ANDRZEJ BIELSKI*

MODELLING OF MASS TRANSPORT IN WATERCOURSES CONSIDERING MASS TRANSFER BETWEEN PHASES IN UNSTEADY STATES. PART I. MASS TRANSFER PROCESS FOR PERIODIC AND APERIODIC CHANGES OF CONCENTRATION

A model most often used for the description of the processes of mass transport through phase boundaries is the model of Whitman. Results of calculations obtained using this model may occasionally considerably differ from the results obtained using diffusion models. Thus an attempt has been made to correct the model proposed by Whitman. The dynamics of the processes of mass transport from a liquid phase (river water) to a solid phase (layer of material in the river bottom) has been analysed. Several equations have been derived describing the rate of absorption with a chemical reaction and periodical changes of the concentration of the analysed substance. An attempt has been made to determine the relation between the concentration gradient and concentration at the phase boundary. In dynamic conditions, the concentration gradient at the phase boundary can be approximated by means of time dependence of a linear combination of concentration, delayed concentration, and concentration derivative at the phase boundary. Analysis of the dynamics of the absorption process with the chemical reaction enabled one to derive an equation describing the stream of the substance penetrating to the inside of the solid phase. Such equations may be used to determine the error generated by the film model of Whitman for the process of mass penetration.

1. INTRODUCTION

More and more complex models have been developed to describe propagation of various kinds of substances in water environment. The models take into consideration transformation rates of substances as well as rates of their interactions with other components of the environment. Therefore, it is possible to describe, in a more accurate way, the actual processes to which the substances are subjected as well as to determine exact substance quantities in a definite place and time. All the models require that numerical values of some parameters be identified; more elaborate models require

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

more parameters to be known. Identification of numerical values of the parameters is usually not easy. Most of the time both specific field investigations and laboratory tests are required. Some investigations and tests allow one to identify just one parameter while in the case of other parameters simultaneous determination of several numerical values is required. Such parameters include: motion resistance coefficient of a flow wave, coefficient of mass dispersion, rate constants of chemical or physical processes that influence that substance.

If biochemical, chemical and physical process rates are considered, appropriate kinetic equations have to be developed. Since the mass transport model for unsteady states (flows varying in time) is very complicated, kinetic equations should remain rather simple. It should be noted however that too much simplifications may result in poor model accuracy. Particularly demanding, in terms of good qualitative description, are processes of mass exchange between different phases (e.g.: atmospheric air–water, water–river sediment, water–algae etc.).

The Whitman model has been most frequently used for description of mass transport through a phase boundary [5, 8, 10, 11]. Results of calculations based on this model may occasionally considerably differ from the results obtained using diffusion models. The differences may be explained by concentration profiles directed along diffusion which are time dependent. Since the Whitman model does not consider such dependences, an attempt to improve the Whitman model has been made.

Kinetics of mass transport in sorption processes may be described by the pseudo second order model [3, 4, 6, 9], however it is useless for desorption processes, because the model does not provide possibility to change the sign of process rate. Consideration of adsorption-absorption effect in mass transport equations needs occasionally some modifications. In the paper, several equations will be derived taking into consideration adsorption-absorption effects, which influence mass transport in natural water systems.

Diffusion processes may be accompanied by chemical and biological ones. The rate of biological and chemical processes proceeding in a separate phase may have a major impact on the concentration of a substance in the liquid phase (water). Therefore, a number of new equations will be derived describing total diffusion rate of a substance into a separate phase accompanied with a simultaneous chemical reaction. The paper focuses on the problems of adsorption-absorption rates in unsteady states.

At the beginning, the concepts of: liquid phase (water) and solid phase (river sediment, e.g. mineral solids, organic solids, rock material, water bound in a sediment, etc.) have been defined. Then it was assumed that the solid phase consists of two compounds where either an adsorption process or chemical/biochemical processes take place but never both these processes occur simultaneously. It was also assumed that no mass transfer occurs between two compounds of the solid phase, and the adsorption refers only to mineral or organic solids deposited at the bottom of the river. On the other hand, absorption refers to water bound in material deposited at the bottom sediment.

It was also assumed that characteristic of river bottom material does not change in time (neither new sediment layers are built up nor erosion proceeds) and there is no water motion in river sediments. Moreover, accumulation of mass of the analyzed substance in cells of microorganisms present in both liquid and solid phases is ignored.

2. DIFFUSION MASS TRANSPORT WITHIN A PHASE

Diffusion of a substance of concentration C accompanied with a chemical or biochemical reaction in a solid phase of a watercourse following monomolecular first order mechanism is expressed by:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial y^2} - k_r C, \tag{1}$$

where the coordinate y is the distance from the phase boundary in the solid phase.
Let us assume for the solid phase:
• initial conditions:

$$C(t=0, y) = 0, \tag{2}$$

$$C(t, y=0) = C_i; \tag{3}$$

• boundary conditions:
– for a layer of unlimited thickness

$$C(t, y \to \infty) = 0, \tag{4a}$$

– for a layer of thickness L

$$\left.\frac{\partial C}{\partial y}\right|_{t, y=L} = 0. \tag{4b}$$

It is hard to precisely determine the thickness of a bottom sediment layer where diffusion process takes place; in theory, the layer may by of any thickness. It was assumed that the analyzed layer would have such thickness that the concentration distribution within the layer would be similar to the distribution in the layer of an infinite thickness.

