ANDRZEJ BIELSKI*

MODELLING OF MASS TRANSPORT IN WATERCOURSES CONSIDERING MASS TRANSFER BETWEEN PHASES IN UNSTEADY STATES. PART II. MASS TRANSPORT DURING ABSORPTION AND ADSORPTION PROCESSES

Equations describing the rate of adsorption and absorption processes and those based on Whitman's model have been analyzed. In the case of unstable states, the mass flux penetrating to the layer of the river sediment and calculated by means of these equations differs from the mass flux calculated from the mass diffusion equation. In order to minimize the discrepancies between the flux determined by Whitman's model and a real flux, the correction factor has been introduced into the concentration gradient equation originated from Whitman's model. This correction factor can be expressed as a time dependence of the product of a certain parameter and the concentration derivative at the phase boundary (solid phase side). The corrected equation for the concentration gradient has been used to derive another equation, describing a general rate of the absorption and adsorption processes at the linear interfacial equilibrium and the chemical reactions occurring in the liquid and solid phases; the chemical reactions follow the first order monomolecular mechanism in unstable states with reference to the liquid phase. Knowing the general rate of the earlier mentioned processes it is possible to construct an advective-dispersion model of mass transport in a river including these particular processes. Such a model contains a term defined as a correction factor referring to the time dependence of the concentration derivative with respect to time. The described model may be also used for simulation of the transport of pollutants undergoing adsorption and absorption in the layer river sediment; the processes occur with a finite and infinitely large rate through the equilibrium states.

1. MASS TRANSPORT IN ABSORPTION AND ADSORPTION PROCESSES

Mass exchange between phases when there is no discontinuity of concentration at the phase boundary has been discussed in our previous paper [1]. In the case of absorption and adsorption, concentrations associated with separate phases may take dif-

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*Cracow University of Technology, Department of Environmental Engineering, ul. Warszawska 24, 31-155 Cracow, Poland, e-mail: abielski@riad.usk.pk.edu.pl

ferent values next to the phase boundary. It is assumed that close to the phase boundary, the equilibrium between these concentrations is reached almost immediately [2]. In a general case, the relationships between these concentrations are described with nonlinear functions and only for sufficiently low concentrations it is possible to use a linear function (Henry's law for the absorption equilibrium or for an adsorption isotherm).

In the case of absorption or adsorption, the analysis of mass transport through a phase boundary may be carried out in a similar way as it was presented previously [1]. However, in such a case it would be necessary to solve the mass transport equation in unsteady states (Eq, (1), [1])) for each phase separately to determine the concentration distribution in a liquid phase and either in adsorption or absorption phases. Such approach to the analysis of mass transport through a phase boundary would result in some major complications in calculations. Therefore, film Whitman's model is used [2–5] to describe the mass transfer rate through a phase boundary.

Numerous other models of mass transfer exist, such as the Higbie penetration model, Danckwerst surface renewal model, Dobbins, Toor and Marchello model, Kisziniewski model, King model [2, 4]. Neither of them provides any possibilities to consider periodic or aperiodic concentration changes at the phase boundary though the models are little more complex than Whitman's model. Just from the perspective of the mass transfer through a phase boundary in rivers, Whitman's model seems to be the most appropriate.

For the specific case of absorption or adsorption without a chemical reaction, the model based on Whitman's model may be described as follows:

$$\frac{dc}{dt} = -\frac{K}{h}\left(c - c^*\right) \tag{1}$$

$$\frac{da}{dt} = \frac{K}{L_0}\left(c - c^*\right) \tag{2}$$

$$a = \Gamma c^* \tag{3}$$

Based on Fick's law (Eq. (23), [1]) [4] and Eq. (1) it may be stated that:

$$-\frac{K}{h}\left(c - c^*\right) = -\left(-\frac{D}{h}\frac{dc}{dy}\right) \tag{4}$$

After introducing Eq. (3) into Eq. (4) the concentration gradient is given by:

$$\frac{dc}{dy} = -\frac{K}{D}\left(c - \frac{a}{\Gamma}\right) \tag{5}$$

Equation (5) refers to the average concentration gradient in the close vicinity of a phase boundary (Fig. 1).
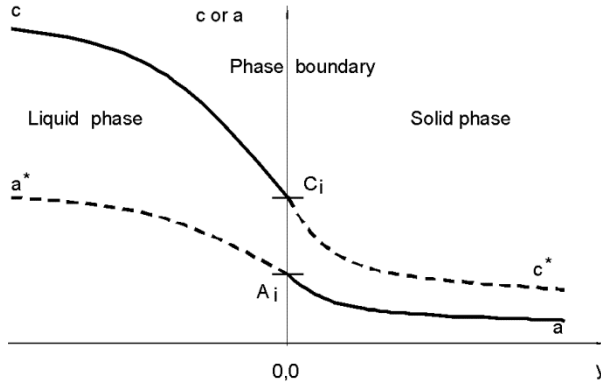

Fig. 1. Distribution of concentrations inside liquid and solid phases.
The dotted lines represent equilibrium concentrations

From Eqs. (2) and (3) it may be concluded that the degree of absorption or adsorption may be described as:

$$a = a\left(t = 0, x\right) + \int_0^t \frac{K}{L_0}\left(c - \frac{a}{\Gamma}\right) d\tau \tag{6}$$

Using Equation (5), Eq. (6) may be transformed into:

$$a = a\left(t = 0, x\right) - \frac{D}{L_0}\int_0^t \frac{dc}{dy} d\tau \tag{7}$$

Substitution of Eq. (7) into Eq. (5) yields to expression for the concentration gradient:

$$\frac{dc}{dy} = -\frac{K}{D}c - \frac{K}{\Gamma L_0}\int_0^t \frac{dc}{dy} d\tau + \frac{K}{D\Gamma} a\left(t = 0, x\right) \tag{8}$$

In Equations (1)–(3) and the following, the equilibrium concentration was denoted as c^*, the concentration at a phase boundary in a liquid phase was denoted as C_i while the concentration in a liquid phase core was denoted as c (Fig. 1). Equations (1) and (2) describe the mass transfer rate through a phase boundary. If concentration c was equivalent to C_i, the coefficient K would be defined as the penetration coefficient in a solid phase.

