after absorbing energy from the sun causing them to be more reactive. Under specific conditions, radiation from the sun can cause chemical reactions known as photochemical reactions. In order for substances to undergo photochemical degradation, they must be located near the water – air interface to be able to absorb solar energy. The general principle for this type of reaction is given by Einstein's law of photochemical equivalence in that the adsorption of one photon can lead to a change in only one particle. This does not imply that the number of molecules that absorb protons must be exactly equal to the number of molecules actually taking part in the reaction. The principle of equivalence applies only to the primary photochemical process and not to the subsequent reaction which can be triggered by photochemical processes [5].

For photochemical reactions, the ratio of the number of particles participating in the reaction to the number of absorbed photons is known as the quantum efficiency (φ) and it can take values other than one. A quantum efficiency less than one occurs when part of the excited particle loses the absorbed energy before it reacts or when the following reactions lead to the recombination of products from the initial reaction. High quantum efficiencies ($10^3 - 10^7$) are caused by chain reactions initiated by photoactivation particles.

Photochemical reactions are commonly found in the natural environment in the process of photosynthesis in green plants, cells with chlorophyll and bacteria containing bacteriochlorophyll.

Through photosynthesis, organic compounds are formed from carbon dioxide, water and the input of solar energy:

$$6CO_2 + 6H_2O + \text{light energy quantum } (h\nu) \rightarrow C_6H_{12}O_6 + 6O_2 \qquad (4.48)$$

Oxidation – reduction reactions are a third important transformation mechanism of substances in the environment. This type of reaction changes the oxidation number of reactive atoms or ions due to either a loss or gain in electrons.

The process of oxidation leads to the loss of electrons by an ion or atom which results in an increase in the oxidation number while reduction leads to a gain in electrons causing a decrease in the oxidation number [22, 30]. It follows that the oxidant receives electrons from the reductant and is itself reduced while the reductant gives up electrons is itself oxidized. In solution, there are no free electrons and thus the electrons given up by an atom or ion must be taken by other atoms or ions. Therefore, the oxidation of a substance must always be accompanied by the reduction of another substance, and vice versa. The combination of coupled oxidation and reduction reactions are called redox reactions. Importantly, in redox reactions the number of electrons accepted by the oxidant always equals the number of electrons donated by the reductant.

In general, redox reactions can be written as follows:

$$\text{Red}_1 \leftrightarrow \text{Ox}_1 + \text{ne} \qquad (4.49)$$

$$\text{Ox}_2 + \text{ne} \leftrightarrow \text{Red}_2 \qquad (4.50)$$

$$\overset{\text{ne}}{\overrightarrow{\text{Red}_1 + \text{Ox}_2}} \leftrightarrow \text{Ox}_1 + \text{Red}_2 \qquad (4.51)$$

An example of a redox reaction in the hydrosphere, occurring above all in groundwater, alters the oxidation state of iron:

$$\frac{1}{2}H_2 \leftrightarrow H^+ + e \qquad \textit{oxidation reaction} \qquad (4.52)$$

$$Fe^{3+} + e \leftrightarrow Fe^{2+} \qquad \textit{reduction reaction} \qquad (4.53)$$

e

$$\frac{1}{2}\overset{\curvearrowright}{H_2 + Fe^{3+}} \leftrightarrow H^+ + Fe^{2+} \quad \textit{redox reaction} \qquad (4.54)$$

Depending on the redox potential and solution pH, iron can exist as Fe^{2+} or Fe^{3+}.

Bacterial conversion is another major mechanism of transforming substances in the aquatic environment. Surface water and groundwater are, in essence, enormous natural biochemical reactors. Microorganisms, diverse in that they include a wide array of morphological and physiological groups of plants and animals at the microscopic scale, inhabit surface water in all its zones. In this respect, microorganisms can be found as a fine suspension in the entire water volume as well as in bottom sediments and on the surface of aquatic plants and underwater objects. Microorganisms are prevalent in groundwater, and above all, are found adsorbed to soil particles. In general, the dominant forms of microorganisms in the aquatic environment are bacteria and algae. The development and dominance of a particular species of bacteria depends on the ecological conditions present in the water, i.e. the abiotic factors (physicochemical composition of water) and biotic factors (the species makeup and their coexistence in the ecosystem).

Bacteria found in surface water are very diverse in terms of their origin. In addition to typical species of aquatic bacteria (autochthonous bacteria), bacteria originating in the soil are released into water bodies from surface runoff. Such bacteria with soil origins can be well adapted to surface water conditions. Another source of bacteria in water bodies is from treated and untreated wastewater released to surface water and groundwater.

The natural biological processes of microorganisms in the aquatic environment transform natural organic matter as well as organic substances of anthropogenic origin. Microorganisms take in nutrients and gases from the water and air while releasing their metabolic products into the water.

Heterotrophic microorganisms oxidize organic compounds using oxygen as the final electron acceptor. Assuming an average composition of organic compounds in municipal wastewater discharged to a receiving body [17], an approximation of the chemical reaction taking place in the receiving body is as follows:

$$C_{10}H_{19}O_3N + 12.5O_2 \rightarrow 10CO_2 + 8H_2O + NH_3 \qquad (4.55)$$

Here, the remaining organic compounds as well as the energy released from oxidation form the building blocks of new cells. The synthesis of heterotrophic biomass having an accepted, average composition [17] through the biodegradation of organic compounds is represented by the following reaction:

$$C_{10}H_{19}O_3N + 1.5NH_3 + 2.5CO_2 \rightarrow 2.5C_5H_7NO_2 + 3H_2O \qquad (4.56)$$

The biochemical kinetics of decomposition for organic substances are described by the Michaelis-Menten equation [24]:

$$r_B = \frac{dC}{dt} = \frac{r_{max} \cdot C}{K_m + C} \tag{4.57}$$

in which

r_{max} – maximum rate of biochemical decomposition [g/m^{3}h],
K_m – Michaelis constant [g/m^3],
C – substrate concentration [g/m^3],
t – time of biochemical decomposition [h].

4.3. Modeling water quality changes in rivers

The goal of developing a model is to have the ability to predict the response of a physical system to various effects. Modeling river systems allows an estimation of the buffering capacity as well as a prediction of the effects of planned investments on the river system. Mass balances and kinetic equations of relevant phenomena are key elements in water quality models of rivers.

The mixing of pollutants is an important phenomenon and a starting point for simulating changes in the water quality of rivers. In most water quality models, complete mixing of the wastewater discharge and receiving body is assumed to occur at or near the discharge point. In actuality, complete mixing rarely occurs; however, this assumption is sufficiently accurate for describing mixing in rivers. Thus, when estimating the potential distance at which there is complete mixing, it is necessary to consider either a single wastewater discharge point versus the possibly advantageous river bottom line discharge design that is perpendicular to the direction of flow. The distance at which there is complete mixing is influenced by several factors including the meander of the river, river depth, flow velocity, and cross section.

The most widely applied method of determining the distance at which complete mixing occurs on the river axis is the equation by Fischer [9]:

$$L_m = 0.03\ V_p s^2 / D_{h_p} \tag{4.58}$$

in which:

L_m – distance from the point of discharge to the nearest point where complete mixing occurs [m],
V_p – average river flow velocity [m/s],
s – river width [m],
D_{h_p} – transverse dispersion coefficient [m^2/s].

If the discharge point is located at the river bank, the distance required to achieve complete mixing is four times longer than if the discharge point would be located along the longitudinal river axis (in the middle of the river). This is because the distance across the river is twice as large for a riverbank discharge point compared to a point located along the longitudinal river axis. Moreover, the required distance for complete mixing can be greatly reduced by using multiple wastewater discharge points located along the transverse river axis (perpendicular to flow). Determining the value of the transverse dispersion coefficient (D_{h_p}) is difficult, although for slow moving rivers it can be estimated from the following equation [9]:

$$D_{h_p} = 0.2H \cdot V_p \qquad (4.59)$$

in which
H – the average depth of the river [m].

Certain discharges, such as cooling water from power plants, mix very slowly due to the difference in density of the discharge and the receiving body that is caused by their contrasting temperatures. In this case, mixing depends on eliminating temperature differences within the system. Thus, the presence of turbulent flow, in addition to heat exchange between the discharge and the river water as well as the atmosphere, promotes mixing.

Assuming complete mixing at the point of discharge, the pollutant concentration (C_0) in the river waste mixture is given by the following equation:

$$C_0 = \frac{Q_r \cdot C_r + q_s \cdot C_s}{Q_r + q_s} \qquad (4.60)$$

in which
Q_r and q_s – volumetric flow of the river and discharge, respectively [m^3/s],
C_r and C_s – river before mixing and discharge pollutant concentration, respectively [g/m^3].

Models predicting changes in the water quality of rivers can be divided into two categories. The first category of models simulates water quality influenced by the natural geological conditions prevailing in the catchment area and not by anthropogenic factors. Water and its natural constituents flow into rivers mainly from groundwater infiltration and surface water runoff. These water sources bring, among others, dissolved salts of calcium, magnesium, sodium and potassium. Such natural constituents are stable; most of them do not undergo chemical and biochemical transformations and their concentration is a function of the volumetric flow of the river.

Models in the second category relate constituents that interact with each other and their presence is caused by direct or indirect contamination from anthropogenic sources. The main water quality parameters in this type of model include dissolved oxygen, dissolved organic compounds measured as BOD_5, different forms of nitrogen and phosphorus, temperature, algae and bacteria. The general balance equation commonly used in the first category of models takes the following form [15, 18]:

$$\frac{\Delta VC}{\Delta t} = QC + \Delta Q_g C_g + \Delta Q_s C_s - \left(Q + \frac{\delta Q}{\delta x}\Delta x\right)\left(C + \frac{\delta C}{\delta x}\Delta x\right) \quad (4.61)$$

in which

- Q – volumetric flow [m^3/s] to the analyzed river section (control volume) having the length Δx [m],
- Q_g – volumetric groundwater flow [m^3/s] to the analyzed river section having the length Δx,
- Q_s – volumetric flow of surface runoff [m^3/s] to the analyzed river section,
- C, C_g, C_s – the respective concentration in the inflow to the analyzed section from the river upstream, groundwater flow and surface runoff respectively [g/m^3],
- V – volume of the analyzed river section [m^3].

Since

$$\left(C\frac{\delta Q}{\delta x} + Q\frac{\delta C}{\delta x}\right)\Delta x = \left(\frac{\delta(CQ)}{\delta x}\right)\Delta x \quad (4.62)$$

and

$$\Delta V = F \cdot \Delta x \quad (4.63)$$

where F is the river cross section perpendicular to flow [m^2], the balance equation can be transformed into the following form:

$$\frac{F\Delta\,xC}{\Delta t\,\Delta x} = \frac{\Delta Q_g}{\Delta x}C_g + \frac{\Delta Q_s}{\Delta x}C_s - \frac{\delta(CQ)}{\delta x} \quad (4.64)$$

Assuming Δx → 0 the general equation of mass flow is as follows:

$$\frac{\delta Q_g}{\delta x}\cdot C_g + \frac{\delta Q_s}{\delta x}\cdot C_s - \frac{\delta(CQ)}{\delta x} = \frac{\delta(FC)}{\delta t} \quad (4.65)$$

For steady state conditions in which accumulation is equal to zero, this equation reduces to

$$\frac{\delta Q_g}{\delta x}\cdot C_g + \frac{\delta Q_s}{\delta x}\cdot C_s - \frac{\delta(CQ)}{\delta x} = 0 \quad (4.66)$$

and integrating yields

$$Q \cdot C = Q_g \cdot C_g + Q_s \cdot C_s \quad (4.67)$$

The previous equation shows that the overall load of the natural constituent passing through the analyzed river section is the sum of the constituent from surface runoff and groundwater. The fraction of the river flow from groundwater is given by the following equation:

$$\frac{Q_g}{Q} = r \quad (4.68)$$

thus

$$\frac{Q_s}{Q} = 1 - r \tag{4.69}$$

equation (4.67) takes the following form:

$$C = r \cdot C_g + (1 - r) C_s \tag{4.70}$$

$$C = r\left(C_g - C_s\right) + C_s \tag{4.71}$$

The concept of basic flow (Q_0), defined as the river flow supplied only by groundwater, can be introduced into the model. Thus, the amount of flow exceeding the basic flow value comes almost exclusively from surface runoff:

$$Q < Q_0 \rightarrow Q = Q_g \qquad \text{and} \;\; C = C_g \tag{4.72}$$

When the river flow rate exceeds the basic flow rate $Q > Q_0$ as defined by

$$Q_g = \alpha\, Q^n \;, \tag{4.73}$$

equation (4.68) takes the following form:

$$r = \frac{\alpha\, Q^n}{Q} = \alpha\, Q^{n-1} \tag{4.74}$$

and equation (4.71) is rewritten as

$$C = C_s + \frac{\alpha}{Q^{1-n}}\left(C_g - C_s\right) \tag{4.75}$$

Figure 4.3 presents a graphical interpretation of the model for the dependencies $\ln Q_g = f(\ln Q)$, $\ln C = f(\ln Q)$ and $\ln r = \ln Q_g/Q = f(\ln Q)$ [15, 18].