Solution of Eqs. (1) with conditions: (2), (3), (4a) in the form of Laplace transformation is as follows:

$$\hat{C} = \frac{C_i}{s}\exp\left(-\sqrt{\frac{s+k_r}{D}}y\right), \tag{5}$$

whereas for conditions: (2), (3), (4b), the solution of Eq. (1) takes the form:

$$\hat{C} = \frac{C_i}{s} \frac{\exp\left(-\sqrt{\dfrac{s+k_r}{D}}\, y\right)}{1+\exp\left(-\sqrt{\dfrac{s+k_r}{D}}\, L\right)} + \frac{C_i}{s} \frac{\exp\left(-\sqrt{\dfrac{s+k_r}{D}}\,(2L-y)\right)}{1+\exp\left(-\sqrt{\dfrac{s+k_r}{D}}\, L\right)}, \qquad (6)$$

where $y \in\ <0, L>$.

If only the thickness of a layer L is large enough and the concentration distribution next to the phase boundary ($y << L$) is examined, Eq. (6) may be approximated with the solution (5). If a complex variable s is substituted with a product: $I\omega$ ($I = \sqrt{-1}$), the transmittance $G = \hat{C}/\hat{C}_i$ can be calculated from Eqs. (5) and (6) as well as corresponding modules $|G|$ (coefficients of attenuation of a concentration amplitude M) and arguments $\arg(G)$ (phase shift φ) [7].

Assume that periodic changes of concentrations C_i at the phase boundary are represented by the function expanding in a trigonometric series in a form of:

$$C_i = \frac{1}{2} A_0 + \sum_{n=1}^{\infty} \left[A_n \sin(n\omega) + B_n \cos(n\omega) \right], \qquad (7)$$

$$\omega = \frac{2\pi}{T}, \qquad (8)$$

where: $(1/2)A_0$ is the average value of concentration C_i, A_n, B_n – the coefficients of trigonometric series, T – period of the concentration function C_i.

In such a case, stabilized changes of concentrations within the layer can be expressed by the following equation:

$$C(y,t) = \frac{1}{2} A_0 M(\omega = 0)$$
$$+ \sum_{n=1}^{+\infty} \left\{ M(n\omega) \left[A_n \sin(n\omega + \varphi(n\omega)) + B_n \cos(n\omega + \varphi\ (n\omega)) \right] \right\}, \qquad (9)$$

where:

$$M(\omega = 0) = |G(\omega = 0)|, \qquad (10)$$

$$M(n\omega) = |G(n\omega)|, \qquad (11)$$

$$\varphi(n\omega) = \arg(G(n\omega)). \qquad (12)$$

When stabilized changes in time occur inside layers of unlimited size and the thickness L, concentration distributions calculated based on Eq. (9) would be similar in these locations where values M and φ are similar [1]. Based on a theoretical analysis of transmit-

tance, one may conclude that the concentration curves get close to each other upon L increasing, decreasing period T and increasing process rate constant k_r [1]. Further discussion focuses on layers for which Eq. (5) is valid.

3. CONCENTRATION GRADIENT AT A BOUNDARY
OF LIQUID AND SOLID PHASES AT UNSTEADY STATES

Let us assume that changes of concentration C_i are stabilized in time at the phase boundary. They can be written as:

$$C_i = C_{i,m} + C_{i,a} \sin(\omega t), \tag{13}$$

where: $C_{i,m}$ – average concentration at the phase boundary, $C_{i,a}$ – concentration amplitude at the phase boundary, $\omega = 2\pi/T$, T is the period of the concentration wave.

If Laplace transformation is $\hat{C}_i$ and the concentration at the phase boundary is C_i ($y = 0$) Eq. (5) may be written in a form:

$$\frac{\hat{C}}{\hat{C}_i} = G(s) = \exp\left(-\sqrt{\frac{s + k_r}{D}}y\right). \tag{14}$$

Equation (14) is a transmittance $G(s)$ of a solid phase that links the concentration transform at the phase boundary $\hat{C}_i$ with the concentration transform $\hat{C}$ inside the phase. In order to pass from a complex domain of Laplace transformations to a frequency domain it is necessary to substitute $s = I\omega$ [7] and then transmittance G will be expressed as:

$$G(I\omega) = \exp\left(-\sqrt{\frac{I\omega + k_r}{D}}y\right). \tag{15}$$

The module $M(y, \omega)$ and the argument $\varphi(y, \omega)$ of the transmittance G are:

$$M(y,\omega) = |G(I\omega)| = \exp\left(-\sqrt{\alpha_M}\cos(\gamma_M)\right), \tag{16}$$

$$\varphi(y,\omega) = \arg(G(I\omega)) = \text{arctg}\left[\frac{\sin\left(-\sqrt{\alpha_M}\sin(\gamma_M)\right)}{\cos\left(-\sqrt{\alpha_M}\sin(\gamma_M)\right)}\right]$$

$$= \text{arctg}\left[\text{tg}\left(-\sqrt{\alpha_M}\sin(\gamma_M)\right)\right] = -\sqrt{\alpha_M}\sin(\gamma_M). \tag{17}$$

(Note the sign of sine and cosine functions while determining argument φ).

$$\alpha_M = \frac{y^2}{D}\sqrt{k_r^2 + \omega^2}, \tag{18}$$

$$\gamma_M = \frac{1}{2}\operatorname{arctg}\left(\frac{\omega}{k_r}\right). \tag{19}$$

(There are two roots of a complex number $k_r + I\omega$. Since the second root ($\gamma_M + \pi$) represents modules $M(y, \omega) \geq 1$, it will not be considered in this case. Due to the presence of a diffusive resistance of mass transport, and since the amount of substance decreases due to the chemical reaction, $M(y, \omega) \leq 1$).