The first term of Eq. (8) refers to absorption or adsorption, while the second one to desorption processes. Let us use model (8) to analyze gradient changes for the concentration presented in Fig. 5 of [1].

Minimization of the product of a sum of squared deviations for both gradient and mass balance allowed one to determine the values of coefficients in Eq. (8). An equation for a concentration gradient has the following form:

$$\frac{dC}{dy} = -420.71 C_i(t) - 1.4790 \times 10^{-4} \int_0^t \frac{dC}{dy} d\tau + 6.5773 \qquad (9)$$

It was assumed that at the moment $t = 0$, the gradient $dC/dy = 0$ though such assumption does not necessarily have to be true. Therefore, a potential error influences the value of a constant – in this case it is 6.5773. A similar assumption may concern the following equations of the same type.
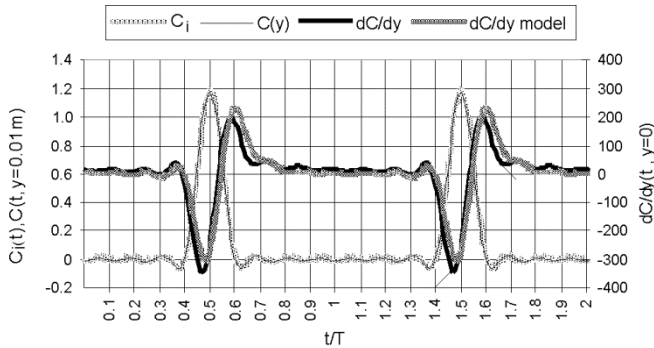

Fig. 2. Concentrations at the phase boundary and at the distance of $y = 1\times10^{-6}$ m
in the solid phase, gradient of concentration at the phase boundary and gradient calculated
using model Eq. (8); $T = 86\,400$ s, $C_{i,a} = 1$ g/m^3, $\Delta\tau = T/16$, $k_r = 1\times10^{-30}$ s^{-1}, $D = 1.7\times10^{-9}$ m^2/s.
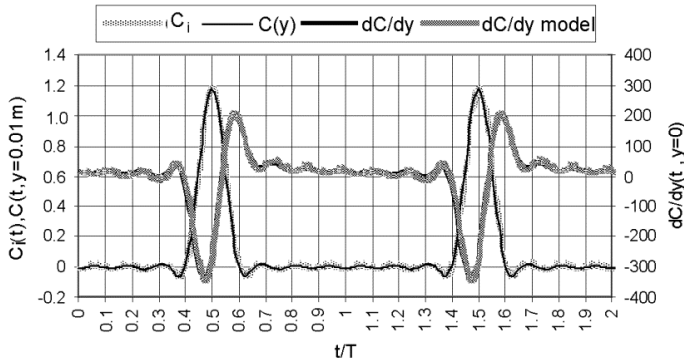The average absolute error for a single gradient value = 27.96 g/m^4

Fig. 3. Concentrations at a phase boundary, concentration at a distance of $y = 1\times10^{-6}$ m
in a solid phase, gradient of concentration at a phase boundary and gradient calculated using
model Eq. (10); $T = 86\,400$ s, $C_{i,a} = 1$ g/m^3, $\Delta\tau = T/16$, $k_r = 1\times10^{-30}$ s^{-1}, $D = 1.71.7\times10^{-9}$ m^2/s.
The average absolute error for a single gradient value is 5.89 g/m^4

Model (8) shows substantial errors in calculations of the mass balance [6] (Fig. 3) and errors in calculations of the concentration gradient (Fig. 2) [6]. Its accuracy may still be improved by introducing a derivative of the concentration with respect to time, as it was proposed in previously (model (26) [1]). Then the model takes the form of:

$$\frac{dC}{dy} = a_1 C_i(t) + a_2 \left.\frac{dC_i}{dt}\right|_t + a_3 \int_0^t \frac{dC}{dy} d\tau + a_4 \tag{10}$$

In the above equation, a constant a_4 represents an initial value of absorption or adsorption – the value is zero in a particular case of an organic tracer introduced in an impulse mode. A term with the concentration gradient integral is responsible for desorption of the material back to a solid phase. The integral of a concentration gradient is proportional to the current value of absorption or adsorption. If the substance present in a solid phase is completely desorbed, the value of the integral is zero.

Minimization of the product of a sum of squared deviations for both gradient and mass balances allowed one to determine the values of the coefficients in Eq. (10) for the concentration curve presented in Fig. 5 of [1]. Now, the equation for the concentration gradient takes the following form:

$$\frac{dC}{dy} = (-224.30)C_i(t) + (-92.478\times10^4)\left.\frac{dC_i}{dt}\right|_t$$
$$+(-4.0725\times10^{-5})\int_0^t \frac{dC}{dy} d\tau + 15.209 \tag{11}$$

Model (11) shows minor errors in calculation of the concentration gradient (Fig. 3) and a mass balance [6]. In Equation (11), the value of a_4 different from zero is related to a periodic occurrence of impulses. Therefore, the average amount of absorbed or adsorbed substance in a solid phase does not approach zero. It may be concluded that hardly any desorption process takes place, hence the concentration gradient should take a positive sign and such situation occurs since a_4 is positive.

Model (10) after its generalization may also be used as a tool for description of processes of absorption or adsorption accompanied with a chemical reaction in both liquid and solid phases.