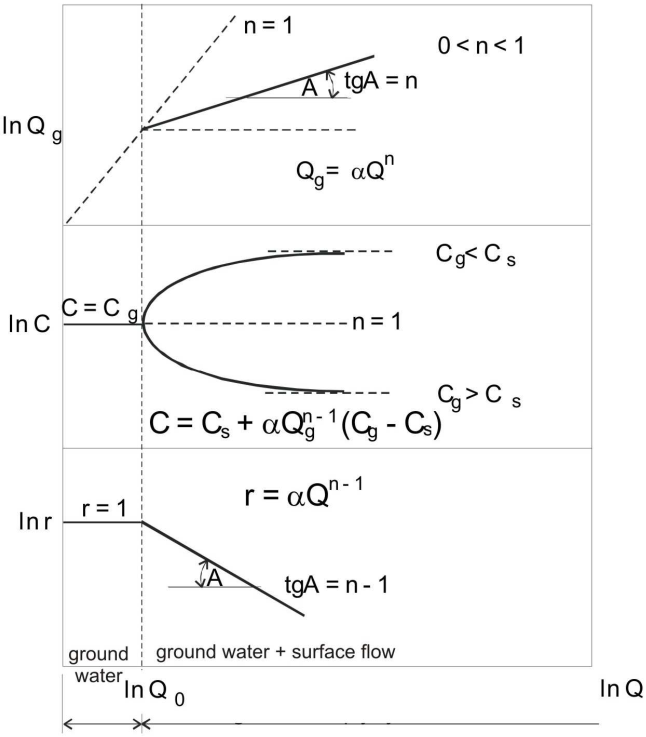

Fig. 4.3. The relationship between river flow and groundwater infiltration into the river, concentration of the analyzed substance and the parameter r.

The Streeter-Phelps model belongs to the second group and is used to simulate the oxygen deficit as a function of the distance from the pollution inflow point as well as the rates of deoxygenation and oxygenation [23, 25]. The rates of deoxygenation and oxygenation vary from river to river and are dependent on local river conditions.

Deoxygenation in rivers is caused by the biodegredation of dissolved natural and anthropogenic organic compounds in addition to the oxygen demand of river sediments.

The amount of oxygen required to stabilize organic pollutants is measured by the biochemical oxygen demand or BOD. Therefore, the biochemical oxygen demand is the leading source of oxygen consumption. The reaction for biochemical deoxygenation is first order; thus, the reaction rate can be described by the following equation:

$$r_{O_2} = -k_B \cdot C_{BOD} \tag{4.76}$$

in which

r_{O_2} – rate of deoxygenation [g/m^{3}d],

k_B – first order reaction rate constant [d^{-1}],

C_{BOD} – BOD of water in the analyzed cross section [gO$_2$/m^3].

Assuming that the river behaves as an ideal plug flow reactor, the mass balance for a differential river element can be described according to equation (3.18) in the form:

$$\frac{dC_{BOD}}{dT_H} = -k_B\, C_{BOD} \tag{4.77}$$

Integrating the previous equation from 0 to T_H and C_{BOD}^{w} to C_{BOD} produces

$$C_{BOD} = C_{BOD}^{w} \exp\left(-k_B T_H\right) \tag{4.78}$$

in which

C_{BOD}^{w} – BOD in the river at the discharge point assuming instantaneous mixing [gO$_2$/m^3],

T_H – hydraulic time of flow required to reach the distance at which the BOD concentration is C_{BOD} [d].

Bottom sediments deposited in a slowly flowing river may be a significant source of oxygen demand in the water. In most cases, however, sediments are mineralized in relatively slow anaerobic processes and the source of the oxygen demand can be located at the water-sediment phase boundary.

In rivers, a large oxygen demand by benthic sediments occurs only in localized areas over short distances. In well managed rivers, organic sediments should not accumulate to the extent that they cause a large oxygen demand affecting the overall balance of oxygen in the river and thus river quality. In situations in which removing sediments is not practical, predicting their effect on the overall oxygen balance is essential. For this task, a commonly used zero order model has the following form:

$$r_{Ben} = \frac{r_{Ben}^{*}}{H} \tag{4.79}$$

in which

r_{Ben} – rate of oxygen uptake by the benthos [g O$_2$/m^3 d],

r_{Ben}^{*} – rate of oxygen uptake [g O$_2$/ m^2 d],

H – average river depth [m].

Typical values in literature [26] of the rate of oxygen uptake r^*_{Ben} depend on the type of river bottom. These values vary from -7 for benthos with filamentous bacteria having a concentration in sediment of about 10 g/m^3 to -4 for municipal wastewater sludge in the area of its discharge to -0.5 for a sandy bottom and to -0.07 for a bottom with a mineral base.

Due to the difference in temperature (T) at the river bottom, the rate of deoxygenation by benthic sediments r_{Ben} should be adjusted as follows:

$$r^T_{Ben} = r^{20}_{Ben} \cdot 1.065^{(T-20)} \tag{4.80}$$

Water in rivers is oxygenated under natural conditions from the absorption of oxygen from the atmosphere and as a result of photosynthesis from aquatic plants and algae. The absorption of oxygen from the atmosphere is often referred to as reaeration. The rate of reaeration from the atmosphere (r_R) is proportional to the dissolved oxygen deficit in water and can be described by the following equation:

$$r_R = k_R \left(C^s_{O_2} - C_{O_2} \right) \tag{4.81}$$

in which

k_R – reaeration constant [d^{-1}],

$C^s_{O_2}$ – saturated concentration of dissolved oxygen [g O$_2$/m^3],

C_{O_2} – dissolved oxygen concentration [g O$_2$/m^3].

The value of the reaeration constant can be estimated using one of many empirical formulas, for example:

$$k_R = \frac{294\left(D_m \cdot V_p\right)^{0.5}}{H^{1.5}} \tag{4.82}$$

in which

D_m – molecular diffusion coefficient of oxygen in water [m^2/d],

V_p – average flow velocity of the river [m/s],

H – average river depth [m].

The value of the molecular diffusion coefficient is dependent on temperature as described by the following equation:

$$D^T_m = D^{20}_m \cdot 1.037^{(T-20)} \tag{4.83}$$

The molecular diffusion coefficient of oxygen in water at a temperature of 20°C is $D_m = 1.76 \cdot 10^{-4}$ m^2/d. Another empirical formula can be used for rivers having a depth from 0.6 m to 3.4 m and a flow velocity from 0.5 m/s to 1.5 m/s:

$$k_R = \frac{5.23 V_p}{H^{1.67}} \tag{4.84}$$

Typical values of the reaeration constant [23] range from 0.1 to 1.15 d^{-1}. For small ponds the value of k_R varies from 0.1 – 0.23 d^{-1}, for large lakes and large rivers with a slow flow velocity 0.23 – 0.46 d^{-1}, for rivers with a fast flow velocity 0.46 – 0.69 d^{-1} and for turbulent streams 0.69 – 1.15 d^{-1}. Values greater than 1.15 d^{-1} are assumed for waterfalls.

The reaeration coefficient is modified for water having a temperature different than 20°C according to the following equation:

$$k_R^T = k_R^{20} \cdot 1.024^{(T-20)} \tag{4.85}$$

Photosynthesis is a process carried out by phytoplankton, especially algae. During the summer, it is the main source of oxygen in lakes and slow flowing rivers.

Photosynthetic organisms, similar to other groups of autotrophic organisms, use CO_2 as their source of carbon. The rapid growth of these organisms can be the reason of carbonate equilibrium upsetting. In addition to carbon, during their growth they also assimilate nitrogen leading to a decrease in the nitrogen concentration in water.

During photosynthesis, the production of oxygen is a function of the algae concentration measured by the amount of chlorophyll, water depth, temperature, sunlight intensity as well as its duration. Since the latter two factors vary throughout the day, aquatic systems with a large algae population often have large variations in the dissolved oxygen concentration. Under extreme conditions, the dissolved oxygen concentration can drop to zero and rise above the saturation level all in one day.

In rivers, the main mass of algae is settled on river bottom. Concerning the oxygen balance, photosynthesis plays the largest role in clear, shallow streams and in eutrophic reservoirs. In general, it is assumed that a dry algae weight equal to or greater than 10 g per cubic meter of water is significant in terms of photosynthesis and thus must be taken into account in the oxygen balance. Estimating the effects of photosynthesis along with the effects of respiration from microorganisms that decrease the amount of dissolved oxygen is very difficult. Although the mechanisms of these processes are well documented in literature, generalized models balancing the effects of such factors are generally absent [26].

The rate of respiration has been measured in controlled laboratory conditions and then extrapolated to natural conditions. The rate of oxygen generation through photosynthesis (r_{Fot}) is described by the empirical relationship similar to the form of equation (4.79):

$$r_{Fot} = \frac{r_{Fot}^{*}}{H} \tag{4.86}$$

Available data for the production of oxygen by photosynthesis shows reported values of r_{Fot}^{*} in the range from 9 gO_2/m^2d for shallow, fast flowing streams to 0.3 gO_2/m^2d for deep, slow flowing rivers [26].

Published values of the rate of respiration r^*_{Res} are within the range from 0.5 to 10 g O_2/m^{2}d. Taking the depth into account, it is possible to determine the actual rate of respiration r_{Res} [g O_2/m^3 d] using a formula analogous to equation (4.86).

The oxygen balance in a volume element of solution (ΔV) taking into account deoxygenation caused by the discharge of wastewater and oxygenation caused by reaeration takes the following form:

$$\frac{\delta C_{O_2}}{\delta t}\Delta V = QC_{O_2}\big|_{x} - QC_{O_2}\big|_{x+\Delta x} + r_{O_2}\Delta V + r_R \Delta V \tag{4.87}$$

Substituting r_{O_2} and r_R with their respective expressions, (4.76) and (4.81), and assuming that $\Delta x \to 0$ simplifies the previous equation to the following form:

$$\frac{\delta C_{O_2}}{\delta t} = -Q\frac{\delta C_{O_2}}{\delta V} - k_B C_{BOD} + k_R\left(C^s_{O_2} - C_{O_2}\right) \tag{4.88}$$

Under steady state conditions $\delta C_{O_2}/\delta t = 0$. Thus, after defining the hydraulic retention time ($V/Q = T_H$) equation (4.88) is transformed to the following form:

$$\frac{dC_{O_2}}{dT_H} = -k_B C_{BOD} + k_R\left(C^s_{O_2} - C_{O_2}\right) \tag{4.89}$$

If the oxygen deficit is defined as

$$D_{O_2} = \left(C^s_{O_2} - C_{O_2}\right) \tag{4.90}$$

the derivative of the oxygen deficit D_{O_2} with respect to the retention time T_H is equal to

$$\frac{dD_{O_2}}{dT_H} = -\frac{dC_{O_2}}{dT_H} \tag{4.91}$$

Using the previous equation together with equation (4.89) the equation concerning the oxygen deficit becomes

$$\frac{dD_{O_2}}{dT_H} = k_B C_{BOD} - k_R D_{O_2} \tag{4.92}$$

By substituting equation (4.78) into the previous equation and transforming it produces the following equation:

$$\frac{dD_{O_2}}{dT_H} + k_R D_{O_2} = k_B C^w_{BOD}\exp\left(-k_B T_H\right) \tag{4.93}$$

For $T_H = 0$, the value of the oxygen deficit D_{O_2} is equal to the initial oxygen deficit at the point of discharge $D_{O_2}^{w}$ assuming instantaneous complete mixing in the system. Integrating equation (4.93) from 0 to T_H and from $D_{O_2}^{w}$ to D_{O_2} produces the classic Streeter-Phelps equation:

$$D_{O_2} = \frac{k_B C_{BOD}^{w}}{k_R - k_B}\left[\exp(-k_B T_H) - \exp(-k_R T_H)\right] + D_{O_2}^{w} \exp(-k_R T_H) \quad (4.94)$$

A plot of the dissolved oxygen concentration in a river according to the Streeter-Phelps equation is presented in Figure 4.4.