Knowing both the module and argument of transmittance, equation describing changes of concentration within the solid phase [7] may be formulated:

$$C = C_{i,m}M(y, \omega = 0) + C_{i,a}M(y, \omega)\sin(\omega t + \varphi(y, \omega)) \tag{20}$$

and the concentration gradient:

$$\frac{\partial C}{\partial y} = C_{i,m}\frac{\partial M(y, \omega = 0)}{\partial y} + C_{i,a}\frac{\partial M(y, \omega)}{\partial y}\sin(\omega t + \varphi(y, \omega))$$

$$+ C_{i,a}M(y, \omega)\cos(\omega t + \phi(y, \omega))\frac{\partial \varphi(y, \omega)}{\partial y}. \tag{21}$$

Especially at the phase boundary ($y = 0$), the gradient may be determined using the following relationship:

$$\left.\frac{\partial C}{\partial y}\right|_{y=0} = -\sqrt{\frac{k_r}{D}}C_{i,m} + \sqrt{\frac{\sqrt{k_r^2 + \omega^2}}{D}}C_{i,a}\sin\left(-\omega\left(t + \frac{\gamma_M}{\omega}\right)\right). \tag{22}$$

In the case of a sinusoidal change of concentration eq. (13) a concentration gradient described by relationship (22) may also be presented in another equivalent form:

$$\left.\frac{\partial C}{\partial y}\right|_{y=0} = a_1 C_i(t) + a_2 \left.\frac{\partial C_i}{\partial t}\right|_t + a_3$$

$$= a_1\left(C_{i,m} + C_{i,a}\sin(\omega t)\right) + a_2 C_{i,a}\omega\cos(\omega t) + a_3. \tag{22a}$$

After comparing right sides of Eqs. (22) and (22a) we have:

$$a_1 = -\sqrt{\frac{\sqrt{k_r^2 + \omega^2}}{D}}\cos(\gamma_M), \tag{22b}$$

$$a_2 = -\frac{1}{\omega}\sqrt{\frac{\sqrt{k_r^2 + \omega^2}}{D}}\,\sin\left(\gamma_M\right), \tag{22c}$$

$$a_3 = C_{i,m}\left(\sqrt{\frac{\sqrt{k_r^2 + \omega^2}}{D}}\,\cos\left(\gamma_M\right) - \sqrt{\frac{k_r}{D}}\right). \tag{22d}$$

Time dependences of both concentrations at phase boundary inside the solid phase and of the concentration gradient are presented in Fig. 1., It should be noted that the concentration gradient slightly accelerates (shift in time, type (γ_M/ω), Eq. (22)) at the phase boundary, if compared with concentration C_i (Fig. 1).
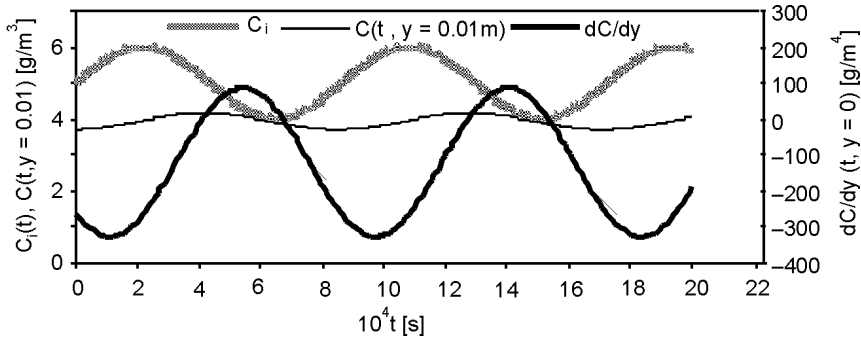

Fig. 1. Time dependences of concentration C_i, concentration gradient $\partial C/\partial y$
at the phase boundary and concentration inside the solid phase $C(t, y = 0.01$ m);
$k_r = 10^{-6}$ s^{-1}, $D = 1.7{\times}10^{-9}$ m^2/s, $C_{i,m} = 5$ g/m^3, $C_{i,a} = 1$ g/m^3, $T = 86\,400$ s

Equation (22) or (22a) may be used to determine the mass flux of a substance diffusing trough the phase boundary to a solid phase, based on the Fick Law [10]:

$$\frac{\partial m}{\partial t} = -DA^*\frac{\partial C}{\partial y}. \tag{23}$$

4. CONCENTRATION CHANGES UNSTABILIZED IN TIME

If changes of concentration of a certain substance do not change in time in a periodic way, the factor defining the value of the concentration gradient in equations describing the mass transfer rate requires modifications. Aperiodic changes of concentration may occur either in the case of occasional pollutant discharges to a watercourse or during tracer experiments, when a specific substance is introduced to a river in an impulse type manner.

