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# Parameter identification and analysis of soluble chemical transfer from soil to surface runoff

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## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Abstract

A two-layer mathematical model is used to predict the chemical transfer from the soil into the surface runoff with ponding water. There are two incomplete infiltration-related parameter  $\gamma$  and runoff-related parameter  $\alpha$  in the analytical solution to the model, which were assumed to be constant in previous studies (Tong et al., 2010). In this study, experimental data are used to identify the variable  $\gamma$  and  $\alpha$  based on the analytical solution. The soil depth of the mixing zone is kept to be constant in different experiments, and the values of  $\gamma$  and  $\alpha$  before the surface runoff occurs are constant and equal to their values at the moment the runoff starts. From the study results, it is found that  $\gamma$  will decrease with the increase of the surface runoff time, the increase of the ponding-water depth,  $h_p$ , or with the decrease of the initial volumetric water content. The variability of  $\gamma$  will decrease with the increase of the initial volumetric water content. Similarly,  $\alpha$  will decrease with time for the initially unsaturated experimental soils, but will increase with time for the initially saturated experimental soils. The larger the infiltration, the less chemical concentration in the surface runoff is. The analytical solution is not valid for experimental soil without any infiltration if  $\alpha$  is expected to be less or equal to 1. The results will help to quantify chemical transfer from soil into runoff, a significant problem in agricultural pollution management.

## 1 Introduction

Chemical transfer from soil to surface runoff during rainfall has become serious agronomic and environmental problems (Baker et al., 1978, 1982; Gao et al., 2004, 2005; Hesterberg et al., 2006; Mulqueen et al., 2004; Tian et al., 2011; Tong et al., 2010; Wallach et al., 2001; Walton et al., 2000; Walter et al., 2007; Yoshinaga et al., 2007; Yu et al., 2011). Agronomic interest pays attention to the loss of soil productivity, whereas environmental interest pays attention to the deterioration of both surface and ground-water quality. Therefore, it is required to study the process of chemical transfer from soil

### Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



to surface runoff and identify the important factors in the process to help us to reduce chemical loss to surface runoff and subsequent pollution.

To study the transfer of soluble chemical in the soil into surface runoff, Ahuja et al. (1981a) proposed the conception of mixing layer (or mixing zone) theory and effective depth of interaction (EDI). It is assumed that there is a region under the soil surface, where soil solution, surface water, and infiltrating water mix instantaneously and that the soil below will supply no chemical for that region. The mixing layer depth is assumed to be constant. This theory was later extended to more general cases (Ahuja and Lehman, 1983; Emmerich et al., 1989; Gao et al., 2004, 2005; Heathman et al., 1985, 1986; Steenhuis and Walter, 1980; Snyder and Woolhiser, 1985; Wang et al., 1998, 1999; Wallach, 1993; Wallach et al., 1988; Wallach and Genuchten, 1990; Zhang et al., 1997, 1999). However, most of these theories do not consider the increasing process of ponding-water before the surface runoff, and there is not much study on the role of incomplete parameters on the process.

By using incomplete mixing theory, Tong et al. (2010) established a two-layer model considering the process of increasing ponding water to predict the soluble chemicals concentration in runoff water from soil. They derived an analytical solution under the assumption that the incomplete mixing parameters related to surface runoff and infiltration water are constant during the whole rainfall process. They applied their model with constant incomplete parameters to analyze two experimental results, one with initially unsaturated soil and the other with initially saturated soil. Their experimental and modeling results clearly showed the differences of the incomplete parameters in the two cases. However, they only assumed that the parameters are constant during the simulation, and they did not analyze the experimental and modeling results with variable incomplete mixing parameters.