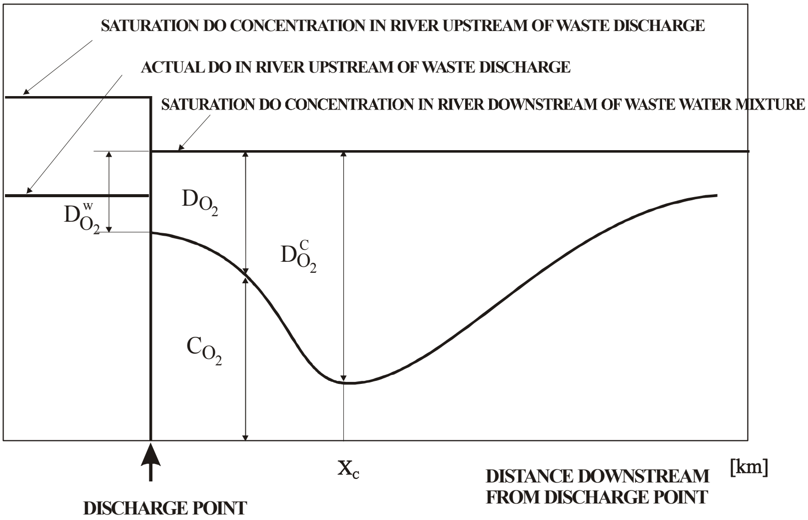

Fig. 4.4. Graphical interpretation of the Streeter-Phelps equation.

The process of biochemical degradation of pollutants using dissolved oxygen begins immediately at the point of discharge in the receiving body. Since atmospheric reaeration is proportional to the oxygen deficit, its value increases with the oxygen deficit. Within the critical distance (x_C) from the point of discharge, the rate of oxygen consumption (r_{O_2}) due to the biochemical degradation of organic matter is equal to the rate of atmospheric reaeration. The critical point indicates the minimum concentration of dissolved oxygen. Beyond the critical point, the rate of reaeration is greater than the rate of oxygen demand resulting in an increase in the dissolved oxygen concentration. The value of the critical dissolved oxygen deficit is the extreme value of the function described by equation (4.94). Thus, its value $\left(D^C_{O_2}\right)$ is determined from the derivative of this function with respect to the hydraulic retention time (equation 4.93) equal to zero. The value of the critical dissolved oxygen deficit is defined by the following equation:

$$D^C_{O_2} = \frac{k_B}{k_R} C^w_{BOD} \exp\left(-k_B T^C_H\right) \tag{4.95}$$

in which T^C_H is the time of flow from the point of discharge to the critical point.

The critical hydraulic retention time (T^C_H) is obtained from the transformed form of the Streeter-Phelps equation (4.94) by inputting the critical deficit as defined in equation (4.95):

$$\frac{k_B}{k_R} C^w_{BOD} \exp\left(-k_B T^C_H\right) = \frac{k_B\, C^w_{BOD}}{k_R - k_B}\left[\exp\left(-k_B T^C_H\right) - \exp\left(-k_R T^C_H\right)\right] + D^w_{O_2} \exp\left(-k_R T^C_H\right) \tag{4.96}$$

$$\frac{k_B}{k_R} C^w_{BOD} \exp\left[T^C_H\left(k_R - k_B\right)\right] = \frac{k_B\, C^w_{BOD}}{k_R - k_B}\left\{\exp\left[T^C_H\left(k_R - k_B\right)\right] - 1\right\} + D^w_{O_2} \tag{4.97}$$

$$\exp\left[T^C_H\left(k_R - k_B\right)\right]\left[\frac{k_B}{k_R} C^w_{BOD} - \frac{k_B\, C^w_{BOD}}{k_R - k_B}\right] = D^w_{O_2} - \frac{k_B\, C^w_{BOD}}{k_R - k_B} \tag{4.98}$$

$$T^C_H = \frac{1}{k_R - k_B} \ln\left[\frac{k_R}{k_B}\left(1 - \frac{D^w_{O_2}\left(k_R - k_B\right)}{k_B C^w_{BOD}}\right)\right] \tag{4.99}$$

Thus, the distance to the critical point from the point of wastewater discharge is

$$x_C = T^C_H \cdot V_f \tag{4.100}$$

Taking into account the initial form of the curve of the oxygen concentration (4.92), the expression for the rate of oxygen production through photosynthesis ($r_{Fot} > 0$), the rate of oxygen consumption from aquatic microorganisms ($r_{Res} < 0$) and the rate of oxygen demand by the benthos ($r_{Ben} < 0$) produces a modified form of the equation representing the curve of the oxygen concentration:

$$D_{O_2} = \frac{k_B C^w_{BOD}}{k_R - k_B}\left[\exp\left(-k_B T_H\right) - \exp\left(-k_R T_H\right)\right] +$$

$$+D_{O_2}^{w}\exp(-k_R T_H)-\frac{r_{Fot}+r_{Res}+r_{Ben}}{k_R}\left[1-\exp(-k_R T_H)\right] \qquad (4.101)$$

One of the primary applications of the Streeter-Phelps model is to determine the acceptable concentration of BOD in effluent discharged into rivers in order to maintain dissolved oxygen concentrations above the assumed critical oxygen deficit. In applying the model, equations (4.95) and (4.99) are used to determine the kinetic parameters of the system by iteration.

To do this, a value of the hydraulic retention time to reach the critical point (T_H^C) is assumed and substituted into equation (4.95) to calculate the value of C_{BOD}^{w}, the initial BOD concentration at the discharge point in the receiving body assuming instantaneous, complete mixing. Then, the value of C_{BOD}^{w} is substituted into equation (4.99) to determine the value of T_H^C. This iteration procedure is repeated until the difference in values obtained and assumed for T_H^C is acceptable.

The Streeter-Phelps method as presented is a classic water quality model in that it predicts changes in the dissolved oxygen concentration in rivers as a function of the discharged pollution load and the distance from the discharge point while taking into account the basic phenomena of oxygen generation and oxygen consumption. It can also be used as the basis to construct water quality models for pollutants besides BOD when it is desired to determine a pollutant discharge rate, the mechanisms of migration as well as the mechanisms and kinetics of pollutant transformation in the hydrosphere.

4.4. Modeling changes in water quality for lakes and artificial reservoirs

Water quality in lakes and reservoirs continually decreases due to natural eutrophication processes and anthropogenic factors. Lakes are classified as being oligotrophic, mesotrophic or eutrophic depending on the availability of biogenic compounds and the intensity of microorganism reproduction. The transition from an oligotrophic lake having high water quality and low productivity to a mesotrophic lake with intermediate water quality and productivity to a eutrophic lake with low water quality and high productivity is an ongoing natural process. With time, oligotrophic lakes become eutrophic lakes irrespective of any environmental protective measures. Human activities can significantly accelerate the eutrophication process. Specifically, natural changes normally occurring in several hundred or thousand years can, with human factors, occur over a time span of just several decades. Such anthropogenic factors include the discharge of untreated or insufficiently treated sewage, surface runoff from agricultural land and polluted atmospheric precipitation [25]. In strongly eutrophic lakes, the population of algae quickly increases leading to algal blooms and changes in the aquatic ecosystem.

Lakes and reservoirs act as non-ideal flow reactors with a long hydraulic retention time. Even a relatively small lake can have a retention time of several days. Therefore, such a system is only marginally sensitive to flow with wind and temperature differences primarily responsible for water movement in the body. Circulation due to wind and temperature is generally sufficient to prevent stratification in shallow lakes. Thus, the water quality in such shallow lakes can be approximated by a completely mixed flow reactor.

Large, deep lakes often have several spaces of circulation that behave like a system of completely mixed reactors in parallel or in series.

Water quality in lakes and artificial reservoirs generally depends more on the process of eutrophication and on temperature than on the BOD concentration and oxygen deficit. Although the dissolved oxygen concentration is related to eutrophication and temperature, these factors represent more of a secondary effect. In practice, an increasing rate of eutrophication is difficult to regulate because biogenic compounds are constantly being recirculated in the aquatic environment. For example, the nitrogen in water is assimilated by algae and aquatic plants. When these organisms die, nitrogen is released into the water and becomes available for other organisms to use. Phosphorous circulates in a similar manner.

In analyzing **mixing in lakes and reservoirs**, it is important to consider that these systems are dominated by long retention times reducing the importance of the inflow and outflow. The primary factors governing mixing are the wind and the difference in water density which is a function of the temperature differences in the water body. For this reason, differences in water density and temperature can be treated as the same factor. Since temperature is an easier parameter to measure than water density, temperature is widely used as a basic parameter in evaluating the mixing in lakes and reservoirs.

Lakes absorb solar radiation and emit energy due to cooling effects caused by air and wind. During warm weather, vertical convection currents are generated in the water body due to the differences in temperature between day and night. Lower lake levels become progressively colder and denser in contrast to the surface layer that is called the epilimnion. A result of this stratification causes the suppression of convection currents. The epilimnion is well mixed compared to the layer below called the metalimnion. The metalimnion has a varying depth and is characterized by a large temperature gradient and often a large oxygen and biogenic compound gradient as well. The hypolimnion, the lowest layer, generally has a constant temperature for the whole year.

In winter, the epilimnion can have a temperature below $4^{o}C$ while the other layers maintain an almost constant temperature profile during the year.

The temperature distribution in a lake is shown for the summer and winter in Figure 4.5.

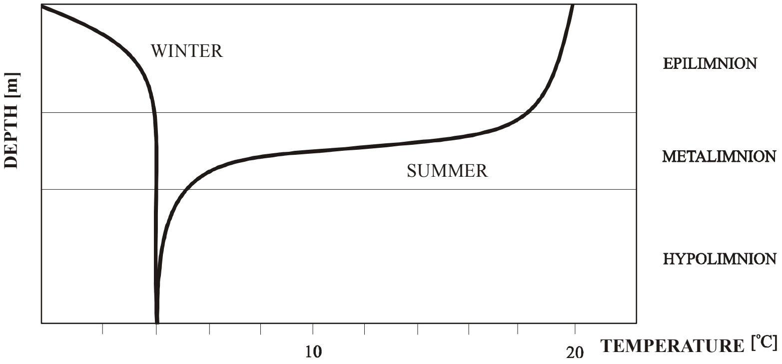

Fig. 4.5. Temperature profile of lakes and reservoirs.

In autumn when the air temperature becomes very cold, the temperature in the epilimnion decreases and when it reaches 4°C the water has its highest density. When the temperature in lower layers is different than 4°C, the lake system is in a state of instability. The vertical movement of water begins and after some time complete mixing takes place. After the end of lake mixing in autumn, the water temperature in the epilimnion is less than 4°C and a further decrease in temperature causes the freezing process to begin.

In addition to autumn, mixing occurs in spring when the upper layer, the epilimnion, heats to 4°C and begins to migrate to the hypolimnion zone. Autumn and spring mixing have a strong influence on water quality through changes in temperature and the concentration of biogenic and organic compounds caused by the movement of the bottom layers. For this reason, it is important to understand the temperature distribution and stratification in lakes and reservoirs when determining their appropriate uses.