In the case of stabilized changes of concentration, it is possible to determine the concentration C in the following moment (shift (γ_M / ω) type, Eq. (22)) just based on the change of concentration in the previous period T. If only a single concentration impulse occurs, determining of the concentration in the following moment is not possible.

An adequate picture of an aperiodic process may be obtained simply through the analysis of penetration into a solid phase when changes of the concentrations follow a function in a form of rectangular impulses. Time lapses between the subsequent concentration impulses next to the phase boundary should be long enough to enable equilibrium between the absorption process and a chemical reaction (Fig. 2).
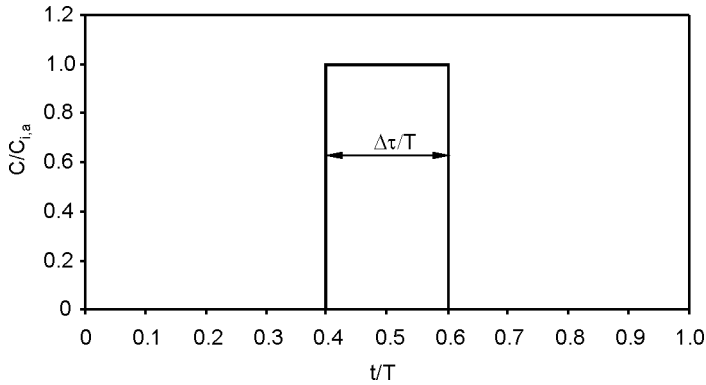

Fig. 2. Rectangular concentration impulse: T – period of function,
$C_{i,a}$ – amplitude of impulse, $\Delta\tau$ – duration of impulse

Expansion of the function presented in Fig. 2 and symmetric to $t/T = 0.5$ in a trigonometric series is as follows:

$$C = \frac{\Delta\tau}{T}C_{i,a} + \sum_{n=1}^{+\infty}\frac{2C_{i,a}}{n\pi}(-1)^n \sin\left(\frac{n\pi}{T}\Delta\tau\right)\cos\left(\frac{2n\pi}{T}t\right), \tag{24}$$

where: T – period of a function, $C_{i,a}$ – amplitude of an impulse, $\Delta\tau$ – impulse duration, $2\pi/T = \omega_0$ – angular velocity for a main harmonic ($n = 1$, fundamental angular velocity).

Let us recall that Eq. (24) describes changes at the phase boundary. Knowing both module (16) and argument of transmittance (17), an equation may be formulated that describes changes of the concentration within the solid phase [7]:

$$C = M\left(y, \omega = 0\right)\frac{\Delta\tau}{T}C_{i,a} + \sum_{n=1}^{\infty}M\left(y, n\omega\right)\frac{2C_{i,a}}{n\pi}(-1)^n$$

$$\times\sin\left(\frac{n\pi}{T}\Delta\tau\right)\cos\left(\frac{2n\pi}{T}t + \varphi\left(y, n\omega\right)\right). \tag{25}$$

Equations (24) and (25) enable one to determine the concentration gradient at the phase boundary in a numeric way (analytical method makes calculations rather complicated in this case). Dependence of the gradient of concentration $(dC/dy)(t)$ on $C_i(t)$ for the case presented in Fig. 1 is an ellipse (Fig. 3).
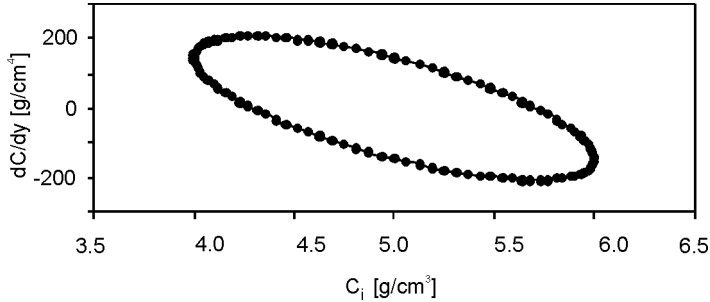

Fig. 3. Concentration gradient vs. concentration at the phase boundary according to $(dC/dy)(t)$ and $C_i(t)$ runs, as presented in Fig. 1

The same dependence developed considering the time lapse $(dC/dy)(t) = f(C_i(t + \Delta t)]$ becomes a line segment at $\Delta t = T/8 = 0.125T$ – this is the maximum value (γ_M /ω) at $k_r = 0$ (for the average value of $C_{i,m} = 5$ g/m^3 gradient $dC/dy = 0$). In case of $\Delta t = 10\ 368$ s $(\Delta t/T = 0.12)$ a distinctly flattened ellipse is obtained (Fig. 4). The concentration gradient at the moment t may be estimated from the value of concentration at the moment $(t + \Delta t)$ or $(t – T + \Delta t)$, when stabilized periodical changes occur, based on the straight line equation. Upon increasing k_r values, the time lapse Δt decreases to zero. In the case of a single concentration impulse or impulses spread long time apart, the dependence of concentration gradient on the concentration is similar to the one described above although not such ideal.
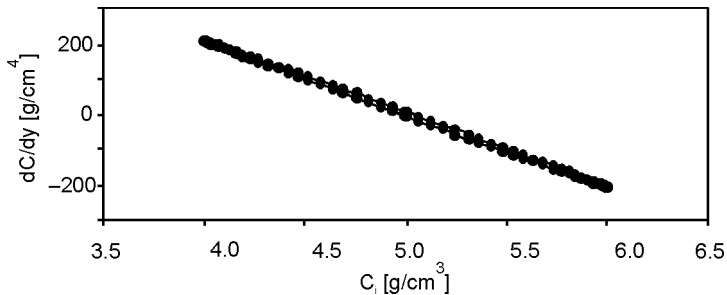