The main objective of this paper is to identify and analyze the variable incomplete mixing parameters for the two-layer model. To make the paper self-contained the two-layer analytical model will be introduced briefly. The analytical solutions will be used to calculate the runoff-related and infiltration-related parameters according to various

## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



initially unsaturated-saturated soil experiments. The experiment equipments and processes have been described in detail by Tong et al. (2010), so the experimental conditions will be introduced only, such as the simulated rainfall intensity, initial soil moisture, the depth of the experimental soil, the depth of ponding-water, the initial saturated chemical concentration, the start time of the ponding-water and the runoff from the rainfall start and the whole time of simulated rainfall for each experiment here, on the basis of the brief introduction of the sketch of the experiment frame in this paper. In the initial stage of the calculation, runoff-related and infiltration-related parameters will be identified, of which the expressions are unknown. The method to find out the parameters will be given at first and then the identified parameters will be analyzed.

## 2 Mathematical model and identification method for incomplete parameters

### 2.1 Analytical model and solution

A simple two-layer model is considered in the study (Fig. 1). The upper layer, also called the whole mixing layer includes the surface ponding-runoff zone and the soil mixing zone (Ahuja et al., 1981a). Similar to the assumptions used by Govindaraju et al. (1996) and Ahuja et al. (1981b), chemicals of the soil mixing layer are the only source of chemical for runoff and infiltration water, and the chemicals are only considered to transport vertically (Steenhuis and Walter, 1980). The chemicals of the soil mixing zone could move to the soil below with the infiltrated water. While the chemicals of the underlying layer could move to the soil mixing zone via the mass diffusion process because of higher chemical concentration of the underlying soil than that of the mixing soil zone. The “net” chemical flux to the underlying soil layer from the soil mixing zone is presented as,  $i\gamma C_w$ , where  $i$  is the soil water infiltration flux,  $\text{cm min}^{-1}$ ;  $C_w$  is the chemical concentration of the soil mixing zone,  $\text{mg l}^{-1}$ . Here it should be noticed that the  $C_w$  is a function of time.  $\gamma$  is the incomplete infiltration-related parameter.

## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



To describe the incomplete solute mixing in the ponding-runoff zone, an incomplete mixing parameter  $\alpha$  was introduced. The chemical concentration of ponding-runoff zone is  $\alpha C_w$ . To simplify the complex processes of chemical transport near the soil surface, it is assumed that the chemical concentration of each zone is uniform, but different with each other. A whole mixing layer includes these two zones. So a simple two-layer model was called for the study system, as shown in Fig. 1.

Based on the mass conservation, the following equation is obtained for the whole mixing layer

$$M_w = C_w [\alpha h_p + h_{\text{mix}} \cdot \theta_s] \quad (1)$$

where  $M_w$  is the mass of soluble chemical in water phase per unit area,  $\mu\text{g cm}^{-2}$ ;  $h_w$  is the water depth in the ponding water, cm;  $h_{\text{mix}}$  is the the soil mixing layer depth, cm;  $\theta_s$  is the saturated water content of the soil mixing zone,  $\text{cm}^3 \text{cm}^{-3}$ .

If the chemical concentration of the rainfall water is assumed to be zero, the following equation can also be obtained based on mass conservation,

$$\frac{d[M_w(t)]}{dt} = -\gamma \cdot i \cdot C_w(t) - \alpha \cdot q \cdot C_w(t) \quad (2)$$

where  $q$  is the specific discharge rate of the surface flow,  $\text{cm min}^{-1}$ ;  $t$  is the time, min.

Equations (1) and (2) can supply a mass conservation model in the kinetic and “static” conditions of the whole mixing layer.