Modeling the water quality in lakes and reservoirs can be quite complicated because it is difficult to simulate many of the occurring phenomena and their interactions. Two examples of this are the effect of heat emission as a function of wind conditions and the dependence of convective mixing and wind generated mixing on wind conditions. Water quality models of lakes and reservoirs can be divided into two broad categories: one dimensional and multidimensional models. One dimensional models are able to accurately describe the phenomena occurring in relatively small and medium sized well mixed lakes and reservoirs. Large lakes and reservoirs are simulated by using stratified models of two or three dimensions while taking time into account [21].

The Froude number, defined as the ratio of inertial force to gravitational force, is a parameter of stability that can be used to indicate the degree of stratification in a water body:

$$Fr = \frac{V_p}{\sqrt{\frac{\Delta\rho}{\rho_0} g\, h}} \qquad (4.102)$$

in which

$V_p = Q/b \cdot h$ – average velocity of flow [m/s],
Q – volumetric flow [m^3/s],
b – average width [m],

h – average depth [m],
$\Delta\rho$ – change in the density of water at a certain depth [kg/m^3],
ρ_0 – reference density assumed to be 1000 [kg/m^3],
g = 9.81 [m/s^2] – gravitational constant.

Well stratified lakes and reservoirs have a Froude number much smaller than 0.1 ($Fr << 0.1$). Weakly stratified lakes and reservoirs have a Froude number in the range of $0.1 < Fr < 1.0$ while completely mixed bodies have a Froude number $Fr > 1.0$.

When constructing a typical conceptual model of a stratified lake or reservoir it is important to determine the correct number of stratified layers, the flow between these layers as well as the inflow and outflow for the system. The number of stratified layers depends on the temperature gradient and locations of flow; however, most stratified lakes and reservoirs have three layers, i.e. the epilimnion, metalimnion and hypolimnion.

Rain water and surface water flow into the epilimnion while groundwater may flow to all layers, although the greatest amount of groundwater flow generally occurs to the hypolimnion since this layer has the largest contact surface with the ground. Outflow from the epilimnion occurs through the natural water course, generally by a stream or river. Water can also leave the system by soil infiltration and evaporation to the atmosphere.

If water is used from the lake or reservoir for consumption, it should be taken from the layer having the most suitable water quality for the intended purpose and thus require the least complicated and cheapest treatment options.

In constructing the simulation model, a mass balance should be made for each layer and each parameter in the mass balance equations can be a function of a set of different parameters. For example, surface inflow (Q_i) is a function of the time of year, atmospheric precipitation and the hydrology of the catchment basin. Evaporation (E) is a function of the time of year, water surface temperature, air temperature and wind velocity. Atmospheric precipitation (P), above all, is a function of the time of year. Flow between the stratified layers (Q_{zi}) is dependent on internal factors, especially the temperature gradient. The outflow (Q_o) of reservoirs is typically controlled while the outflow from lakes is a function of the natural drainage from the upper layer, the epilimnion.

The mass balance for the ith layer in a reservoir or lake can be written as follows:

$$\frac{\delta V_i}{\delta t} = Q_{i_i} + Q_{z_{i-1}} + Q_{z_{i+1}} + P - E - Q_{z_i} - Q_o \pm Q_{g_i} \qquad (4.103)$$

in which

V_i – volume of water of the ith layer [m^3],
Q_{i_i} – volumetric inflow to the surface of the ith layer [m^3/time],
$Q_{z_{i-1}}$ – volumetric outflow from the layer i - 1 [m^3/time],
$Q_{z_{i+1}}$ – volumetric outflow from the layer i + 1 [m^3/time],
P – intensity of atmospheric precipitation [m^3/time],
E – intensity of evaporation [m^3/time],
Q_o – volumetric outflow from the system [m^3/time],
Q_{g_i} – volumetric inflow or outflow of groundwater [m^3/time].

A three layered system with surface inflow and outflow along with a water intake for human use from the metalimnion layer (Q_{O_2}) is presented in Fig. 4.6. The mass balance for such a system as described as follows:

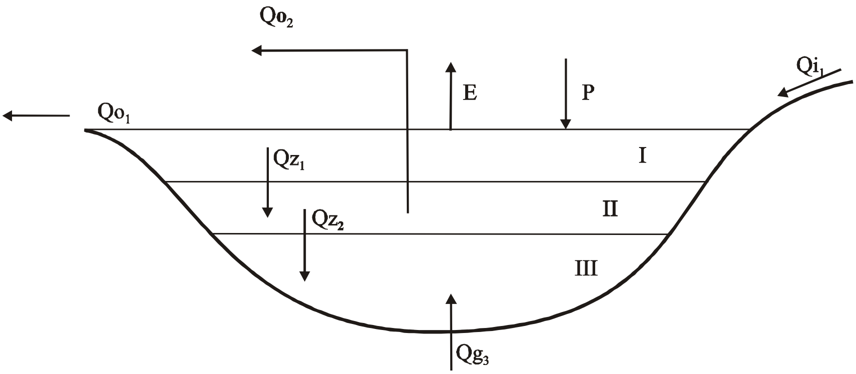

Fig. 4.6. Flow diagram of a lake or reservoir.

$$\frac{\delta V_1}{\delta t} = Q_{i_1} + P - E - Q_{o_1} - Q_{z_1} \qquad (4.104)$$

$$\frac{\delta V_2}{\delta t} = Q_{z_1} - Q_{z_2} - Q_{O_2} \qquad (4.105)$$

$$\frac{\delta V_3}{\delta t} = Q_{z_2} + Q_{g_3} - Q_{o_3} \qquad (4.106)$$

Solving the mass balance requires determining each parameter. External factors can be measured using conventional hydrological methods. The description of the internal flow between stratified layers is based on a thermal energy balance, which can be presented in the following form:

$$\frac{\delta E_i}{\delta t} = \left(e_i - e_o + e_{sz}\right)_i - \left(e_{A_i} - e_{A_{i+1}}\right) - \left(e_{D_i} - e_{D_{i+1}}\right) \qquad (4.107)$$

in which

E_i – heat accumulated in the ith layer [J],

e_i, e_o, e_{sz} –heat accumulated from the inflow to the ith layer, outflow from the ith layer and heat supplied by solar radiation, respectively [J/s],

e_{Ai} – heat of advection [J/s],

e_{Di} – heat of dispersion [J/s].

Substituting the definitions of the following parameters into equation (4.107):

$$E_i = c_W \cdot \rho \cdot V_i \cdot T_i \tag{4.108}$$

$$e_{i_i} = c_W \cdot \rho \cdot Q_{i_i} \cdot T_{i_i} \tag{4.109}$$

$$e_{o_i} = c_W \cdot \rho \cdot Q_{o_i} \cdot T_{o_i} \tag{4.110}$$

$$e_{sz_i} = (1-\beta) q_{sl} \cdot \exp(-\xi z) f_z \cdot \Delta z \tag{4.111}$$

$$e_{A_i} = c_W \cdot \rho \cdot Q_{z_i} \cdot T_{z_i} \tag{4.112}$$

$$e_{D_i} = c_W \cdot \rho \cdot D_h \cdot f_z \cdot \frac{\partial T}{\partial z} \tag{4.113}$$

produces

$$T_i \frac{\delta V_i}{\delta t} = \left(Q_{i_i} T_{i_i} - Q_{o_i} T_{o_i}\right) - \left(Q_{z_i} T_{z_i} - Q_{z_{i+1}} T_{z_{i+1}}\right) +$$

$$- f_z \left(D_{h_i} \frac{\delta T_i}{\delta z} + D_{h_{i+1}} \frac{\delta T_{i+1}}{\delta z} \right) + \frac{1}{c_w \rho} (1-\beta) q_{sl} \exp(-\xi z) f_z \Delta z \tag{4.114}$$

in which

q_{sl} – solar radiation flux [J/m^2·s],
c_w – specific heat of water [J/kg·K],
ρ – density of water [kg/m^3],
β – utilization of solar radiation,
z – depth [m],
Δz – thickness of layer [m],
ξ - mass extinction coefficient,
f_z – surface area at depth z [m^2],
D_h – dispersion coefficient [m^2/s],
T – temperature [K].

In order to simulate the flow between layers, it is first necessary to determine the previously mentioned parameters. The coefficient of dispersion (D_h), utilization of solar radiation (β) and the mass extinction coefficient (ξ) are difficult to estimate which limits the possibilities of applying the model [21].

Ecological models represent another category of models for lake and reservoir systems. These kinds of models define the relationships between phytoplankton, zooplankton and fish. Plants and organisms living in the benthos are analyzed as a separate component in the ecosystem [14]. A conceptual model of an ecological system is presented in Figure 4.7.

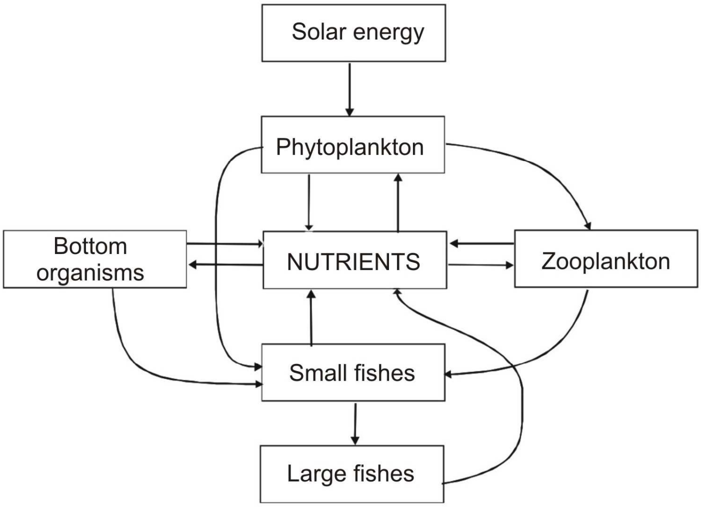

Fig. 4.7. Diagram of a model for an ecological system.

The growth of phytoplankton is dependent on the availability of organic compounds and nutrients in the case of bacteria and on the availability of nutrients and sunlight in the case of algae. In lakes and reservoirs, the dominant phytoplankton are photosynthetic organisms. For this reason, the phytoplankton population tends to concentrate near the surface of the water body. The main parameters in estimating the concentration of phytoplankton are time and intensity of sunlight, temperature and turbidity (which affects the degree of extinction). Notably, growth in the phytoplankton population increases turbidity causing the extinction of radiation. In this way, the growth in the phytoplankton population is governed by this feedback process and somewhat self regulating.

Zooplankton feed on phytoplankton and for this reason they also reside at the surface of the water body. The growth rate of zooplankton depends on temperature and the amount of available phytoplankton. In the majority of analyses, it is assumed that the population growth rate of zooplankton corresponds to a first order reaction. The growth rate factor of zooplankton is estimated by conducting laboratory tests.

In analyses, fish and benthic organisms are treated in a similar way as zooplankton. Normally, the fish population does not play a significant role in affecting the water quality. Models generally take the opposite approach in that they simulate how water quality affects the populations of species, the number of species and changes occurring in fish [14].

Since the concentration of biogenic compounds and temperature are factors limiting the growth of phytoplankton, ecological models must be combined with hydrodynamic models to simulate the water quality in lakes and reservoirs. Biogenic compounds such as nitrogen and phosphorus enter lakes and reservoirs from wastewater discharge, agricultural surface runoff and polluted atmospheric precipitation. In lakes and reservoirs the movement of nutrients is described by using a mass balance.

The circulation of phosphorus in lakes and reservoirs after a sudden addition of inorganic phosphorus can be simulated by a steady state model. [1, 10, 12]. Phosphorus circulation between three sets is shown schematically in Figure 4.8.

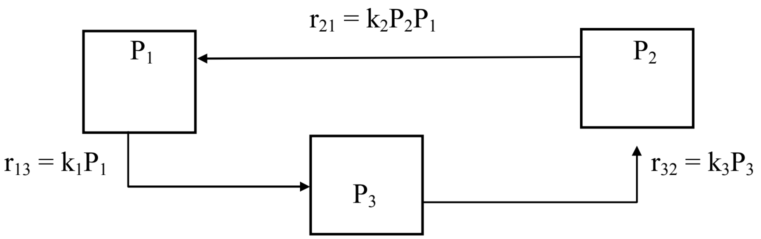

Fig. 4.8. Diagram of phosphorus circulation in lakes and reservoirs.