Fig. 4. Concentration gradient vs. concentration at the phase boundary according to $(dC/dy)(t)$ and $C_i(t+\Delta t)$ runs, as presented in Fig. 1 $(\Delta t = 10\ 368$ s$)$

Assume that a series of concentration impulses at the phase boundary is defined using first seven components of the sum in Eq. (24). Concentration runs at the phase

boundary, concentrations at the distance $y = 10^{-6}$ m at the solid phase side and concentration gradients at the phase boundary are presented in Fig. 5. Dependences of concentration gradients on concentration $(dC/dy)(t) = f(C_i(t))$ and $(dC/dy)(t) = f(C_i(t + \Delta t))$ for various Δt are presented in Figs. 6–8.
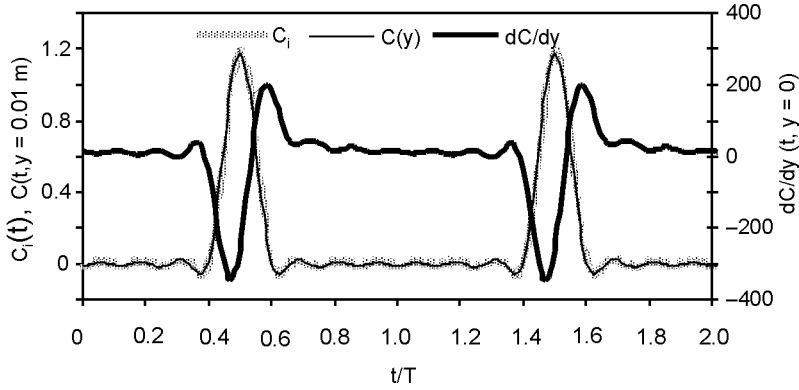

Fig. 5. Concentrations at the phase boundary, concentration at the distance
$y = 10^{-6}$ m at the solid phase side and concentration gradient at the phase boundary:
$T = 86400$ s, $C_{i,a} = 1$ g/m^3, $\Delta\tau = T/16$, $k_r = 10^{-30}$ s^{-1}, $D = 1.7 \times 10^{-9}$ m^2/s
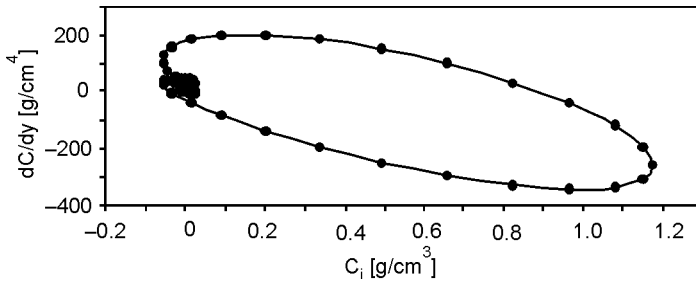

Fig. 6. Concentration gradient vs. concentrations at the phase boundary
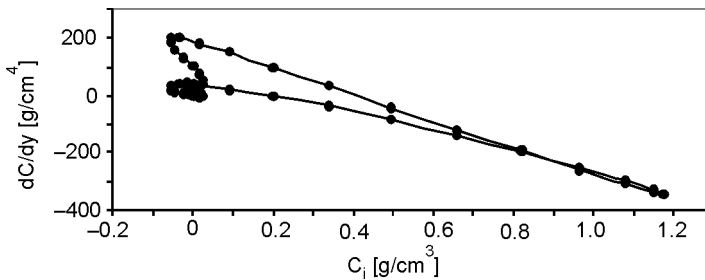according to $(dC/dy)(t)$ and $C_i(t)$ runs, as presented in Fig. 5 ($\Delta t = 0$)

Fig. 7. Concentration gradient vs. concentration at the phase boundary
according to $(dC/dy)(t)$ and $C_i(t + \Delta t)$ runs, as presented in Fig. 5 ($\Delta t = 0.03T$)
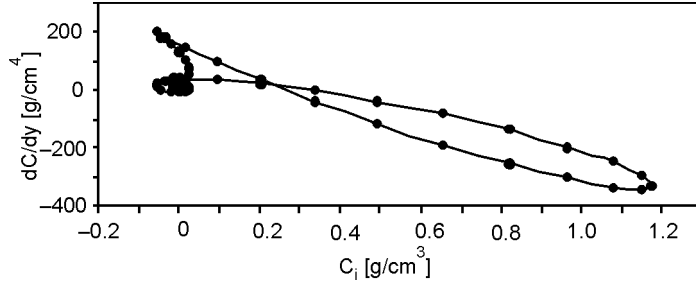
Fig. 8. Concentration gradient vs. concentration at the phase boundary
according to $(dC/dy)(t)$ and $C_i(t+\Delta t)$ runs, as presented in Fig. 5 ($\Delta t = 0.04T$)

Plots presented in Figs. 7 and 8 form closed curves that are much more flat than the curve in Fig. 6. Irregular scatter of points close to the concentrations approaching zero is probably caused by oscillations and lack of ideal steady state conditions (Fig. 5).