At the first time period there exists no ponding-water on the soil surface, so the infiltration rate for soil was equal to rainfall rate with both initially saturated and unsaturated experimental soils. The initial saturated chemical concentration (i.e., KCl in this paper) was  $C_0/\text{mg l}^{-1}$ , thus the Eq. (2) can be solved as

$$C_w(t) = C_0 \cdot \exp \left[ -\frac{\gamma \cdot p \cdot (t - t_{sa})}{h_{\text{mix}} \cdot \theta_s} \right] \quad (3)$$

## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



During the period from the ponding start ( $t_p$ /min) to the runoff start ( $t_r$ /min), the average soil infiltration rate was  $i_{1p}$ /cm min<sup>-1</sup>, so the increasing depth of ponding water was  $h_p(t) = (\rho - i_{1p}) \cdot (t - t_p)$ . All the time and infiltration rate parameters are obtained from the experiments. The initial concentration  $C_w(t_p)$  can be obtained from Eq. (3), so the chemical concentration of the soil mixing layer is:

$$C_w(t) = C_w(t_p) \cdot \left[ \frac{\alpha \cdot (\rho - i_{1p}) \cdot (t - t_p) + h_{\text{mix}} \cdot \theta_s}{h_{\text{mix}} \cdot \theta_s} \right]^{\frac{-\gamma \cdot i_{1p}}{\alpha \cdot (\rho - i_{1p})}} \quad (4)$$

During the time from the runoff start ( $t_r$ /min) to the steady runoff start ( $t_s$ /min), the average soil infiltration rate was  $i_{2p}$ /cm min<sup>-1</sup>, and the ponding-water depth was constant and maximum as  $h_p(t_r)$ /cm. Initial concentration of mixing soil  $C_w(t_r)$  can be gotten by putting  $t_r$  to Eq. (4), so the chemical concentration of runoff was presented as:

$$\alpha \cdot C_w(t) = \alpha \cdot C_w(t_r) \cdot \exp \left\{ \left[ \frac{-\gamma \cdot i_{2p} - \alpha \cdot (\rho - i_{2p})}{\alpha \cdot h_p(t_r) + h_{\text{mix}} \cdot \theta_s} \right] \cdot (t - t_r) \right\} \quad (5)$$

During the time from the steady runoff start ( $t_s$ /min) to the rainfall end ( $t_e$ /min), the infiltration rate was constant as  $i_s$ /cm min<sup>-1</sup>. Similarly, initial chemical concentration in runoff ( $\alpha C_w(t_s)$ ) could be obtained according to Eq. (5), so the solute concentration in runoff was obtained as,

$$\alpha \cdot C_w(t) = \alpha \cdot C_w(t_s) \cdot \exp \left\{ \left[ \frac{-\gamma \cdot i_s - \alpha \cdot (\rho - i_s)}{\alpha \cdot h_p(t_r) + h_{\text{mix}} \cdot \theta_s} \right] \cdot (t - t_s) \right\} \quad (6)$$

## 2.2 Identification method for incomplete parameters

Before the surface runoff starts, the runoff-related incomplete parameter  $\alpha$  and infiltration-related incomplete parameter  $\gamma$  are constant and equal to their values at

the moment when surface runoff starts. The soil mixing zone depth is constant all the time. As described above, if  $\gamma$  and  $\alpha$  are still constant after runoff occurs, the concentration in the surface runoff  $C/\text{mg l}^{-1}$  at any time  $t$  (min) can be expressed as Eqs. (5) and (6). Both expressions are of the same exponential forms, so  $C$  can be rewritten after the runoff start as following for simplicity:

$$C(t) = \alpha \cdot C_r \cdot \exp \left\{ \left[ \frac{-\gamma \cdot i_r - \alpha \cdot (p - i_r)}{\alpha \cdot h_p + h_{\text{mix}} \cdot \theta_s} \right] \cdot (t - t_r) \right\} \quad (7)$$

Where  $C_r$  ( $\text{mg l}^{-1}$ ) is the soluble chemical concentration of the mixing layer when the surface runoff starts,  $i_r$  is the soil infiltration rate during the surface runoff,  $\text{cm min}^{-1}$ .