In Figure 4.8, P_1 represents the amount of phosphorus in the biomass of living organisms, P_2 the phosphorus in an inorganic form and P_3 the phosphorus in nonliving, organic material. Parameter r_{ij} represents the rate of flow from form "i" to form "j" in g/m^3d. The flow of phosphorus from set P_1 to set P_3 resulting from the death of aquatic biomass and the flow of phosphorus from set P_3 to P_2 caused by the decomposition of organic matter can be estimated for the purposes of analyses as being controlled by the donor concentration. This implies that the rate of flow between the different sets is described in the same manner as a first order reaction:

$$r_{13} = k_1P_1 \tag{4.115}$$

$$r_{32} = k_3P_3 \tag{4.116}$$

The flow from set P_2 to P_1 is controlled by both donors and receptors. The receptors are controlled by the fact that a greater concentration of living biomass means a greater rate in the collection of inorganic constituents previously a part of biomass:

$$r_{21} = k_2P_2P_1 \tag{4.117}$$

However, a large amount of inorganic phosphorus P_2 does not lead to an increase in decomposition and in this respect the flow from set P_3 to P_2 increases. Similarly, a high value in set P_3 does not cause an increase in the death rate and therefore does not influence the increase in flow from set P_1 to P_3.

The first step in analyzing a system in response to a phosphorus load is to determine the numerical values of the rate constants k_1, k_2 and k_3. The determination of the rate constants is done experimentally in the specific sets. The basic requirement for steady state conditions is for there to be no accumulation in the system meaning system inflow equals outflow. Thus, the following equations can be written:

$$k_2P_2P_1 = k_1P_1 \tag{4.118}$$

$$k_3P_3 = k_2P_2P_1 \tag{4.119}$$

$$k_1P_1 = k_3P_3 \tag{4.120}$$

Equation (4.120) is an identity in relation to equations (4.118) and (4.119). This means that the previous system of equations may not be used to determine the three constant rates of flow. To overcome this limitation, it can be assumed that the average retention time of phosphorus in living biomass is four days (4 d). From this, the retention time of phosphorus can be written as the ratio of the amount of phosphorus in biomass (P_1) to the rate of flow to set P_3, i.e. k_1P_1:

$$\frac{P_1}{k_1P_1} = 4 \tag{4.121}$$

thus

$$k_1 = 0.25 \tag{4.122}$$

Therefore the values of constants k_2 and k_3 are

$$k_2 = 0.25\ (P_2)^{-1} \tag{4.123}$$

$$k_3 = 0.25\ (P_3)^{-1}P_1 \tag{4.124}$$

The next step in the analysis is to determine the new values in the sets after phosphorus loading caused by an accidental discharge and then after the system reaches new steady state conditions.

New values of the sets (P_i^*) must fulfill the steady state conditions in equations (4.118), (4.119) and (4.120) because the constant flow rate of phosphorus between the sets does not change. The resulting new steady state conditions are as follows:

$$(P_2)^{-1}P_2^*P_1^* = P_1^* \tag{4.125}$$

$$(P_3)^{-1}P_1P_3^* = (P_2)^{-1}P_2^*P_1^* \tag{4.126}$$

$$P_1^* = (P_3)^{-1}P_1P_3^* \tag{4.127}$$

Equation (4.125) shows that the amount of phosphorus in set P_2 does not change ($P_2^* = P_2$). After adding an amount of phosphorus P_d to the closed phosphorus circulation system, the mass balance is as follows:

$$P_1^* + P_2^* + P_3^* = P_d + P_1 + P_2 + P_3 \tag{4.128}$$

and after substitutions:

$$P_1^* + P_2 + (P_1)^{-1}P_3P_1^* = P_d + P_1 + P_2 + P_3 \tag{4.129}$$

$$P_1^* = \frac{(P_d + P_1 + P_3)P_1}{P_1 + P_3} \tag{4.130}$$

$$P_3^* = \frac{(P_d + P_1 + P_3)P_3}{P_1 + P_3} \tag{4.131}$$

It is important to note that the solution to this problem does not depend on the set to which the additional phosphorus (P_d) was added. As mentioned, the content in set P_2 is not affected by the phosphorus addition due to the steady state equation (4.118) for this set:

$$P_2 = k_1 k_2^{-1} \tag{4.132}$$

A similar situation occurs for the circulation of nitrogen in a reservoir. Nitrogen compounds in dead organic matter in sediments undergo the process of ammonification. In the aquatic environment, nitrifying bacteria oxidize ammonium to nitrite, which is the first phase of nitrification:

$$NH_4^+ + 1.5\,O_2 \rightarrow NO_2^- + 2H^+ + H_2O + 66\text{kcal} \tag{4.133}$$

and they then oxidize nitrite to nitrate, which is the second phase of nitrification:

$$NO_2^- + 0.5\,O_2 \rightarrow NO_3^- + 17\text{kcal} \tag{4.134}$$

Nitrogen is an essential constituent for bacteria with ammonia and organic nitrogen being the most important constituents for new cell synthesis. The assimilation of nitrate or nitrite first requires their reduction to ammonium [17]:

$$NO_3^- \rightarrow NO_2^- \rightarrow NO \rightarrow NOH \rightarrow NH_2OH \rightarrow NH_4^+ \tag{4.135}$$

$$NO_3^- + 2H^+ + H_2O \rightarrow NH_4^+ + 2O_2 - 80\text{ kcal} \tag{4.136}$$

Under certain conditions, denitrification can occur. Denitrification is the biochemical reduction of nitrate or nitrite to nitrogen gas with the simultaneous oxidation of organic compounds. The oxidation of organic compounds provides the source of carbon and energy for the heterotrophic bacteria carrying out denitrification:

$$NO_3^- \rightarrow NO_2{}^- \rightarrow NO \rightarrow NOH \rightarrow N_2 \tag{4.137}$$

The denitrification of nitrate with methanol as the carbon source is described by the following reactions:

$$NO_3^- + 0.33CH_3OH \rightarrow NO_2^- + 0.67H_2O + 0.33CO_2 + \text{energy} \tag{4.138}$$

$$NO_2^- + 0.5CH_3OH \rightarrow 0.5N_2 + 0.5CO_2 + 0.5H_2O + OH^- + \text{energy} \tag{4.139}$$

Nitrogen, the product of denitrification, is a weakly soluble gas and thus the excess from denitrification is emitted to the atmosphere. Nitrogen in the form of ammonia and organic nitrogen is used by the populations of algae and zooplankton. When these organisms die, they release nitrogen into the water in the form of organic nitrogen. In addition, nitrogen is also absorbed to the water from the atmosphere [3].

Comprehensive limnological models take into account the most important phenomena occurring in water bodies:

- ecological model, i.e. models of phytoplankton, zooplankton, dissolved oxygen, benthic biocenosis and the interactions between these models,
- nitrogen circulation model,
- phosphorus circulation model,
- dissolved oxygen model,
- model of water circulation in a lake or reservoir [3].

Modeling the quality of water in lakes and reservoirs is quite difficult. This is due to a number of complicated, interactive phenomena such as weather conditions that play a large role in determining water quality, but are very challenging or practically impossible to simulate. These facts, coupled with the long system response time to external factors, generally preclude the verification of proposed models.

Despite the significant limitations in modeling lake and reservoir systems, such modeling is often justified and indeed beneficial to address three main issues:

- hypothetically identify the reasons for the current state of water quality,
- predict the water quality and the populations of microorganisms while maintaining the current ecosystem conditions in the lake or reservoir,
- predict the reaction of the hydrosphere to external changes in the ecosystem.

Addressing these issues allows for the proper management of the lake or reservoir ecosystem, especially for when changes are planned. An equally important goal of modeling is to accurately predict the quality and quantity of water in a lake or reservoir used for multi purpose engineering applications, i.e. water supply, energy, flood protection, recreation and navigation.

4.5. Modeling of groundwater quality

The basic source of water for economic purposes and for human existence is groundwater. In the past, the treatment of groundwater was traditionally limited to deironing, removing manganese, and adding chlorine for disinfection or oxidation. Often, only the disinfection treatment step was applied and not always on a continual basis. Increasingly, groundwater sources are becoming polluted with compounds requiring the use of highly specialized, effective water treatment technologies.

Prior to designing the well and treatment systems, it is necessary to develop a reliable water quality model taking into consideration actual and possible factors that could affect the water composition and availability. This entails accounting for trends in the demand of water, the volume of the aquifer along with the source and supply of aquifer regeneration. Evaluating at the macro level the time at which the groundwater resource is depleted can be done using a non-steady state model [1, 10, 12].

This kind of non-steady state model can be formulated by including a constant per capita water demand while taking into account population growth. Under these conditions the initial growth rate of groundwater consumption will be associated with an increase in human population, defined by the population growth rate M [%]. With a fixed, annual population growth rate the consumption of groundwater will increase exponentially.

In analyzing groundwater systems, it is commonly assumed that steady state conditions prevail when there is no water taken from the aquifer for human use. In this respect, groundwater recharge to the aquifer equals the outflow from the aquifer. The outflow from the groundwater system, i.e. consumption, can be described by the following equation:

$$Q(t) = Q(0)\exp(r \cdot t) \tag{4.140}$$

The initial conditions are specified at time $t = 0$. The constant of the water consumption rate (r) having the units [1/year] is determined from the following equation:

$$Q(1) = (1 + 0{,}01M)Q(0) \tag{4.141}$$

and

$$\exp[r(1)] = 1 + 0.01M \tag{4.142}$$

$$r = \ln(1 + 0.01M) \tag{4.143}$$

If Z(t) is the size of the groundwater resource at time t, its rate of change can be defined by the following equation:

$$\frac{dZ}{dt} = -Q(0)\exp(r \cdot t) \tag{4.144}$$

Separating variables and integrating from $t = 0$ to $t = t$ and from $Z = Z(0)$ to $Z = Z(t)$ yields

$$\int_{Z(0)}^{Z(t)} dZ = -\int_{0}^{t} Q(0)\exp(r \cdot t)dt \tag{4.145}$$

$$Z(t) - Z(0) = -\frac{Q(0)}{r}\exp(r \cdot t) + \frac{Q(0)}{r} \tag{4.146}$$

and after transformation:

$$Z(t) = Z(0) + \frac{Q(0)}{r}[1 - \exp(r \cdot t)] \tag{4.147}$$

For groundwater resources with known consumption trends, the following equations can be used to determine the time, t_w, at which the resource is completely depleted meaning when $Z(t) = 0$:

$$Z(0) + \frac{Q(0)}{r}[1 - \exp(r \cdot t)] = 0 \tag{4.148}$$

$$t = t_w = \frac{1}{r}\ln\left[1 + \frac{r\,Z(0)}{Q(0)}\right] \tag{4.149}$$

For example, the time until the world's aquifers are depleted can be theoretically simulated from the year 1980. The total groundwater resource is assumed to be $Z(0) = 8.3 \cdot 10^6$ km^3 while the total initial groundwater consumption for 1980 is about $Q(0) = 220$ km^3/year. The estimated annual population growth rate is $M = 2\%$ meaning $r = 1.98 \cdot 10^{-2}$ 1/year. Assuming that groundwater recharge equals 75% of water consumption, the time until complete groundwater depletion is $t_w = 348.7$ years.

A similar analysis can be made to determine the time of depletion for local groundwater resources.

Groundwater resources are finite and thus should be exploited sustainably and protected against anthropogenic pollution.

Predicting groundwater quality requires identifying possible sources of contamination. In its natural state, groundwater contains a variety of chemicals and dissolved gases. Most chemical species in groundwater are ionic in form. These species come directly from the rock and/or soil of the geological layers or from the microbial degradation of organic matter in these layers. Factors negatively affecting groundwater quality can be described as being from either natural (geogenic) processes or human influences (anthropogenic). Notably, the natural degradation of groundwater is often greatly accelerated by human activities. Anthropogenic contamination can enter an aquifer directly or through infiltration as groundwater recharge. In addition, various geotechnical activities can cause groundwater contamination [13].