If the reaction proceeds in solid phase with the rate $(-k_r a)$, the concentration gradient has the following form:

$$\frac{dc}{dy} = -\frac{K}{D}c - \left(\frac{K}{\Gamma L_0} + k_r\right)\int_0^t \frac{dc}{dy} d\tau + \frac{K}{D\Gamma}a(t=0,x) - \frac{Kk_r}{D}\int_0^t c\, d\tau \tag{12}$$

In such a situation, the concentration gradient is expressed using the relationship similar to Eq. (10) including also the concentration integral in function of time (under a momentary assumption that: $c \Leftrightarrow C_i$)

$$\frac{dC}{dy} = a_1 C_i(t) + a_2 \left.\frac{dC_i}{dt}\right|_t + a_3 \int_0^t \frac{dC}{dy} d\tau + a_4 + a_5 \int_0^t C_i d\tau \tag{13}$$

If the term including the concentration differential with respect to time is ignored in the above equation, the gradient and mass balance values are calculated with errors [6].

Based on Fick's law (Eq. (23), [1]) [4] and the concentration gradient (Eq. (12)) rates r of absorption or adsorption accompanied with a chemical reaction with respect to a liquid phase may be calculated as:

$$r = -\frac{dm}{dt}\frac{1}{V^*} = -\left(-D\frac{A^*}{V^*}\frac{dc}{dy}\right) = \frac{D}{h}\frac{dc}{dy}$$

$$= -\frac{K}{h}c - \left(\frac{K}{\Gamma L_0} + k_r\right)\int_0^t \frac{D}{h}\frac{dc}{dy} d\tau + \frac{K}{h\Gamma}a(t=0,x) - \frac{Kk_r}{h}\int_0^t c\, d\tau \tag{14}$$

$$= -\frac{K}{h}c - \left(\frac{K}{\Gamma L_0} + k_r\right)\int_0^t r\, d\tau + \frac{K}{h\Gamma}a(t=0,x) - \frac{Kk_r}{h}\int_0^t c\, d\tau$$

Since the overall process rate in the liquid phase is:

$$r_{og} = r - k_c c \tag{15}$$

(rate of chemical reaction is $(-k_r c)$), based on Eq. (14), the following may be written:

$$r_{og} = -\left(\frac{K}{h} + k_c\right)c - \left(\frac{K}{\Gamma L_0} + k_r\right)\int_0^t r_{og}\, d\tau + \frac{K}{h\Gamma}a(t=0,x)$$

$$- \left[\frac{Kk_r}{h} + k_c\left(\frac{K}{\Gamma L_0} + k_r\right)\right]\int_0^t c\, d\tau \tag{16}$$

Considering a differential of concentration with respect to time in the equation for an overall process rate in a liquid phase, Eq. (16) takes the form:

$$r_{og} = a_1' C_i + a_2' \left.\frac{dC_i}{dt}\right|_t + a_3 \int_0^t r_{og}\, d\tau + a_4' + a_5' \int_0^t C_i\, d\tau \tag{17}$$

under the assumption that $c \Leftrightarrow C_i$.

Parameter $a_2' = (D/h)a_2$ because after inserting the gradient equation, for example Eq. (13) to Eq. (14), the parameter a_2 will be multiplied through fraction (D/h).

In the case of the concentration related to the core of a liquid phase, it may be written that:

$$r_{og} = a_1'\, c + a_2' \left.\frac{dc}{dt}\right|_t + a_3' \int_0^t r_{og}\, d\tau + a_4' + a_5' \int_0^t c\, d\tau \tag{18}$$

Equation (18) describes a general process rate of absorption and adsorption at a linear interphase equilibrium accompanied with chemical reactions taking place in both solid and liquid phases; the reactions follow a monomolecular first order reaction mechanism, at an unsteady state with respect to a liquid phase. Parameters a_1', a_4', a_5' and probably a_2' (uncertainty origins from both analysis of a mass transport equation that includes absorption or adsorption processes carried on through an equilibrium states and Eq. (16)) depend on the water level h.

Coefficients $a_1', a_2', a_3, a_4', a_5'$ are characteristic of a certain type of wave. By changing wave parameters, e.g. the period T, number of harmonics, impulse duration, etc., parameters of Eq. (18) change as well.

2. POLLUTANT TRANSPORT MODEL

Advection-diffusion transport of any substance in natural water courses may be accompanied with chemical and/or physical processes such as absorption and adsorption. The absorption and adsorption process rates are expressed as functions depending on concentrations of the analyzed substances within the phases participating in transport (e.g. liquid phase – water, solid phase related with water course sediment).

Substituting the overall rate (Eq. (18)) into a pollutant transport equation [7–14]:

$$\frac{\partial c}{\partial t} + V\frac{\partial c}{\partial x} = \frac{1}{A} \cdot \frac{\partial}{\partial x}\left(E_x A \frac{\partial c}{\partial x}\right) + r_{og} \tag{19}$$

we arrive at an equation where the concentration derivative with respect to time is multiplied by a coefficient higher than 1 $(1+|a_2'|)$. Such a situation is similar to the one that occurs in the mass transport equation which takes into account processes of adsorption or absorption proceeding through the equilibrium states.

Using a classical approach of the mass transport model with other processes proceeding with no equilibrium, the set of equations would be expressed as follows (case with a linear isotherm):

$$\frac{\partial c}{\partial t} + V\frac{\partial c}{\partial x} = \frac{1}{A} \cdot \frac{\partial}{\partial x}\left(E_x A \frac{\partial c}{\partial x}\right) - \frac{K}{h}\left(c - c^*\right) - k_c c \tag{20}$$

$$\frac{da}{dt} = \frac{K}{L_0}\left(c - c^*\right) - k_r a \tag{21}$$

$$a = \Gamma c^* \tag{22}$$

The set of equations does not have any additional term assigned to the concentration differential with respect to time, therefore calculations based on from Eqs. (20)–(22) would not give an accurate results.