After the surface runoff occurs, the incomplete parameters  $\gamma$  and  $\alpha$  are assumed to become variable. Of course, if they are still constant, all the variable values are the same. Time steps is divided into  $t_1, t_2, \dots, t_m$  after the surface runoff according to the sampling time, and the corresponding incomplete parameters are  $\gamma_j$  and  $\alpha_j, i_{rj}$  are infiltration rates at the time stage,  $t_j$  ( $j = 1, 2, 3, \dots, m$ ). So during the first time step of  $t_1$ ,

$$C(t) = \alpha_1 \cdot C_r \cdot \exp \left\{ \left[ \frac{-\gamma_1 \cdot i_{r1} - \alpha_1 \cdot (p - i_{r1})}{\alpha_1 \cdot h_p + h_{\text{mix}} \cdot \theta_s} \right] \cdot (t - t_r) \right\} \quad t_r < t \leq t_r + t_1 \quad (8)$$

During the time step  $t_2$ , the surface runoff concentration can be expressed as:

$$C(t) = C(t_r + t_1) / \alpha_1 \cdot \alpha_2 \cdot \exp \left\{ \left[ \frac{-\gamma_2 \cdot i_{r2} - \alpha_2 \cdot (p - i_{r2})}{\alpha_2 \cdot h_p + h_{\text{mix}} \cdot \theta_s} \right] \cdot (t - t_r - t_1) \right\} \quad t_r + t_1 < t \leq t_r + t_1 + t_2 \quad (9)$$

20 ...

**Parameter identification and analysis of soluble chemical transfer**

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



During the time step  $t_m$ , the runoff concentration is

$$C(t) = C(t_r + t_1 + t_2 + \dots + t_{m-1}) / \alpha_{m-1} \cdot \alpha_m \cdot \exp \left\{ \left[ \frac{-\gamma_m \cdot i_{rm} - \alpha_m \cdot (\rho - i_{rm})}{\alpha_m \cdot h_p + h_{mix} \cdot \theta_s} \right] \cdot (t - t_r - t_1 - t_2 - \dots - t_{m-1}) \right\}$$

$$t_r + t_1 + t_2 + \dots + t_{m-1} < t \leq t_r + t_1 + t_2 + \dots + t_{m-1} + t_m \quad (10)$$

- 5 The time  $t_r, t_r + t_1, t_r + t_1 + t_2, \dots, t_r + t_1 + t_2 + \dots + t_m$ , are the experimental sampling periods. So if the experimental data are known at these time points, the incomplete parameters value of  $\gamma$  and  $\alpha$  can be obtained to fit the experimental data by changing one and keeping the other one constant or changing both of them sometimes, which is a process to find out  $\gamma$  and  $\alpha$ . In order to explore the parameters of  $\gamma$  and  $\alpha$ ,  $h_{mix}$  is
- 10 assumed to be constant during all the time of every experiment.

### 3 Experimental conditions

For the paper completeness, the experimental frame is presented in Fig. 2. The parameters for different experiments are presented in Table 1. Two kinds of soil were used in the experiment, one is fine loam sieved 2 mm, and the other one is even sand.

15 A certain 5–10 mm-diameter gravel below the experimental soil was used as a filter layer, a 5 cm-depth of filter layer ( $h_f/\text{cm}$ ), a depth of experimental soil and ponding-water ( $h_e/\text{cm}^{-1}$  and  $h_p/\text{cm}^{-1}$ ), and runoff water from the bottom to the top in every experiment (Fig. 2). The bulk density  $\rho_s/\text{g cm}^{-3}$  and saturated volumetric water content  $\theta_s$  for the fine loamy experimental soil are 1.4 and 0.476, while they are 1.47 and

20 0.443 for the sandy experimental soil, respectively. The experiment is conducted with three cases of the fine loamy soil and seven cases of the sandy soil. The surface runoff is at the height of 25 cm above the experimental box bottom.  $h_{\text{drain}}/\text{cm}$  is introduced, which is the drainage outlet height from the experimental box bottom to indicate different drainage conditions. In the fine loam experiments, the infiltration water from the

Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion





bottom was obtained with free drainage, which means that the  $h_{\text{drain}}$  is 0 in Table 1. The saturated infiltration rate is larger than rainfall intensity rate for the sand experiments with free drainage, so ponding-water and surface runoff did exist at all. The drainage outlet height was set above the experimental box bottom in order to get ponding-water and surface runoff for sand experiments, which means that  $h_{\text{drain}}$  is greater than 0 in Table 1. The average infiltration rate ( $i$  shown in Table 1) during the surface runoff was obtained according to the water balance based on the water collected and the total simulated rainfall water. Moreover, the measured error is not taken into account here.

## 4 Identification results and discussion

As shown in Figs. 3c–12c, the soluble chemical concentration KCl in surface runoff decrease with time. Based on the experiments results, the parameters identification results and corresponding modeled data are obtained during the time of the surface runoff in Figs. 3–12.

### 4.1 Results for the fine loam experiments

The results for the fine loam experiments (cases 1, 2, 3) are shown in Figs. 3–5. The infiltration-related parameter  $\gamma$  decreases with time for all these three cases, and it can even become less than 0 though they are positive at first. This is because that  $\gamma$  is a “net” infiltration of soluble chemical including both advection (downward due to the leached infiltration water) and diffusion (upward due to the concentration gradient) processes. When the infiltration process plays a more important role than that diffusion does at early time,  $\gamma$  is positive. However, infiltration decreases gradually when the soil become saturated. On the other hand, the soluble chemical of the soil mixing layer moved into the soil below, which make the chemical concentration of the soil mixing layer decrease while the chemical concentration in the soil below the soil mixing layer increases. Therefore, the upward concentration gradient become greater, and it

## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

leads to the larger upward diffusion. When the upward diffusion plays a more important role than that of the downward infiltration,  $\gamma$  becomes negative. The calculated  $\gamma$  in Figs. 3b–5b shows that the stronger the upward diffusion, the larger the absolute value of  $\gamma$ .

Furthermore, as listed in Table 1, experimental soil in case 1 is initially unsaturated and the maximum ponding-water depth  $h_p$  (ponding-runoff depth shown in Fig. 2) is much larger than that in case 2. The soluble chemical leached from the soil mixing layer by the infiltration water is much larger in case 1 than in case 2 even though the infiltration rates ( $i$  in Table 1) for both cases are almost the same. The same reason can also be used to explain why the parameter value of  $\gamma$  in Fig. 3b is a little less than that in Fig. 4b on average, and the soluble chemical concentration in surface runoff in Fig. 3c is also less than that in Fig. 4c.

Similarly, the initial volumetric water content of the experimental soil in case 3 is very close to the saturated water content ( $\theta_s$  shown in Table 1), and there is almost no infiltration water during the experiment as the value of  $i$  is so small. Therefore, there is less downward leached chemical from the soil mixing layer, so the value of  $\gamma$  in case 3 is much smaller than that in cases 2 and 1 as demonstrated in Fig. 5b. At the same time, there was much more soluble chemical in the soil mixing layer in case 3 than those in cases 1 and 2, so was the chemical concentration in the surface runoff on average. For the initially unsaturated experimental soil in case 1,  $\gamma$  varies all the time during the surface runoff. While for the initially saturated experimental soil in case 2,  $\gamma$  has only three different constant values.  $\gamma$ 's variation in case 3 is between those in cases 1 and 2 since the initial volumetric water content in case 3 is between them.  $\gamma$  varies continuously at the early time in case 3, and gradually reaches a constant at the last time. These results are due to the small variation of infiltration rate in the saturated soil and constant average infiltration rates during the surface runoff (Table 1). It is concluded that the closer the initial volumetric water to the saturated water content, the smaller variation the infiltration-related incomplete parameter  $\gamma$  during the surface runoff.