Potential sources of groundwater contamination generally include the majority of human activities. One common source of groundwater pollution is from the accidental spillage of organic and inorganic chemicals to the ground surface. Once on the ground surface, these chemicals can migrate and infiltrate into the subsurface causing long term contamination of the groundwater.

Sources of groundwater contamination include the following:

- acid rain (nitrogen and sulfur oxides),
- agriculture (artificial and natural fertilizers, pesticides and herbicides),
- application of chemicals during snow plowing (chlorides of sodium and potassium),
- disposal of wastewater through a drain well (a variety of organic and inorganic chemicals, radionuclides, etc.),
- poorly designed/operated landfills for municipal, hazardous and industrial waste (organic and inorganic chemicals, radionuclides, bacteria, etc.),
- mining (mining often results in the draining and thus depletion of aquifers),
- salt water intrusion (inorganic salts),
- unsustainable exploitation of groundwater resources.

Groundwater flow is a very important, but also very complicated element in the quantitative analysis of groundwater quality. Most groundwater flow models are characterized by a high degree of simplification. The basic empirical relationship describing the movement of water through a porous medium is Darcy's law [8, 27]:

$$V_p = k_f \frac{dh}{dl} \tag{4.150}$$

in which

V_p – average discharge per unit area [m/s],

$\frac{dh}{dl}$ – hydraulic gradient, change in head divided by the length of flow,

k_f – hydraulic conductivity (permeability coefficient) [m/s].

The hydraulic conductivity is dependent on the properties of the porous layer and on the density of water, which is a function of temperature. Its value can be estimated based on the empirical formula by Allen-Hazen:

$$k_f = C(0.7 + 0.03T)d_{10}^2 \tag{4.151}$$

in which

T – water temperature [°C],

d_{10} – is the particle (grain) size diameter that 10% of the sample by weight is finer than [mm],

d_{60} – is the particle size diameter that 60% of the sample by weight is finer than,

C – is the coefficient of particle characteristics, related to the coefficient of uniformity CU = d_{60}/d_{10}:

C = 1000–1200 for CU = 1
C = 800 for CU = 2–4
C = 500 for CU = 5

Generally, formula (4.151) is used for soil with a spatially constant grain size distribution having a d_{10} value between 0.1 and 3.0 mm and a coefficient of uniformity CU ≤ 5,0.

For clean sands and a water temperature of 10°C, the Allen-Hazen formula simplifies to the following form:

$$k_f = 1.16 \cdot 10^{-2} d_{10}^2 \tag{4.152}$$

The Schlichter formula also gives a relatively good empirical approximation of the hydraulic conductivity k_f for homogeneous layers having a d_{10} value of between 0.01 and 5.0 mm:

$$k_f = c_T c_p d_{10}^2 \tag{4.153}$$

in which

c_T – coefficient dependent on temperature,
c_p – coefficient depending on the porosity of the layer

For a water temperature of T = 10°C, the previous equation takes the following form:

$$k_f = 7.8 \cdot 10^{-2} c_p \cdot d_{10}^2 \qquad (4.154)$$

the parameter c_p can be estimated from the following relationship:

$$c_p = 0.385\ (\varepsilon_g - 0.25) \qquad (4.155)$$

in which ε_g is the layer porosity.

The value of the hydraulic conductivity varies greatly depending on the type of soil [25]:

- for clay $k_f < 10^{-8}$ m/s,
- for peat $k_f = 10^{-8}$–10^{-7} m/s,
- for sandy or silty clay $k_f = 10^{-7}$–10^{-6} m/s,
- for fine grained clayey sand $k_f = 10^{-6}$–10^{-5} m/s,
- for fine grained sand $k_f = 10^{-5}$–10^{-4} m/s,
- for coarse grained sand $k_f = 10^{-4}$–10^{-3} m/s,
- for gravelly sand $k_f = 10^{-3}$–10^{-2} m/s,
- for gravel $k_f > 10^{-2}$ m/s.

The flow Q_w [m^3/s] through a cross section of soil or rock with an area of F_w [m^2] is described by

$$Q_w = F_w \cdot k_f \frac{dh}{dl} \qquad (4.156)$$

The application of the previous equation to model groundwater flow requires the assumptions that the porous medium is homogeneous and completely saturated. The Dupuit-Forchheimer method can be applied to estimate the flow of groundwater for a steady state system with a water table. This method assumes that the flow lines are horizontal and parallel; thus, effects of transverse dispersion are not accounted for. If the aquifer is regenerated by infiltrating surface water and groundwater flow is unidirectional (L), the mass balance for a differential element volume can be written as follows:

$$\frac{\delta V}{\delta t} = Q\big|_L - Q\big|_{L+\Delta L} + P_i s\ dL \qquad (4.157)$$

in which

V – volume of analyzed flow [m^3],
Q – volumetric flow rate [m^3/s],
P_i – rate of groundwater recharge through soil surface [m^3/m^{2}s],
s – width of the analyzed section [m].

Assuming steady state conditions, simplifying the expressions, dividing by sdL and assuming $\Delta L \to 0$ produces

$$-\frac{d\left(\frac{Q}{s}\right)}{dL} + P_i = 0 \tag{4.158}$$

Since parameter Q is defined by

$$Q = V_p \cdot h \cdot s \tag{4.159}$$

equation (4.158) can be written in the following form:

$$-\frac{d\left(V_p \cdot h\right)}{dL} + P_i = 0 \tag{4.160}$$

Substituting the velocity of flow in direction L with Darcy's law (4.150), in which the negative sign means a decrease in pressure, into equation (4.160) produces the following equation:

$$k_f \frac{d^2h}{dl^2} + P_i = 0 \tag{4.161}$$

Solving the previous equation by adopting appropriate boundary conditions and assuming a large range of values for P_i gives

$$h = \left(h_o^2 - \frac{P_i}{k_f} L^2\right)^{1/2} \tag{4.162}$$

in which

h is the thickness of the aquifer at distance L in the direction of flow from the cross sectional area of the inflow to the analyzed section,

h_o is the thickness of the aquifer at the point when L = 0.

Contaminants infiltrating into groundwater from the surface can have different distributions in an aquifer. One extreme result is the very quick, complete distribution of a pollutant throughout an aquifer. The opposite extreme occurs when a very small contaminant plume forms and mixes minimally with the water in the aquifer (Fig. 4.9) [8, 27].

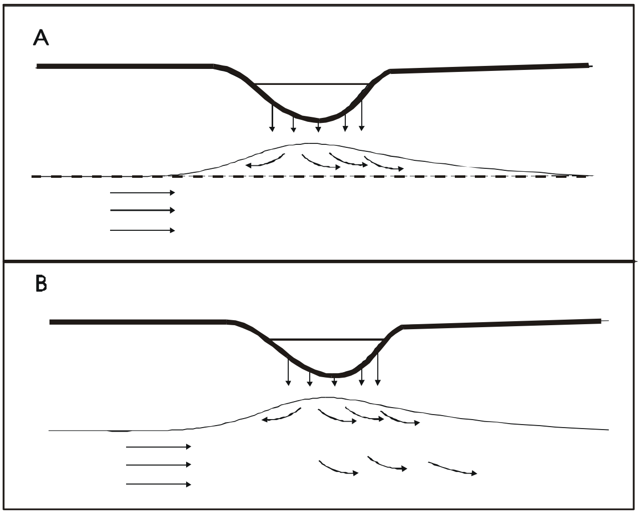

Fig. 4.9. Characteristics of contaminant distribution in groundwater (A – contaminants forming a small plume above the aquifer, B – contaminants completely distributed throughout the aquifer).

Applying Darcy's law and the balance equation allows the determination of the pollutant concentration (C_{ST}) in well located in the direction of groundwater flow and in the area of the groundwater recharge zone which is the source of the contamination. The equation for this model is a function of the depth of mixing:

$$C_{ST} = \frac{h \cdot k_f \cdot i \cdot C_g + V_{inf} \cdot d \cdot C_{sc}}{h \cdot k_f \cdot i + V_{inf} \cdot d} \qquad (4.163)$$

in which

h – depth of mixing [m],

i – hydraulic gradient,

C_g – concentration of the analyzed pollutant in groundwater at the point of infiltration [g/m^3],

C_{sc} – concentration of the analyzed pollutant in wastewater [g/m^3],

V_{inf} – velocity of wastewater infiltration [m/d],

d – length of the groundwater recharge zone in the direction of groundwater flow [m],

k_f – hydraulic conductivity [m/d].

This equation gives just an approximation of the mixing process since it does not take into consideration the properties of the groundwater recharge zone and the effects of transverse dispersion in the aquifer.

The transport of unreactive pollutants in groundwater, as in the case of surface water, is mainly governed by advection and hydrodynamic dispersion. The differential equation for transport by advection and dispersion has been presented earlier (equation 4.17). As mentioned, the solution of this equation depends on the adopted initial and boundary conditions [6].
For a constant initial concentration value (C_0) the following conditions are assumed:

$$C(L, 0) = 0 \qquad L \geq 0 \qquad (4.164)$$

$$C(0, t) = C_0 \qquad t \geq 0 \qquad (4.165)$$

$$C(\infty, t) = 0 \qquad t \geq 0 \qquad (4.166)$$

For these boundary conditions, the following solution of equation (4.17) is obtained [27]:

$$\frac{C}{C_0} = \frac{1}{2}\left[\operatorname{erfc}\left(\frac{L - V_p t}{2\sqrt{D_h t}}\right) + \exp\left(\frac{V_p L}{D_h}\right)\operatorname{erfc}\left(\frac{L + V_p t}{2\sqrt{D_h t}}\right)\right] \qquad (4.167)$$

in which

C – pollutant concentration at distance L [g/m^3],
C_0 – initial pollutant concentration [g/m^3],
L – distance from the point of pollutant entry [m],
V_p – average flow velocity in direction L [m/s],
t – time of flow [s],
D_h – coefficient of hydrodynamic dispersion in the direction of flow [m^2/s],
erfc – complementary error function.

$$\operatorname{erfc}(\psi) = 1 - \operatorname{erf}(\psi) \qquad (4.168)$$

$$\operatorname{erf}(\psi) = \frac{2}{\pi}\int_0^{\psi} \exp(-t^2)\, dt \qquad (4.169)$$

$$\operatorname{erf}(-\psi) = -\operatorname{erf}\psi \qquad (4.170)$$

The values of the function $\operatorname{erf}(\psi)$ are presented in Table 4.1.

Table 4.1. Values of the function erf(Ψ) [25].

Ψ	**erf(Ψ)**	**Ψ**	**erf(Ψ)**
0	0	1.1	0.880205
0.05	0.05637	1.2	0.910314
0.1	0.112463	1.3	0.934008
0.15	0.167996	1.4	0.952285
0.2	0.222703	1.5	0.966105
0.25	0.276326	1.6	0.976348
0.3	0.328627	1.7	0.983790
0.35	0.379382	1.8	0.989091
0.4	0.428392	1.9	0.992790
0.45	0.475482	2.0	0.995322
0.5	0.520500	2.1	0.997021
0.55	0.563323	2.2	0.998137
0.6	0.603856	2.3	0.998857
0.65	0.642029	2.4	0.999311
0.7	0.677801	2.5	0.999593
0.75	0.711156	2.6	0.999764
0.8	0.742101	2.7	0.999866
0.85	0.770668	2.8	0.999925
0.9	0.796908	2.9	0.999959
0.95	0.820891	3.0	0.999978
1.0	0.842701	-	-

In analyzing the concentration at a very large distance from the entry point of the pollutant, the second term in equation (4.167) may be omitted. In this case, equation (4.167) simplifies to the following form:

$$\frac{C}{C_0} = \frac{1}{2}\left[\operatorname{erfc}\left(\frac{L - V_p \cdot t}{2\sqrt{D_h \cdot t}}\right)\right] \tag{4.171}$$

This calculation is performed for times slightly smaller and larger than the theoretical flow time and at different distances from the pollution entry point.

An example of the changes in relative concentration of an unreactive pollutant for a particular time, at different distances from the entry point and with varying degrees of dispersion is given in Figure 4.10 [6, 19].