Introduction of a new term at a differential $\partial c/\partial t$ in Eq. (20) leads to a model that consists of three equations:

$$\left(1 - \frac{D}{h} a_2\right)\frac{\partial c}{\partial t} + V\frac{\partial c}{\partial x} = \frac{1}{A} \cdot \frac{\partial}{\partial x}\left(E_x A\frac{\partial c}{\partial x}\right) - \frac{K}{h}\left(c - c^*\right) - k_c c \tag{23}$$

$$\frac{\partial a}{\partial t} = \frac{K}{L_0}\left(c - c^*\right) - \frac{D}{L_0} a_2 \frac{\partial c}{\partial t} - k_r a \tag{24}$$

$$a = \Gamma c^* \tag{25}$$

Integrated with respect to time, Eq. (24) yields the dependence:

$$a(x,t) = \int_0^t \left(\frac{K}{L_0}\left(c(x,\tau) - c^*(x,\tau)\right) - k_r a(x,\tau)\right)d\tau$$
$$- \frac{D}{L_0} a_2 c(x,t) + \frac{D}{L_0} a_2 c_0(x) + a_0(x) \tag{26}$$

which may be easier to use in numerical applications.

To solve the set of the above equations, the following conditions have to be formulated:

1. Initial condition:

$$C(x, t = 0) = C_0(x) \tag{27}$$

2. Boundary conditions related to:
a) concentration changes in the initial cross-section:

$$C(x = 0, t) = C_p(t) \tag{28}$$

b) changes of the concentration gradient in the final cross-section (Neumann's condition [15–19]:

$$\left.\frac{\partial C}{\partial x}\right|_{x = L_{odc}, t} = 0 \tag{29}$$

(L_{odc} is the length of the water course segment)

3. Initial condition for adsorption or absorption:

$$a(x, t = 0) = a_0(x) \tag{30}$$

It should be noted, however that if a thermodynamic equilibrium exists between the phases at the initial moment, Eq. (25) or a similar one resulting from the actual isotherm has to be true. In particular, for a pure solid phase:

$$a(x, t = 0) = 0 \tag{31}$$

though, if an interfacial equilibrium exists, concentrations in a liquid phase are also zero, at the initial moment.

3. THEORETICAL ANALYSIS OF THE MASS TRANSPORT MODEL INCLUDING ABSORPTION OR ADSORPTION RATES

The mass transport model, including absorption and/or adsorption, comprises three equations: advection and diffusion in a liquid phase (Eq. (23)), absorption and/or adsorption rate (Eq. (24)) and interfacial equilibrium equation (Eq. (25), in this case Henry's law). Equations (23) and (24) meet the conditions of the mass conservation law for the system [6].

If adsorption or absorption processes proceed through the equilibrium states, it may be shown that the model of mass transport fulfils the equations:

$$\left(1 + \Gamma \frac{L_0}{h}\right) \frac{\partial c}{\partial t} + V \frac{\partial c}{\partial x} = \frac{1}{A} \frac{\partial}{\partial x}\left(A E_x \frac{\partial c}{\partial x}\right) + r + \frac{q_L}{A}(c_d - c) \tag{32}$$

whereas the rate of changes of adsorption or absorption level is [6]:

$$\frac{\partial a}{\partial t} = \frac{K}{L_0}\left(c - \frac{a}{\Gamma}\right) + \Gamma \frac{\partial c}{\partial t} \varepsilon \tag{33}$$

Comparing Equations (33) and (24), as well as considering Eq. (25), the following relationship is obtained:

$$-Da_2 \Leftrightarrow \Gamma L_0 \varepsilon \tag{34}$$

A similarity of Eqs. (33) and (24) means that the set of Eqs. (23)–(25) may be used to simulate mass transport accompanied with adsorption/absorption processes proceeding at a finite rate through the equilibrium states. It may also be used in both cases simultaneously, when the sediment material consists of fractions that show different physicochemical affinity to a substance transported in the water phase.

4. IDENTIFICATION OF A MASS TRANSPORT MODEL
ACCOMPANIED WITH ABSORPTION PROCESSES

The set of Eqs. (23)–(25) was used to describe propagation of copper sulfate in water. Water passed through a glass pipe partially filled with glass balls; the pipe length L_{odc} was ca. 0.70 m, its diameter d ca. 3 cm. In order to obtain very accurate results of measurements, the experiment was conducted in the laboratory. The pipe was slightly tilted up from its horizontal position and its upper end was equipped with an air release valve. This way the volume of a gas phase that built up over the water surface (air and water vapour) could be minimized. Water flowed over the entire cross-section of the pipe and only at the very end of the pipe both gas phase and free water level were present. Flow-through conductometric sensors were mounted at the both sides of the pipe to measure the conductivity in a real time. After calibration of sensors, it was possible to convert the measured conductivity into copper sulfate concentration. Along the lower end of a pipe wall glass balls were placed; the ball diameter was 3 mm, thickness of a ball layer ca. 1.13 cm.

A polyethylene capillary was introduced inside the layer of glass balls and close to the air release valve, at the upper end of the pipe. The capillary enabled one to draw a sample from the inside of the glass ball layer. The layer of the glass balls together with water immobilized inside the layer was considered a solid phase with mostly absorption properties. Adsorption of copper ions on glass is very low if compared with their absorption in water that filled the space between glass balls. Therefore, it was absorption that was considered a leading process in a layer of balls. It was assumed that water motion in the interspace between balls is negligible if compared with the main stream motion over the glass ball layer and is therefore not considered in the transport of copper sulfate. During the experiment, water of high purity (specific conductivity of about 1 µS/cm) was used as a liquid phase. Conductivity of pure water was used as a reference value to calculate the copper sulfate concentration. Conductivity measurements were performed including the temperature compensation coefficient of 0.02 °C^{-1}. Temperature of 25 °C was the reference temperature. All conductivity measurements were automatically converted to the values at the reference temperature. It was found that the relationship between specific conductivity S [µS/cm], and the concentration C [mol $CuSO_4 \cdot 5H_2O$/m^3] was as follows:

$$C = S^{1.0566}\left(3.7361 \times 10^{-3} + 5.4493 \times 10^{-6} S^{0.65704}\right) \tag{35}$$

(Note: The values of the specific conductivity S in Eq. (35) are the readings of the conductometers for which the measuring constants were set in such a way as to make their readings identical. Hence, the results of Eq. (35) may slightly differ from the real values.)