**Parameter  
identification and  
analysis of soluble  
chemical transfer**

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



**Parameter  
identification and  
analysis of soluble  
chemical transfer**

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

For the initially unsaturated experimental soil in case 1, the soluble chemical in the soil mixing layer has been leached into the soil below it, so the chemical concentration in the soil mixing layer decreases, which will decrease the chemical concentration gradient between the surface runoff water and the water in soil mixing layer. Thus, the chemical diffusion from the soil mixing layer into the surface runoff will decrease with time if the depth of the ponding-water on the soil surface keeps unchanged. This result can explain why the runoff-related parameter  $\alpha$  decreases all the time during the surface runoff, as shown in Fig. 3a. However,  $\alpha$  increased with time in cases 2 and 3 (Figs. 4a and 5a), and in both cases,  $\alpha$  varies at the early time, then gradually reaches a constant value. For the same reason, the infiltration rate varies much larger for the initially unsaturated soil than that for the initially saturated soil in the whole simulated rainfall experiments, but the averaged constant infiltration rate is used in the modeling simulation of every experiment. Therefore, for the chemical transport, the infiltration plays a major role during the surface runoff for the initially unsaturated soil in case 1, while diffusion became more important in cases 2 and 3, which results in the increase of  $\alpha$  with time in cases 2 and 3. Since infiltration rate is so small (Table 1) in case 3 and the initial volumetric water content is very close to the saturated water content, the increasing rate of  $\alpha$  is larger than that in case 2 during the early time of the surface runoff. However, at the late surface runoff time, the infiltration rate becomes steady and much close to the averaged constant value as shown in Table 1. Therefore, the value of the runoff-related parameter  $\alpha$  becomes constant at late time, as shown in Figs. 4a and 5a.

Furthermore,  $\alpha$ 's values in the fine loam experiments in cases 1–3 are all less or equal to 1, which mean that soluble chemical concentration in the surface runoff is less than or equal to that in the soil mixing layer. The chemical concentration in the soil mixing layer decreases with surface runoff time, and becomes zero at very late time of the surface runoff process, so that it mixes completely with the surface runoff water. This result explains why  $\alpha$ 's values in Figs. 4a and 5a are the constant values of 1 during the late time of the surface runoff.

Comparing case 1 with cases 2 and 3, it is found that the soluble chemical concentration in the surface runoff of case 1 is smaller than these in cases 2 and 3. This is maybe because of the less initial volumetric water content, or the larger depth of the ponding-water in the soil surface, or the less simulated rainfall intensity, or the greater averaged constant value of the infiltration rate during the time of the surface runoff for experimental soil in case 1 than that in cases 2 and 3.

## 4.2 Results for the sand experiments

Figures 6–12 displayed the sand experimental results in cases 4–10 (Table 1). The experimental setting is the same as those for loam experiments and results are also listed in Table 1. The results show that only infiltration water can be measured from the drainage outlet in the cases 4, 5, 7 and 8 (called controlled infiltration water hereafter) while there is no drainage water at all in cases 6, 9 and 10 (called restrained infiltration water hereafter).

Same as the conclusions made above for the loam experiments, the infiltration-related incomplete parameter  $\gamma$  is variable for the initially unsaturated experiments in case 4 (Fig. 6), while  $\gamma$  remains almost unchanged for initially saturated experiments in cases 5, 6, 8, and 9 (Figs. 7, 8, 10 and 11). To conform to the modeled data in Tong et al. (2010), parameters  $\alpha$  and  $\gamma$  are constant values in cases 7 and 8 (Figs. 9 and 10). So it can be seen that the modeled results shown in Figs. 9c and 10c are the same as those in Tong et al.'s (2010). In the initially unsaturated experiment of case 10,  $\gamma$  is also constant, which is quite different from case 4's results. The results could be explained as that the initial volumetric water content in case 10 is much closer to the saturated water content than that in the case 4. The parameter  $\gamma$  can take arbitrary value because the infiltration rate is 0 in cases 6, 9, 10, so the constant value of  $\gamma$  before the surface runoff is displayed in Figs. 8b, 11b, 12b.