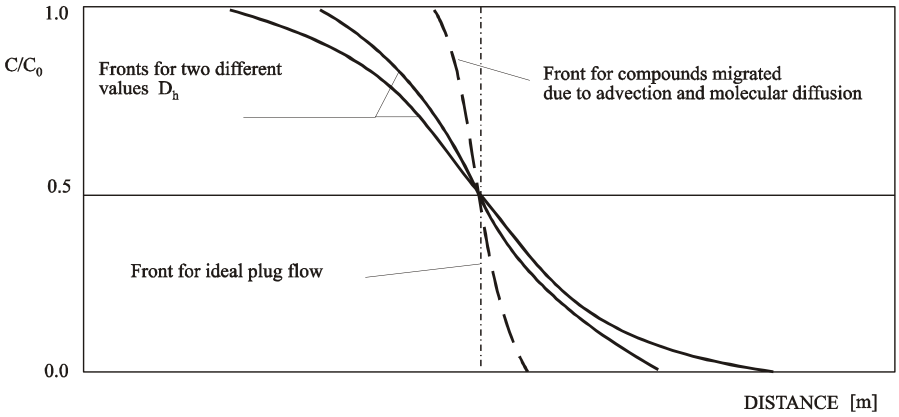

Fig. 4.10. Breakthrough curves for different pollutant transport mechanisms.

Contaminants often migrate to and are present in groundwater. Once there, they can be transported by various mechanisms or undergo change as a result of chemical or biochemical reactions. In addition, pollutants can be retained by adsorption in the saturated and unsaturated zones.

Phosphates, a common groundwater contaminant, react with multivalent cations in the soil. Thus, their migration to an aquifer is related to the sorption capacity of the soil in the layer. The front at which phosphorus sorption capacity is exhausted moves slowly in the direction of groundwater flow until the sorption capacity is completely exhausted

Ammonium ions are easily adsorbed on the surface of clay particles where under favorable conditions they can be oxidized to nitrite and nitrate by nitrifying bacteria. Furthermore, these oxidation products can be assimilated by plants and bacteria or can be transported by advection, dispersion and diffusion.

Heavy metal ions are adsorbed on the surface of clay particles and migrate, as in the case of phosphates, depending on the sorption capacity of the soil. Increasingly, groundwater contamination is anthropogenic in origin. Solvents often present in groundwater include trichloroethane (TCE), herbicides, fumigants, dibromochloropentan (DBCP) and many types of pesticides such as lindane and dieldrin.

The mass transport of reactive contaminants through porous media is described by equation (3.45). In this equation, the reaction rate component may include adsorption, hydrolysis, precipitation, redox reaction(s) or a combination of these processes.

Adsorption is the most common process affecting groundwater quality. When the processes of dispersion and diffusion in pollutant transport are omitted, the mass balance equation takes the following form:

$$\left(1-\varepsilon_g\right)\frac{\delta x}{\delta t}\rho_g\Delta V+\varepsilon_g\frac{\delta C}{\delta t}\Delta V=\varepsilon_g V_f FC\big|_L-\varepsilon_g V_f FC\big|_{L+\Delta L} \qquad (4.172)$$

in which

x – mass of pollutant adsorbed per dry unit mass of clay [g/g],
ρ_g – soil density [g/m^3],
ε_g – porosity of the soil layer,
F – cross sectional area of flow [m^2],
C – pollutant concentration in the flow [g/m^3],
ΔV – volume element of the aquifer [m^3],
V_f – flow velocity [m/h],
L – distance from the pollution entry point [m].

The pollutant distribution between the soil and water can be introduced in the analysis using the coefficient of distribution (partition) K_{SD}, which is defined by the following equation:

$$K_{SD}=\frac{x}{C}\ [\mathrm{m^3/h}] \qquad (4.173)$$

and since

$$(K_{SD})\frac{\delta C}{\delta t}=\frac{\delta x}{\delta t} \qquad (4.174)$$

and assuming $\Delta L\to 0$ the following form of equation (4.172) is obtained:

$$-V_f\frac{\delta C}{\delta L}=\left[1+\frac{\left(1-\varepsilon_g\right)\rho_g}{\varepsilon_g}K_{SD}\right]\frac{\delta C}{\delta t} \qquad (4.175)$$

Since

$$\frac{\delta L}{\delta t}=V_{p(0.5)} \qquad (4.176)$$

where $V_{p(0.,5)}$ is the average velocity at the points of concentration $C = 0.5C_0$ [m/s] the following equation can be written:

$$-\frac{V_f}{V_{f(0.5)}}=1+\frac{\left(1-\varepsilon_g\right)\rho_g}{\varepsilon_g}K_{SD} \qquad (4.177)$$

The value of the distribution coefficient can be approximated from the following empirical formula:

$$K_{SD}=6.3\cdot 10^{-7}\cdot f\cdot K_{OW} \qquad (4.178)$$

in which

f – fraction of organic carbon in the soil [g/g],
K_{OW} – coefficient of distribution between octanol and water.

The values of the coefficient of distribution K_{OW} for selected organic compounds often responsible for groundwater pollution are given in Table 4.2 [25].

Table 4.2. Values of the coefficient of distribution for selected organic compounds.

Compound	Chemical Formula	K_{OW}
Benzene	C_6H_6	$3.032\cdot10^{-1}$
Carbon tetrachloride	CCl_4	$4.345\cdot10^{-1}$
Chlorobenzene	C_6H_5Cl	$3.962\cdot10^{-1}$
Chloroform	$CHCl_3$	$2.900\cdot10^{-1}$
DDT	$C_{14}H_9Cl_5$	$6.972\cdot10^{-1}$
Phenol	C_6H_60	$1.732\cdot10^{-1}$

4.6. Example calculations

EXAMPLE 1

Determine the distance required for complete mixing of discharged wastewater in a river having the width S = 20 m and depth H = 3 m. The average velocity of the river is $V_f = 0.1$ m/s and the coefficient of transverse dispersion D_{h_p} can be determined from equation (4.59):

$$D_{h_p} = 0.2\cdot H\cdot V_f = 0.2\cdot 3\cdot 0.1 = 0.06\ m^2/s$$

Calculations can be conducted for a single discharge point (Fig. 1) at a distance from the riverbank of 0.5, and 10 m and for three discharge points (Fig. 2) located 5, 10 and 15 m from the riverbank.

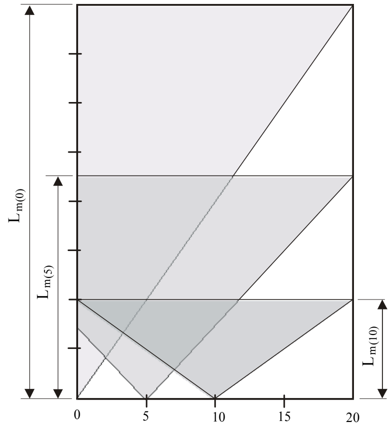

Fig. 1

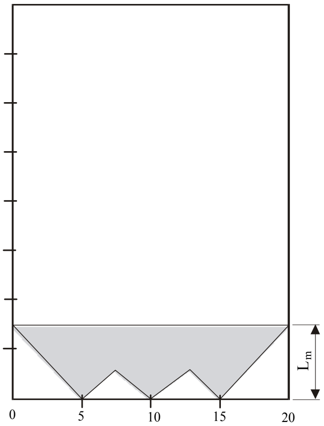

Fig. 2

The Fischer equation (4.58) is used for the calculations:

$$L_m = 0.03 \cdot V_p \cdot s^2 \cdot D_{h_p}^{-1}$$

$$L_{m(0)} = \frac{0.03 \cdot 0.1 \cdot (2 \cdot 20)^2}{0.06} = 80\ \text{m}$$

$$L_{m(5)} = \frac{0.03 \cdot 0.1 \cdot [2 \cdot (20-5)]^2}{0.06} = 45\ \text{m}$$

$$L_{m(10)} = \frac{0.03 \cdot 0.1 \cdot 20^2}{0.06} = 20\ \text{m}$$

The distance required for complete mixing of wastewater in the river with three discharge points is described by the following proportion:

$$\frac{L_m}{5} = \frac{L_{m(5)}}{20-5}$$

$$L_m = \frac{5 \cdot 45}{15} = 15\ \text{m}$$

EXAMPLE 2

Determine the maximum allowable BOD$_5$ value in wastewater $\left(C_{BOD_5}^{s}\right)$ discharged at a rate of q = 0.5 m^3/s to a river with a volumetric flow of Q = 4.5 m^3/s and initial respective dissolved oxygen and BOD$_5$ concentrations of $C_{O_2} = 7.5\ \text{g}\ O_2/\text{m}^3$ and $C_{BOD_5}^{r} = 4\ \text{g}\ O_2/\text{m}^3$.

The maximum allowable BOD$_5$ concentration in wastewater is a function of the defined minimum allowable dissolved oxygen concentration $\left(C_{O_2}\right)_{min} = 6.0\ \text{g}\ O_2/\text{m}^3$ that occurs in the river at a distance from the discharge point.

From laboratory testing, the first order reaction constant of BOD$_5$ value decreasing at 20°C is $k_B = 0.21\ \text{d}^{-1}$.

The reaeration constant of oxygen in water at 25°C is $k_R = 0.37\ \text{d}^{-1}$.

The initial oxygen deficit $\left(D_{O_2}^{w}\right)$ and the oxygen deficit at the critical point $\left(D_{O_2}^{C}\right)$ can be determined knowing that the saturation concentration of oxygen in water at the temperature of 25°C is $\left(C_{O_2}^{s}\right)_{min} = 8.2\ \text{g}\ O_2/\text{m}^3$.

$$D_{O_2}^{w} = 8.2 - 7.5 = 0.7\ \text{g}O_2/\text{m}^3$$

$$D_{O_2}^{C} = 8.2 - 6.0 = 2.2 \text{ gO}_2 / \text{m}^3$$

Equation (2.36) can be used to adjust the reaction constant k_B from 20°C to 25°C. The temperature coefficient θ for temperatures greater than 20°C is $\theta = 1.056$. Thus,

$$k_B = 0.21 \cdot 1.056^{(25-20)} = 0.27 \text{ d}^{-1}$$

Determining the values of BOD_5 in a river from the wastewater discharge point $\left(C_{BOD_5}^{w}\right)$ to the critical point $\left(T_H^{k}\right)$ is done by iteration using equations (4.95) and (4.99):

$$D_{O_2}^{C} = \frac{k_B}{k_R} C_{BOD_5}^{w} \exp\left(-k_B \, T_H^{C}\right)$$

$$T_H^{C} = \frac{1}{k_R - k_B} \ln\left[\frac{k_R}{k_B}\left(1 - \frac{D_{O_2}^{w}\left(k_R - k_B\right)}{k_B \, C_{BOD_5}^{w}}\right)\right]$$

A value of T_H^{C} is assumed and substituted into the first equation to determine the value of $C_{BOD_5}^{w}$.The determined value is then substituted into the second equation to obtain a value of T_H^{C}. This procedure is repeated until the two values of T_H^{k} are similar.