Numerical experiments confirm that an increase of a chemical process rate constant k_r enhances the effect of flattening of the closed curves. Shapes of curves in Figs. 4, 7 and 8 suggest that the concentration gradient may be approximated by:

$$\frac{dC}{dy} = a_1'\left[C_i\left(t+\Delta t_1\right)-C_{i,m}\right]+a_3'\left[C_i\left(t-\Delta t_2\right)-C_{i,m}\right]+a_4', \qquad (26)$$

where: a_1', a_3' and a_4' – constants, Δt_1, Δt_2 – time shifts.

Since during a single impulse the subsequent concentration values are not known, their values may be estimated by differentiating the concentration with respect to time:

$$\frac{dC}{dy} = a_1'\left[C_i\left(t\right)+\frac{dC_i}{dt}\bigg|_t \Delta t_1 - C_{i,m}\right]+a_3'\left[C_i\left(t-\Delta t_2\right)-C_{i,m}\right]+a_4'$$

$$= a_1'C_i\left(t\right)+a_1'\frac{dC_i}{dt}\bigg|_t \Delta t_1 + a_3'C_i\left(t-\Delta t_2\right)+a_4$$

$$= a_1'C_i\left(t\right)+a_2\frac{dC_i}{dt}\bigg|_t + a_3C_i\left(t-\Delta t_2\right)+a_4, \qquad (27)$$

where: a_1, a_2, a_3, a_4 – constants.

Calculation of the previous values using a derivative dC_i/dt may not give accurate results when Δt_2 is too high. In the case of an impulse function, its approximated average value $C_{i,m}$ should be assumed zero, since the function is a positive fraction of another function that has been developed as a result of an odd analytical impulse continuation (impulse oscillation around zero). If any oscillation around the non-zero value would occurred, the average value would have varied along the watercourse length (x – linear coordinate). Let us assume that the concentration of the substance in

the core of the liquid phase is equal to the concentration at the phase boundary of liquid and solid phases ($C_i \approx \tilde{C}$). In such a case, the values $C_{i,m}(x)$ should be calculated from appropriate stationary mass transport models referring to a liquid phase. A detailed discussion on this topic has been presented elsewhere [1].

If sinusoidal concentration changes occur (Fig. 1), the theoretical concentration gradient calculated from Eqs. (24) and (25) ($\Delta y = 10^{-6}$ m) may be precisely approximated with the model (27) (Fig. 9). In this particular case we have:

$$\frac{dC}{dy} = -141.653839581284\left(C_i(t) - C_{i,m}\right)$$

$$-201.210089726553 \times 10^4 \left.\frac{d\left(C_i(t) - C_{i,m}\right)}{dt}\right|_t, \qquad (28)$$

where $\Delta t = 864$ s is the time step used for numerical calculations of a derivative with respect to time.
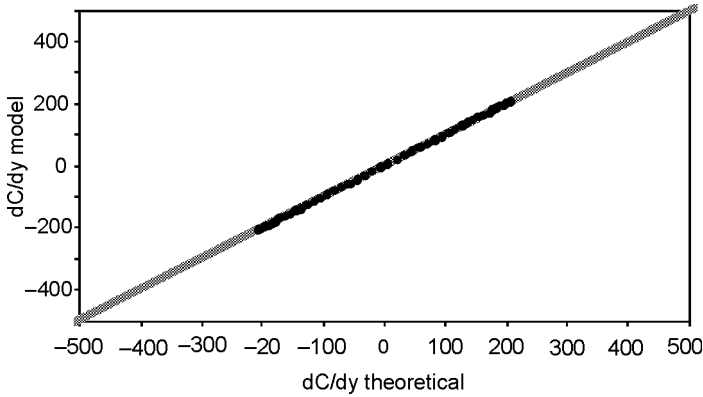

Fig. 9. Fitting of the gradient model (27) to the gradient calculated
numerically using Eqs. (24) and (25) (theoretical gradient) for
a sine concentration curve, as presented in Fig. 1 (the average
absolute error for a single value of gradient is 3.78×10^{-7} g/m^4)

Coefficients of Eq. (28) are approximately equal to the respective theoretical ones: $a_1 = -146.25$ m^{-1}, Eq. (22b), $a_2 = -201.11 \times 10^4$ s/m, Eq. (22c), $a_3 = 0$ g/m^4, Eq. (22d) (a_3 is equivalent of a_4 in Eq. (27); a_3 approaches zero since a difference between concentration and the average was used in calculations).