4.1. EXPERIMENTAL RUNS

1 M copper sulfate solution was injected with a syringe to the water stream passing through the pipe connected to the exit electrode. Characteristic of an input impulse is presented in Fig. 4. In practice, the volume of a copper sulfate solution injected to the water did not change the flow volume of $Q = 3.48$ cm^3/s. The volume of the pipe V^* that extended over the layer of glass balls was estimated as ca. 228 cm^3. Based on this volume, the average hydraulic detention time in the system ($t_m = 228$ cm^3 /3.48 cm^3/s = 65.59) as well as the average velocity $V = 0.70$ m/65.59 s = 1.067×10^{-2} m/s were calculated. It should be noted that, the velocity calculated this way is lower than the real mass advection velocity; the difference may be attributed to the boundary layer present next to glass balls. Therefore, the actual volume V^* of the liquid core was smaller than 228 cm^3 and the estimated velocity V was just an approximation of the real advection velocity.
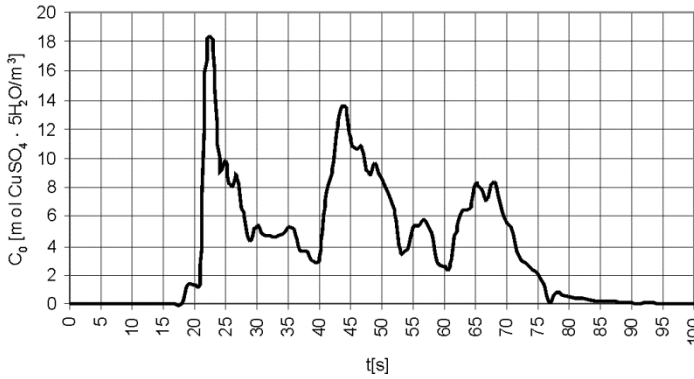

Fig. 4. Characteristic of the input impulse

Once the copper sulfate solution was introduced into the water stream, the conductivity measurements were performed every 1 s and every 2 s, at the inlet and outlet of the system, respectively. Measurements were recorded automatically with a computer.

4.2. ESTIMATION OF MODEL PARAMETERS

In simulation calculations the model was used that comprised Eqs. (23)–(25). Additionally, a complementary variable S_{T6} and porosity of a balls layer ε_0 were introduced to the model. Finally, the model could be written as:

$$\left(1 - \frac{\dfrac{D}{h}}{S_{T6}} a_2\right)\frac{\partial c}{\partial t} + VS_{T6}\frac{\partial c}{\partial x} = \frac{1}{A} \cdot \frac{\partial}{\partial x}\left(E_x A \frac{\partial c}{\partial x}\right) - \frac{K}{\dfrac{h}{S_{T6}}}\left(c - c^*\right) - k_c c \qquad (36)$$

$$\frac{\partial a}{\partial t} = \frac{K}{\varepsilon_0 L_0}\left(c - c^*\right) - \frac{D}{\varepsilon_0 L_0}a_2\frac{\partial c}{\partial t} - k_r a \tag{37}$$

$$a = \Gamma c^* \tag{38}$$

The constant S_{T6} was introduced in order to compensate for the error caused by a rather rough determination of an advection velocity V. Since the velocity V increased along with a decrease of the water depth h, the term (h/S_{T6}) in Eq. (36) appeared. Porosity ε_0 of the layer of glass balls in Eq. (37) resulted from the assumption that copper salts were absorbed mostly by water that filled void spaces between balls. Therefore, based on the mass balance, thickness of the layer of glass ball L_0 had to be multiplied by ε_0.

The values of some model parameters were assumed for the calculations: $h = 0.0109$ m, $V = 0.0107$ m/s, $A = 3.26\times10^{-4}$ m^2, $k_c = 0$, $\varepsilon_0 = 0.409$, $L_0 = 0.0113$ m, $k_r = 0$. The main goal of the experiment was to determine the values of the parameters or expressions: E_x, Da_2, K, Γ and S_{T6}, based on the experimental results.

The parameter values of model (Eqs. (36)–(38)) were identified using measurements of copper sulfate concentration in water passing through the installation. Additionally, the measurements of the concentration of copper sulfate in a layer of glass balls were considered (absorption point in Table 1). The values of model parameters were determined by minimizing the sum of squared deviations between measured and calculated values. The function was minimized according to the simplex method of Nelder–Mead [20, 21].

Table 1

Results of estimation of the model parameters[a]

Parameter or expression	One absorption point	One absorption point	Initial values		No absorption point	Two absorption points
			No absorption point	No absorption point v2		
1	2	3	4	5	6	7
E_x [10^{-4} m^2/s]	1.0236	0.61180	1.0829	5.2839	0.69805	0.42996
Da_2 [10^{-3} m]	−1.2966	–	−0.64980	−7.9260	–	–
K [10^{-5} m/s]	8.6887	22.870	6.8685	23.236	10.849	22.873
Γ	1.0976	0.70157	1.0007	2.4553	0.68493	1.0156
S_{T6}	1.3146	1.3874	1.2030	6.9646	1.2136	1.3676
Average absolute error model fitting [mol CuSO$_4$·5H$_2$O/m^3]	0.002098	0.005491	0.004133	0.004407	0.006549	0.009507

[a]Coordinates of the experimental absorption point: $t = 92$ s, $c = 2.430$ mol CuSO$_4$·5H$_2$O/m^3, coordinates of the theoretical absorption point $t = 180$ s, $c = 1.637$ mol CuSO$_4$·5H$_2$O/m^3.