$T_{Ha}^{C} = 2.0$ d:

$$2.2 = \frac{0.27}{0.37} C_{BOD_5}^{w} \cdot \exp\left(-0.27 \cdot 2\right)$$

$$C_{BOD_5}^{w} = \frac{2.2 \cdot 0.37 \exp\left(0.27 \cdot 2\right)}{0.27} = 5.17 \text{ gO}_2 / \text{m}^3$$

$$T_H^{C} = \frac{1}{0.37 - 0.27} \ln\left[\frac{0.37}{0.27}\left(1 - \frac{0.7\left(0.37 - 0.27\right)}{0.27 \cdot 5.17}\right)\right] = 2.64 \text{ d}$$

$T_{Ha}^{C} = 2.4$ d:

$$C_{BOD_5}^{w} = 3.0148 \exp\left(0.27 \cdot 2.4\right) = 5.76 \text{ gO}_2 / \text{m}^3$$

$$T_H^{k} = 10 \ln\left[1.37\left(1 - \frac{0.07}{0.27 \cdot 5.76}\right)\right] = 2.69 \text{ d}$$

T_{Ha}^{C} = 2.6 d:

$$C_{BOD_5}^{w} = 3.0148 \exp\left(0.27 \cdot 2.6\right) = 6.08 \, gO_2 / m^3$$

$$T_{H}^{C} = 10 \ln\left[1.37\left(1 - \frac{0.07}{0.27 \cdot 6.08}\right)\right] = 2.71 \, d$$

T_{Ha}^{C} = 2.7 d:

$$C_{BOD_5}^{w} = 3.0148 \exp\left(0.27 \cdot 2.7\right) = 6.25 \, gO_2 / m^3$$

$$T_{H}^{C} = 10 \ln\left[1.37\left(1 - \frac{0.07}{0.27 \cdot 6.25}\right)\right] = 2.72 \, d$$

T_{Ha}^{C} = 2.75 d:

$$C_{BOD_5}^{w} = 3.0148 \exp\left(0.27 \cdot 2.75\right) = 6.33 \, gO_2 / m^3$$

$$T_{H}^{C} = 10 \ln\left[1.37\left(1 - \frac{0.07}{0.27 \cdot 6.33}\right)\right] = 2.73 \, d$$

T_{Ha}^{C} = 2.73 d:

$$C_{BOD_5}^{w} = 3.0148 \exp\left(0.27 \cdot 2.73\right) = 6.3 \, gO_2 / m^3$$

$$T_{H}^{C} = 10 \ln\left[1.37\left(1 - \frac{0.07}{0.27 \cdot 6.3}\right)\right] = 2.73 \, d$$

The determined time of flow for the critical point to be achieved is T_{H}^{C} = 2.73 d and the BOD$_5$ concentration at the discharge point in the river assuming immediate, complete mixing is $C_{BOD_5}^{w} = 6.3 \, gO_2 / m^3$.

The maximum allowable BOD$_5$ concentration in wastewater discharged to the river is used in the balance equation (4.60):

$$C_{BOD_5}^{s} = \frac{C_{BOD_5}^{w}\left(Q + q\right) - C_{BOD_5}^{r} \cdot Q}{q} = \frac{6.3\left(4.5 + 0.5\right) - 4 \cdot 4.5}{0.5} = 27.0 \, gO_2 / m^3$$

EXAMPLE 3

Determine the maximum allowable BOD$_5$ value in wastewater $C^{s}_{BOD_5}$ discharged to a river using the data given in example 2 while also taking into account the oxygen uptake by the benthos $r_{Ben} = -0.26\ gO_2/m^3d$. The critical dissolved oxygen deficit with benthos oxygen uptake is the extreme case of the function described in equation (4.101) with the values of r_{Fot} and r_{Res} equal to zero. The value $D^{C}_{O_2}$ is determined from the derivative of this function with respect to the hydraulic retention time equaling zero.

$$\frac{dD_{O_2}}{dT_H} = k_B\ C^{w}_{BOD_5}\ \exp\left(-k_B T_H\right) - k_R D_{O_2} - r_{Ben}$$

$$D^{C}_{O_2} = \frac{k_B}{k_R} C^{w}_{BOD_5}\ \exp\left(-k_B T^{C}_{H}\right) - \frac{r_{Ben}}{k_R}$$

The critical hydraulic retention time $\left(T^{C}_{H}\right)$ determined from the transformed form of equation (4.101) taking into account the value of $D^{k}_{O_2}$ in the previous equation has the following form:

$$T^{C}_{H} = \frac{1}{k_R - k_B} \ln\left[\frac{k_R}{k_B} - \frac{k_R D^{w}_{O_2}\left(k_R - k_B\right) + r_{Ben}\left(k_R - k_B\right)}{k^2_B\ C^{w}_{BOD_5}}\right]$$

The values of T^{C}_{H} and $C^{w}_{BOD_5}$ are determined using the same method as in example 2:

$T^{C}_{Ha} = 2.4\ d$:

$$2.2 = \frac{0.27}{0.37} C^{w}_{BOD_5} \cdot \exp\left(-0.27 \cdot 2.4\right) - \left(-\frac{0.26}{0.37}\right)$$

$$C^{w}_{BOD_5} = \frac{\left(2.2 - \dfrac{0.26}{0.37}\right)\exp\left(0.27 \cdot 2.4\right) \cdot 0.37}{0.27} = 3.92\ gO_2/m^3$$

$$T^{C}_{H} = \frac{1}{0.37 - 0.27} \ln\left[\frac{0.37}{0.27} - \frac{0.37 \cdot 0.7\left(0.37 - 0.27\right) - 0.26\left(0.37 - 0.27\right)}{0.27^2 \cdot 3.92}\right] = 3.14\ d$$

T_{Ha}^{C} = 2.8 d:

$$C_{BOD_5}^{w} = 2.052\exp(0.27\cdot 2.8) = 4.37\ gO_2/m^3$$

$$T_H^C = 10\ln\left[1.37 + \frac{0.0001}{0.073\cdot 4.37}\right] = 3.15\ d$$

T_{Ha}^{C} = 3.15 d:

$$C_{BOD_5}^{w} = 2.052\exp(0.27\cdot 3.15) = 4.8\ gO_2/m^3$$

$$T_H^C = 10\ln\left[1.37 + \frac{0.0001}{0.073\cdot 4.8}\right] = 3.15\ d$$

The determined critical time of flow is $T_H^k = 3.15\ d$ and the BOD_5 concentration at the discharge point in the river is $C_{BOD_5}^{w} = 4.8\ gO_2/m^3$.

The maximum allowable concentration of BOD_5 in wastewater discharged to the river is

$$C_{BOD_5}^{w} = \frac{4.8\,(4.5+0.5) - 4\cdot 4.5}{0.5} = 12.0\ gO_2/m^3$$

This example takes into account the oxygen uptake by benthos causing a significant decrease in the allowable BOD_5 concentration in discharged wastewater. In this analysis, the BOD_5 concentration in wastewater must be decreased by 55% compared to the situation in which the there is no oxygen uptake by the benthos.

EXAMPLE 4

Estimate the stability of lake with a medium length (L), depth (h) and width (b) of 10 km, 0.05 km and 2 km, respectively. The flow rate is Q = 300 m^3/s.

The density of the water in summer varies from $\rho = 996.23$ kg/m^3 at the surface to 999.97 kg/m^3 at the bottom of the lake. Assume a reference density value of $\rho_o = 1000$ kg/m^3. The average flow velocity is

$$V_f = \frac{Q}{b\cdot h} = \frac{300}{2000\cdot 50} = 0.003\ m/s$$

The critical Froude number is

$$\mathrm{Fr}=\frac{V_p}{\sqrt{\frac{\Delta\rho}{\rho_o}g\,h}}=\frac{0.003}{\sqrt{\frac{999.97-996.23}{1000}\cdot 9.81\cdot 50}}=2.215\cdot 10^{-3}$$

Since the determined Froude number is much smaller than 0.1, the analyzed lake is considered well stratified.

EXAMPLE 5

A lake with a surface of $F = 8{\cdot}10^7\ m^2$ is fed by a stream with a flow of $Q = 15\ m^3/s$ and a phosphorus concentration of $C_s = 0.02\ g/m^3$. There is an additional phosphorus load from a point source having the value of L = 1.0 g/s.
Assuming that the rate of phosphorus compounds sedimentation is $V_s = 10$ m/year $= 3.17{\cdot}10^{-7}$ m/s, determine the average phosphorus concentration in the lake and the maximum phosphorus load (L) that can be discharged in the lake while limiting the process of eutrophication corresponding to a phosphorus concentration in the lake of $C_d = 0.01\ g/m^3$.
The mass balance for steady state conditions is as follows:

$$Q\,C_s+L=QC+V_s\cdot F\cdot C$$

and

$$C=\frac{Q\,C_s+L}{Q+V_s\cdot F}=\frac{15\cdot 0.02+1}{15+3.17\cdot 10^{-7}\cdot 8\cdot 10^{7}}=0.0322\ g/m^3$$

From this calculation, the phosphorus concentration in the lake is more than three times higher than the maximum concentration allowable for limiting eutrophication.
In order to obtain phosphorus concentrations in the lake below C_d, phosphorus loading into the lake L may not be greater than

$$L=C_d\,(Q+V_sF)-QC_s=0.01\left(15+3.17\cdot 10^{-7}\cdot 8\cdot 10^{-7}\right)-15\cdot 0.02=0.1036\ g/s$$

Thus, the phosphorus load discharged should be reduced by 90%.

EXAMPLE 6

Leachate from a 100 m x100 m landfill infiltrates into the ground at a velocity of $V_{inf} = 0.1$ m/d and the phenol concentration in the leachate is $C_o = 200\ g/m^3$.
Determine the influence of the depth of mixing and the effects of sorption on the phenol concentration in the aquifer. Specifically, determine the phenol concentration in a well at a distance of 100 m from the landfill in the direction of

groundwater flow. Groundwater flow parameters and aquifer characteristics are as follows:

k_f – hydraulic conductivity = 30 m/d,

$\frac{dh}{dl}$ – hydraulic gradient = 0.023,

f – fraction of organic carbon in the soil = 0.5 g/g,

ε_g – porosity of the aquifer = 0.4,

ρ_g – soil density of the aquifer = 2100 kg/m^3.

The coefficient of distribution between octanol and water for phenol is $K_{OW} = 1.732 \cdot 10^{-1}$.

Assuming that the upstream groundwater flowing to the landfill has a phenol concentration of zero, the mass balance equation (4.163) simplifies to the following form:

$$C_{ST} = \frac{V_{inf} \cdot d \cdot C_o}{h \cdot k_f \cdot \frac{dh}{dl} + V_{inf} \cdot d}$$

in which h is the depth of mixing [m], d is the length of the recharge zone in the direction of groundwater flow that is d = 100 m in this example.

The phenol concentration in groundwater can be determined as a function of the depth of mixing: with assumption that phenol is not removed from leachate stream flowing to the surface of groundwater

$$C_{ST} = \frac{0.1 \cdot 100 \cdot 200}{h \cdot 30 \cdot 0.23 + 0.1 \cdot 100} = \frac{2000}{h \cdot 0.69 + 10}$$

h = 0 m, $C_{ST} = \frac{2000}{10} = 200\ g/m^3$

h = 25 m, $C_{ST} = \frac{2000}{25 \cdot 0.69 + 10} = 73.4\ g/m^3$

h = 50 m, $C_{ST} = \frac{2000}{50 \cdot 0.69 + 10} = 44.94\ g/m^3$

h = 75 m, $C_{ST} = \frac{2000}{75 \cdot 0.69 + 10} = 32.39\ g/m^3$

h = 100 m, $C_{ST} = \frac{2000}{100 \cdot 0.69 + 10} = 25.32\ g/m^3$

If the soil does not have sorption capabilities, the previous concentrations are expected in the analyzed well.

The coefficient of distribution can be determined:

$$K_{SD} = 6.3 \cdot 10^{-7} \cdot f \cdot K_{ow} = 6.3 \cdot 10^{-7} \cdot 0.5 \cdot 1.732 \cdot 10^{-1} = 5.452 \cdot 10^{-8}$$

The average migration velocity of the concentration points C = 0.5 C_{ST} (equation 4.177) can be determined:

$$V_{p\ (0.5C_{ST})} = \frac{k_f \dfrac{dh}{dl}}{1 + \dfrac{(1-\varepsilon_g)\,\rho_g}{\varepsilon_g} K_{SD}} = \frac{30 \cdot 0.023}{1 + \dfrac{(1-0.4)}{0.4} \cdot 2100 \cdot 5.452 \cdot 10^{-8}} = 0.69\ \mathrm{m/d}$$

The time since the first flow of leachate from the landfill to when it reaches a concentration of C = 0.5 C_{ST} in the well can be determined:

$$t = L \cdot V_{p\ (0.5C_{ST})}^{-1} = \frac{100}{0.69} = 145\ \ d$$

The first appearance of phenol in the well C < 0.5 C_{ST} occurs several days earlier. After 145 days, the phenol concentration quickly increases to the value corresponding to the depth of mixing (C_{ST}).

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