For an impulse concentration change (Fig. 5), the following equations were obtained:

$$\frac{dC}{dy} = -210.78 C_i(t) - 90.27 \times 10^4 \left. \frac{dC_i}{dt} \right|_t + 77.782 C_i(t - 8640) + 16.718, \qquad (29)$$

$$\frac{dC}{dy} = -201.83 C_i(t) - 110.46 \times 10^4 \left. \frac{dC_i}{dt} \right|_t + 25.229. \qquad (30)$$

Values of the coefficients in Eqs. (29) and (30) were determined after minimizing of a sum of squared deviations between theoretical gradient values, calculated from Eqs. (24) and (25), and the values calculated from the model (27).
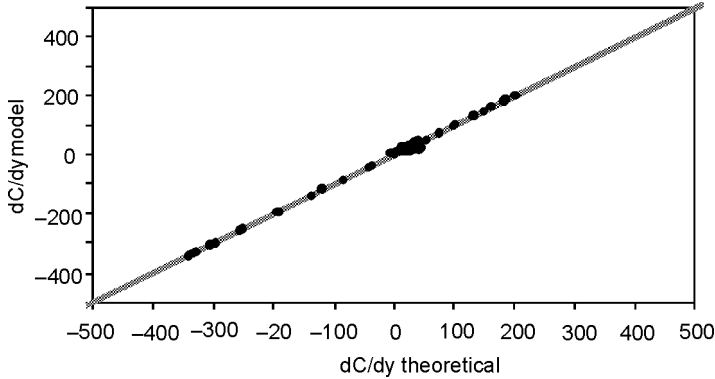

Fig. 10. Fitting of the gradient model (27) to the gradient calculated numerically using Eqs. (24) and (25) (theoretical gradient) for an impulse of concentration, as presented in Fig. 5 (the average absolute error for a single value of gradient is 7.36 g/m^4)
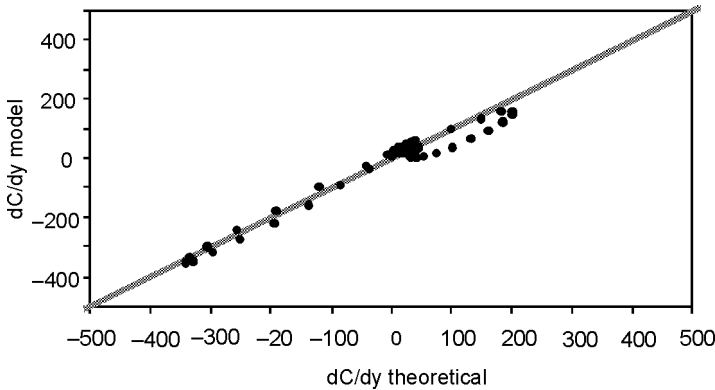

Fig. 11. Fitting of the gradient model (27) to the gradient calculated numerically using Eqs. (24) and (25) (theoretical gradient) for an impulse of concentration, as presented in Fig. 5 (the average absolute error for a single value of gradient is 21.69 g/m^4)

Figures 10 and 11 show the results of gradient calculations from Eqs. (29) and (30), respectively. The equations approximate a theoretical value of gradient with a different accuracy; in practice, poor accuracy of Eq. (30) seems quite sufficient. The equation is much easier to use since it does not require memorizing a series of concentrations delayed with respect to a current time t by Δt_2 in all river cross-sections x_i during numerical solving of the mass transport equation.

In model (27) term a_4 is responsible for a substance desorption for a single concentration impulse and its value is proportional to the average desorption rate. Due to desorption from a solid phase, some concentrations in a liquid phase remain different from zero, irrespective of time of impulse duration. Such an effect is a consequence of the assumption that a series of concentration impulses at the phase boundary is described using seven first elements of the sum in Eq. (24).

During identification of the mass transport model, based on the concentration measurements of a tracer fed into a watercourse in an impulse-type mode and using Eq. (27), it is necessary to introduce some complementary functions. The functions depend on such parameters as distance coordinate x, time t and tracer hydraulic detention time; all the parameters attenuate a desorption effect related to the value of the coefficient a_4 ($a_4 \neq 0$) [2]. Equations like (27) may also be used in models describing both absorption and desorption with a chemical reaction in a solid phase. [2].

4. SUMMARY AND CONCLUSIONS

The first part of the paper focuses on a detailed analysis of dynamics of mass transport from a liquid phase (river water) to a solid phase (river sediment). A series of relationships was developed describing concentration gradient for a periodic concentration changes of the substance. From theoretical analysis of transmittance for a solid phase it may be concluded that changes of concentration within solid phases of different thickness would become similar in the case when: solid phase thickness increases, concentration wave period decreases, rate constant of a substance decay within the solid phase increases.

At the phase boundary (solid phase side), the concentration gradient increases upon time shifts, with respect to the concentration function assuming that a substance decay takes place or none process occurs. A time shift varies within the range of $< 0, 1/8 >$ of a concentration function period.

The concentration gradient at the phase boundary (solid phase side) may be calculated based on the concentration changes and a derivative of a concentration with respect to time at the phase boundary. In the case of sine concentration changes, concentration gradients (Eq. (22a)) calculated using this method are accurate. Such a method of estimation of the concentration gradient may also be used when the concentration at the phase boundary changes in other then a sinusoidal mode.

Knowledge of concentration gradient enables one to develop an equation describing the mass flux penetrating into the solid phase. Such an equation may also be used to estimate the error in the mass penetration model if calculated using the Whitman film model. Neglecting the dispersion effects along the river bed in natural water bodies at a steady state results in serious errors. Then, application of advection models may be just accurate in many cases.