The parameter,  $\alpha$ , in cases 4 and 5 decreases with time and becomes smaller than 1.0 in the controlled infiltration condition. These results can also be attributed to the same reason as that described for the case 1, the decrease of the soluble chemical

## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



concentration in the soil mixing layer will reduce the chemical concentration gradient between the soil mixing layer and the surface runoff water.

However,  $\alpha$  increase with the time during the surface runoff in cases 6, 9, 10 under the condition of restrained infiltration and with very large initial volumetric water content, and its value becomes much larger than 1.0. These results can be explained as that in these cases, the rainwater infiltrated into the soil surface at the early time with the increase of the ponding-water, the chemical concentration in the soil mixing layer decreased with the leached water. The soluble chemical in the soil below the soil mixing layer increased at the same time. Since there is no infiltration water in the drainage outlet, so there will be no water to infiltrate into the soil surface after a certain time, except the water exchanges between the two layers. Without infiltrated water, the soluble chemical concentration gradient between the soil mixing layer and the soil below it is the major driving force for chemical transport, so the soluble chemical in the soil below the soil mixing layer will diffuses into the soil mixing layer. However, it is assumed that soluble chemical in the soil mixing layer is the only source of chemical in infiltration and runoff water, and there will be no soluble chemical that transfer into the soil mixing layer. Therefore,  $\alpha$  increases with time and even reaches the value more than 1 based on this assumption. It is can also be concluded that the analytical model proposed by Tong et al. (2010) is only valid for the case without restrained infiltration if  $\alpha$  is considered to be less or equal to 1.

For cases 6 and 10,  $\alpha$  slightly decreases in the very short early time of the surface runoff, which is probably due to the deeper pond-water depth ( $h_p = 0.3$  cm in Table 1) than that in the case 9 ( $h_p = 0.2$  cm), and some rainwater infiltrates into the soil after the start of the surface runoff. This is consistent with the assumption applied in the model development, so  $\alpha$  decreases. After some time, as the same reason explained above, there is some soluble chemical into the soil mixing layer, so  $\alpha$  increases with time.

Comparing the experimental and simulated results for cases 4, 5 and 7 under the condition of controlled infiltration with those in cases 6, 9, 10 under the condition of

## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

the restrained infiltration, one can see that the soluble chemical concentrations of the surface runoff in cases 4, 5 and 7 are much smaller than those in cases 6, 9 and 10. So the infiltration or drainage condition is a very important factor that affects the soluble chemical transfer from the soil into the surface runoff.

5 However, for case 8, the soluble chemical concentration in the surface runoff with controlled infiltration is much larger than those in the controlled infiltration cases 4, 5 and 7, and the chemical concentration is at the same order of magnitude as those in cases 6, 9 and 10 with restrained infiltration. This phenomenon could be attributed to the shallower ponding-water in case 8 ( $h_p = 0.2$  cm in Table 1) than that in other controlled infiltration cases 4, 5 and 7 (Table 1). From these results it is can be concluded that, the depth of ponding-water on the surface will significantly affect soluble chemical transfer from the soil into the surface runoff.

### 4.3 Comparison of the fine loam and sand experiments

Both  $\gamma$  and  $\alpha$  vary with the time during the surface runoff process for the initially unsaturated experimental fine loam in case 1 and initially unsaturated experimental sand in case 4.  $\gamma$  takes three constant values in three stages in case 2 of the initially saturated experimental fine loam and also in case 5 of the initially saturated experimental sand. On the other hand,  $\alpha$  increases with time in case 2 for the fine loam experiment, but decreases with time in case 5 for the sand experiment. The values of  $\alpha$  for both soils are within 0 to 1. Saturated hydraulic conductivity in the sand is much larger than that in the fine loam, so the infiltration rate in the sand soil is faster than that in the fine loam even though the sand is under the condition of the controlled infiltration. As discussed above, the larger the infiltration rate during the time of the surface runoff, the more accurate the proposed model based on the assumption that there is no chemical source for the soil mixing layer. So the value of  $\alpha$  will decrease in sand experiment as expected in Tong et al. (2010). Moreover, the greater infiltration rate leads to more soluble chemical loss downward in case 5, so the upward transfer of chemical from the