From the mathematical point of view, the model parameters may also be determined if concentration measurements in a layer of glass balls are not considered (Ta-

ble 1, columns 4 and 5). In such a case, tough approximation of the model parameters may by ambiguous due to a multiminimum character of the sum of squared deviations between calculated and measured concentrations. The results presented in column 2 of Table 1 served as a basis for the essential plots that were later compared to the plots referring to the columns 3, 4 and 6.
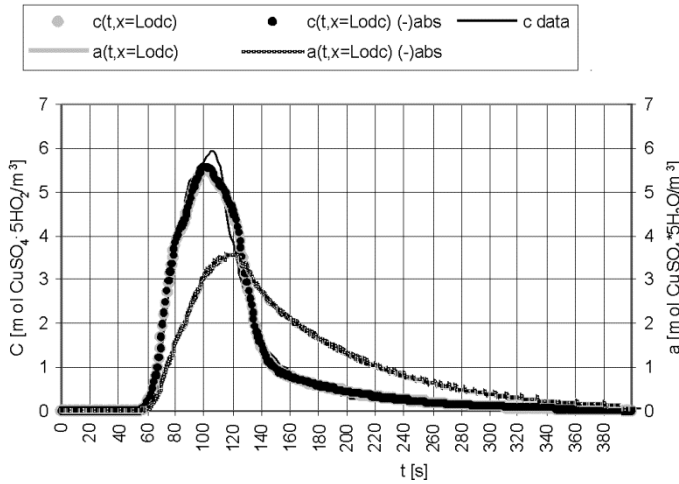

Fig. 5. Concentration *c* and absorption *a* curves obtained from the model (Eqs. (36)–(38))
for data with absorption (Table 1, column 2) and without absorption ((−)abs) (Table 1, column 4)
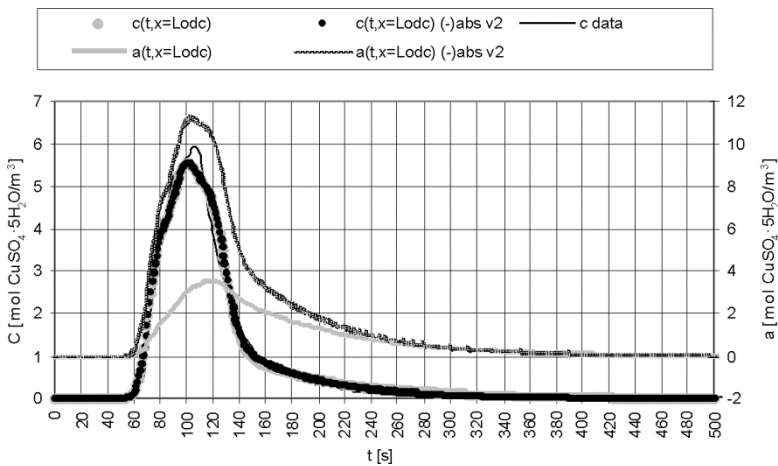

Fig. 6. Concentration *c* and absorption *a* curves obtained from the model Eqs. (36)–(38)
for data with absorption (Table 1, column 2) and without absorption ((−)abs v2) (Table 1, column 5)

Model parameters that have been determined based on the data both including and neglecting absorption level may assume similar or significantly different values (Ta-

ble 1, columns: 2, 4 and 5). If the values are similar, the curves representing concentration c and absorption level a (Fig. 5) are also similar. Depending on the input values of model parameters, rather poor probability of the model parameters may be obtained after minimization of the sum of squared deviations (Table 1, column 5). A low value of the average absolute error of the model fitting, if compared with other errors, does not guarantee that the parameters values are accurate (Table 1, column 5). Curves of concentration c are in this case also similar, but the absorption level assumes irrational values (Fig. 6; concentrations in the absorption layer cannot exceed in this case concentrations in the liquid phase). The value of the absorption coefficient Γ is close to 1.0 in this experiment (for the system water in a liquid phase – water in a solid phase of glass balls). The value of 2.4553 (Table 1, column 5) cannot refer to this phase system, although such a value is entirely correct just from the mathematical point of view. Questionable value of the coefficient Γ causes that the values of other parameters should also be considered as unlikely.

From the above discussion, it may be concluded that if the model (36)–(38) is to be used to analyze the quantity of substance in an absorption layer, it is necessary to obtain information on concentrations in this layer. Estimation of model parameters based on concentrations in just a mobile liquid phase may give wrong estimates. The results of actual measurements concerning liquid phase are usually used while modelling processes of pollutant transport in rivers, lakes, sea etc. Such approach may result in poor estimation of model parameters. It should be stressed that transport of any substance in any medium (natural or man-mad, e.g. pipe, wastewater drain, chemical reactor) is always accompanied with absorption and/or adsorption processes – to less or more extend. Absorption processes may also be analyzed with respect to dead zones in units that carry the flow. Therefore, if the theoretical model has to describe accurately the course of the real-life processes, it is recommended to use the specific measuring data that enable one to determine the model parameter values. It should be noted that in the case of natural water bodies: rivers, lakes, sea etc., the values of Da_2 and Γ are not known. Evaluation of the values of the parameters using other methods would not be much reliable. Therefore, they have to be estimated simultaneously with the values of other model parameters, and as such require the specific data.