When cyclic concentration changes at the phase boundary may be described with a single harmonic function, the points of graph developed based on the concentration values and the concentration gradient at the same time instant form a closed curve – an ellipse. It may be noticed that the curve of the concentration gradient vs. delayed concentration gets more flat or it becomes a line segment. When time dependence of concentration can be described as couple of harmonics, the effect of curve flattening also occurs though it is not as ideal as in case of a single harmonic. The effect of curve flattening was used in construction of the model describing a relationship between the concentration gradient and concentration. The proposed model may also be used for description of the dependence of the concentration gradient on concentration when both absorption and desorption processes occur with a chemical reaction. In some specific cases, the model structure may be simplified just by ignoring an element referring to a delayed concentration. A simplified model is slightly less accurate than its complete version. In dynamic conditions, the concentration gradient at the phase boundary may be approximated using combination of linear concentration, delayed concentration and concentration derivative, all at the phase boundary with respect to time.

Numerical experiments showed that an increase of the constant rate of a chemical process enhanced the effect of curve flattening. Following the increase of the rate constant, the accuracy of model (27) improves while the coefficients a_2 and a_3 approach zero.

Increase of chemical process rate causes that changes of the concentration gradient at the phase boundary follow the changes of the concentration at the phase boundary.

The mass exchange problems presented in the paper focused on continuous changes of concentration at the phase boundary. The problems related to mass exchange when concentrations at the phase boundary are not continuous (e.g., absorption and adsorption processes occur) will be discussed elsewhere.

SYMBOLS

$(1/2)A_0$ – average concentration C_i, g/m^3
A – surface area, m^2
A^* – surface normal to diffusion direction, m^2
A_n, B_n – coefficients of a trigonometric series, g/m^3
C, c – concentration, g/m^3
$C^\sim$ – concentration in the phase core, g/m^3
$C_m^\sim$ – average concentration within a phase core, g/m^3

$C^{\sim}_{m,0}$ – average concentration in the phase core at an initial river cross-section, g/m^3

$C^{\sim}_{m,srd}$ – average value of the average concentration in the phase core for watercourse segment, g/m^3

$C^{\sim}_a$ – concentration amplitude in the phase core, g/m^3

$C^{\wedge}$ – Laplace transformation of a concentration function

C_i – concentration at the phase boundary, g/m^3

$C_{i,m}$ – average concentration at the phase boundary, g/m^3

$C_{i,a}$ – concentration amplitude at the phase boundary, g/m^3

$C^{\wedge}_i$ – Laplace transformation of a concentration at the phase boundary, g/m^3

D – diffusion coefficient, m^2/s

E_x – longitudinal dispersion coefficient, m^2/s

E_z – coefficient of vertical turbulent diffusion (perpendicular to athe solid phase surface), m^2/s

G – transmittance

h – water level or the average water level in a river, m

i – drop of a water level in a watercourse, unless stated otherwise

I – imaginary unit, $I = (-1)^{1/2}$

k_r – process rate constant, 1/s

k_w – mass transfer coefficient at a liquid phase side, m/s

$k_{z,og}$ – overall equivalent rate constant for all processes occurring in both liquid and solid phases, s^{-1}

L, L_0 – thickness of a solid phase layer, m

L_{odc} – length of watercourse segment, m

M – transmittance module $|G|$

m – weight, g

$r(C^{\sim})$ – 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

$\mathrm{re}(...)$ – real part of complex variables

$\mathrm{im}(...)$ – imaginary part of complex variables

s – complex variables

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 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

$\Delta t_1, \Delta t_2$ – 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 constant

SUBSCRIPTS AND SUPERSCRIPTS

i	–	concentration at the phase boundary
a	–	amplitude
m	–	average value
$\sim$	–	phase core, in the case of concentration
$\wedge$	–	Laplace transformation

REFERENCES

[1] BIELSKI A., *Selected aspects of mass transfer rate determination between phases in the watercourse. Part I. Analysis of the influence of periodical concentration changes on mass transport through phase boundary*, Cracow University of Technology, Techn. Bull., 2, 2006.

[2] BIELSKI A., *Selected aspects of mass transfer rate determination between phases in the watercourse. Part II. Analysis of the influence of aperiodical concentration changes on mass transport through phase boundary*, Cracow University of Technology, Techn. Bull., 2, 2006.

[3] DALI-YOUCEF N., OUDDANE B., DERRICHE Z., J. Hazardous Mater. A, 2006, 137, 1263.

[4] JIMENEZ- CEDILLO M.J., OLGUIN M.T., FALL C., J. Hazardous Mater. 2009, 163, 939.

[5] KEMBŁOWSKI Z., MICHAŁOWSKI S., STRUMIŁŁO C., ZARZYCKI R., *Theoretical basis of chemical and process engineering*, WNT, Warsaw, 1985 (in Polish).

[6] KULA I., UGURLU M., KARAOGLU H., CELIK A., Biores. Techn., 2008, 99, 492.

[7] LUYBEN W.L., *Process modeling, simulation, and control for chemical engineers*, McGraw-Hill, New York, 1973.

[8] *Management of Health and Environmental Hazards*, web adress: http://www2.cyf.gov.pl, files adresses: http://www2.cyf.gov.pl/przewodnik

[9] ZHANG M.H., ZHAO Q.L., ZHENG X.B., YE F., Coll. Surf.A, Physicochem. Eng. Aspects, 2010, 362, 140.

[10] POHORECKI R., WROŃSKI S., *Kinetics and thermodynamics of chemical process engineering*, WNT, Warsaw, 1977 (in Polish).

[11] SZARAWARA J., SKRZYPEK J., *Basics of chemical reactor engineering*, WNT, Warsaw, 1980 (in Polish).