Determination of concentrations in an absorption layer is difficult since measurements in this layer cause turmoil that interfere with the absorption process. In the experiment, in order to determine the concentration a, the sample volume of ca. 0.1 cm^3 was taken from the layer core.

Assume that the product Da_2 serves only as a correction factor for Whitman's model to compensate for unsteady state conditions. Then, based on the estimated value -1.2966×10^{-3} m (Table 1, column 2), using equations published elsewhere (Eqs. (19), (22c) [1]) and assuming that the chemical process rate constant k_r is 0 and the average wave period $T \approx 200$ s, it is possible to determine the value of the effective coefficient of turbulent diffusion from a liquid to solid phase. In this case

$D = E_z = 1.06 \times 10^{-7}$ m^2/s; the value is ca. 106 times higher than the molecular diffusion coefficient for copper sulfate.
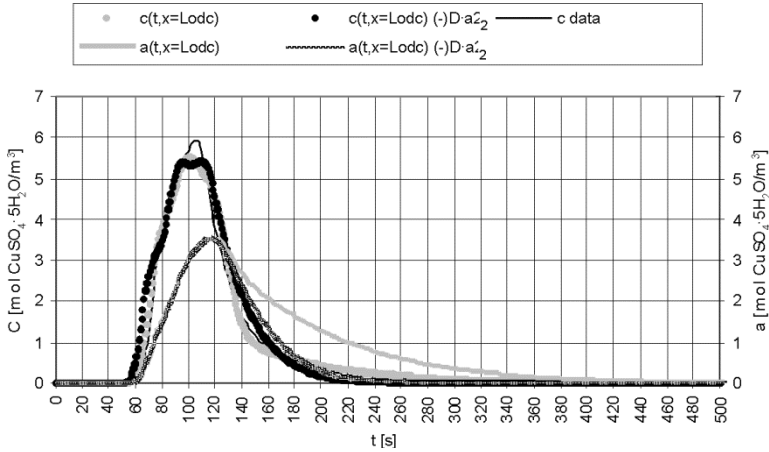

Fig. 7. Concentration c and absorption a curves obtained from the model (Eqs. (36)–(38)) (Table 1, column 2) and model (Eqs. (36)–(38)) without term Da_2 ((–)Da_2) (Table 1, column 3)
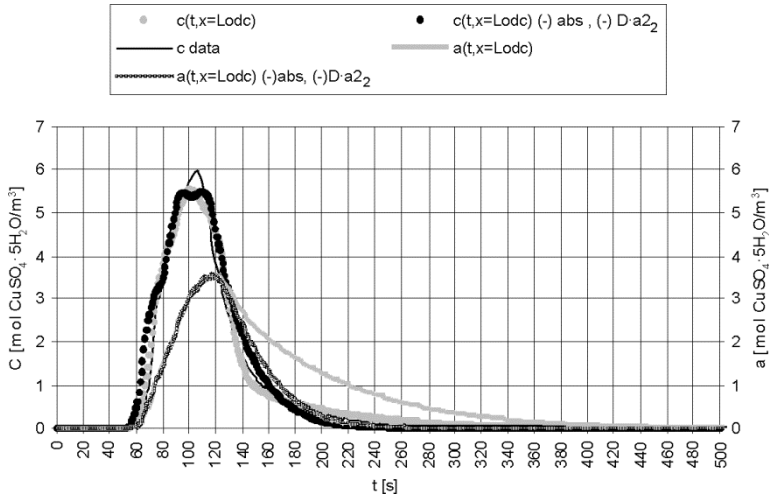

Fig. 8. Concentration c and absorption a curves using model (Eqs. (36)–(38)) for the data including absorption (Table 1, column 2) and model (Eqs. (36)–(38)) without term Da_2 ((-)Da_2) for the data without absorption ((–)abs) (Table 1, column 6)

Neglecting the term Da_2 in the model (Eqs. (36)–(38)) makes the model less accurate (the average absolute error of the model fit increases, Table 1, columns 3 and 6; Figs. 7 and 8). Absorption coefficients Γ are lower than the theoretical one, which is close to one. Also other values of the model parameters differ, specially the ab-

sorption rate constant K. Major differences occur also between the values of model parameters presented in Table 1, columns 3 and 6, and the values of a complete model parameters with absorption (Table 1, column 2). Neglecting the term Da_2 in the model (Eqs. (36)–(38)) results in lower model accuracy in terms of concentration c and absorption level a (Figs. 7 and 8).

If two absorption points were considered in estimation of model parameters (Eqs. (36)–(38), neglecting term Da_2), the measured one and the one from the theoretical calculations using the complete model (Table 1, column 2), the absorption level a would be improved (Fig. 9) but the average absolute error of the model fit would reach its maximum value (Table 1, column 7).
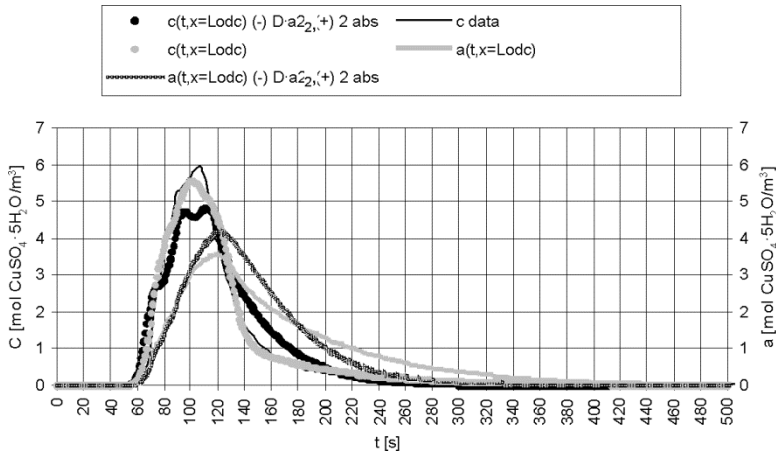

Fig. 9. Concentration c and absorption a curves obtained from model (Eqs. (36)–(38)) for the data including absorption (Table 1, column 2) and model (Eqs. (36)–(38)) without term Da_2 (($-$)Da_2) for data considering two absorption points (($+$)2 abs) from measurements and theoretical calculations (Table 1, column 7)

If the term Da_2 is neglected, fitting of the model (Eqs. (36)–(38)) becomes inadequate and its description of the real-life processes becomes less accurate. The same conclusion is true for the model of Eqs. (23)–(25). The described model has been also used for tracer transport modelling in the Colorado River, USA.

5. SUMMARY AND CONCLUSIONS

Application of Whitman's model for description of mass penetration due to absorption and adsorption mechanism in the solid phase enables one to determine the mass flux. The calculated flux values may differ from the real values depending on the character of concentration changes in time at the phase boundary. Analysis of dynamics of concentration changes within the solid phase, obtained due to integration of the

equation of diffusion in unsteady states, enables one to determine the real mass flux with respect to time. In order to decrease the discrepancies between the mass flux calculated from Whitman's model and the real mass flux, it is necessary to introduce the correction factor to the equation describing the concentration gradient close to the phase boundary in a solid phase. The correction factor may be expressed as the product of a certain parameter and the concentration derivative with respect to time, at a phase boundary. The parameter is equivalent to the coefficient a_2 (Eq. (22c), [1])) and therefore, it would be a function of: the concentration wave period, rate constant of chemical processes and the diffusion coefficient. The model comprises Eqs. (23)–(25) including the correction factor that incorporates the concentration derivative with respect to time. The model may be applied to simulate transport of pollutants which are subjected to adsorption or absorption processes in a river sediment layer. The processes proceed at a finite and an infinitely large rates through the equilibrium states. Therefore, the coefficient a_2 stands for the correction factor improving accuracy of Whitman's model and the parameter characterizing adsorption/absorption processes proceeding through the equilibrium states, simultaneously.

Model (23)–(25) was used to describe mass transport in a measuring apparatus; the experiments were conducted in a lab and in a full-scale model (river). The model accuracy improved when the term Da_2 was different from zero. Knowing the value of this term, one can estimate the effective coefficient of turbulent diffusion in the direction of the phase boundary, where the mass transport occurs.

SYMBOLS

$(1/2)A_0$ – average concentration C_i, g/m³
A – surface area, m²
A^* – surface normal to diffusion direction, m²
A_n, B_n – coefficients of a trigonometric series, g/m³
C, c – concentration, g/m³
$\tilde{C}$ – concentration in a phase core, g/m³
$\tilde{C}_m$ – average concentration within a phase core, g/m³
$\tilde{C}_{m,0}$ – average concentration in a phase core at an initial river cross-section, g/m³
$\tilde{C}_{m,\text{srd}}$ – average concentration in a phase core for a water course segment, g/m³
$\tilde{C}_a$ – concentration amplitude in a phase core, g/m³
$\hat{C}$ – Laplace transformation of a concentration function
C_i – concentration at a phase boundary, g/m³
$C_{i,m}$ – average concentration at a phase boundary, g/m³
$C_{i,a}$ – concentration amplitude at a phase boundary, g/m³
$\hat{C}_i$ – Laplace transformation of a concentration at a phase boundary, g/m³
D – diffusion coefficient, m²/s
E_x – longitudinal dispersion coefficient, m²/s
E_z – coefficient of vertical turbulent diffusion (perpendicular to a solid phase surface), m²/s

f	–	function
G	–	transmittance
g	–	acceleration of gravity
h	–	water level or the average water level in a river, m
i	–	drop of a water level in a water course, unless stated otherwise
I	–	imaginary unit,
k_r	–	process rate constant, 1/s
k_w	–	coefficient of mass transfer at a liquid phase side, m/s; in the case of few different phases indexes: 1, 2, etc. are used; units may differ depending on the formula
$k_{z,og}$	–	overall equivalent rate constant for all processes occurring in liquid and solid phases, s^{-1}
L, L_0	–	thickness of a solid phase layer, m
L_{odc}	–	length of water course segment, m
M	–	transmittance module $|G|$
m	–	mass, g
$r(\tilde{C})$	–	process rate in the liquid phase core, g/(m^3·s)
r_{og}	–	total process rate, g/(m^3·s)
R_h	–	hydraulic radius, m],
re(...)	–	real part of complex variables
im(...)	–	imaginary part of complex variables
s	–	complex variable
t	–	time, s
t_{01}, t_{02}	–	time of appearing and disappearing of a concentration impulse in a initial river cross-section, s
t_{k1}, t_{k2}	–	time of appearing and disappearing of a concentration impulse in a final river cross-section, s
T	–	period of a function, s
V	–	velocity, m/s
V_{srd}	–	average velocity, m/s
V^*	–	liquid phase volume, m^3
x	–	linear coordinate (longitudinal for a river), m
y	–	linear coordinate, m

GREEK SYMBOLS

α_M, γ_M	–	complementary parameters
Δt	–	time difference or time shift, s
$\Delta t_1, \Delta t_2$	–	time shifts, s
$\Delta t_0, \Delta t_k$	–	time differences, s
$\Delta \tau$	–	impulse time, s
φ	–	argument of transmittance G, rad
ω	–	angular velocity, rad/s
ω_0	–	angular velocity for the main harmonic, rad/s
Ω_1, Ω_2	–	integration constants

SELECTED SUBSCRIPTS

i	–	concentration at a phase boundary
a	–	amplitude, unless the list of variables states otherwise
m	–	average value, unless the list of variables states otherwise

SELECTED SUPERSCRIPTS

~	–	phase core (in the case of concentration)
^	–	Laplace transformation

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