**Parameter identification and analysis of soluble chemical transfer**

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



mixing soil layer to the surface runoff is less in case 5 than that in case 2, which is suggested in Figs. 4c and 7c.

## 5 Conclusions

In this study, a method was introduced to find out the variable incomplete infiltration-related parameter  $\gamma$  and runoff-related parameter  $\alpha$  on the basis of both the analytical solution to the model proposed by Tong et al. (2010) and the fine loam and sand experimental data. The value of  $h_{\text{mix}}$  is constant during all the time for each experiment, and the values of  $\gamma$  and  $\alpha$  keep unchanged before the surface runoff takes place and their values are the same as the values at the moment the runoff starts. According to the analysis of the identified results, it is found that  $\gamma$  will decrease with the time after the surface runoff starts. The study results indicate that the variability of the infiltration-related incomplete parameter  $\gamma$  will decrease during the surface runoff when the initial volumetric water content approaches the saturated water content. With the increase of the ponding-water depth,  $h_p$ , on the soil surface and decrease of the less initial volumetric water content, the chemical leached by the infiltration water will increase, and the upward diffusion will increase at the bottom of the soil mixing layer due to the chemical concentration gradient, the  $\gamma$  will decrease correspondingly. Similarly,  $\alpha$  will decrease with time for the initially unsaturated experimental soils, but will increase with time for the initially saturated experimental soils because the decrease of chemical gradient with time between the surface runoff and the soil mixing layer by infiltration water. With the increase of the infiltration, the chemical concentration in the surface runoff will decrease. It should be pointed out that the proposed analytical model is not valid for the condition without any infiltration if the  $\alpha$  is still expected to be less or equal to 1 as shown in Tong et al. (2010).

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### Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures



Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



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### Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion







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# HESSD

9, 3901–3931, 2012

## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion



## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

**Table 1.** Experimental parameters for different cases.

soil type	case number	$C_0$ mg l <sup>-1</sup>	$\theta_0$ cm <sup>3</sup> cm <sup>-3</sup>	$P$ cm min <sup>-1</sup>	$i$ cm min <sup>-1</sup>	$h_{\text{mix}}$ cm	$h_e$ cm	$h_p$ cm	$h_{\text{drain}}$ cm	$t_p$ min	$t_r$ min	$t_s$ min	$t_e$ min
fine loam	1	62 957.8	0.1	0.093	0.0282	0.44	18	2	0	23	55	99	184
	2	62 957.8	0.476	0.097	0.0284	0.1	19.5	0.5	0	0	6	11	123
	3	62 957.8	0.42	0.098	0.0057	0.1	19.5	0.5	0	0.5	5	10	67
sand	4	25997.3	0.046	0.098	0.0195	0.2	19.5	0.5	23	6.2	79	98	224
	5	62 960	0.443	0.097	0.0363	0.2	19.5	0.5	22	0	7.5	7.5	180
	6	62 960	0.443	0.097	0	0.02	19.5	0.3	>25	0	3.5	3.5	125
	7	25 997.3	0.046	0.097	0.0119/0.0067	1.5	19.5	0.5	23.2	75	80	88	198
	8	62 960	0.443	0.098	0.0322	0.1	19.5	0.2	23	0	2.5	2.5	146
	9	62 960	0.443	0.097	0	0.02	19.5	0.2	>25	0	2.5	2.5	203.5
	10	62 960	0.28	0.098	0	0.1	19.5	0.3	>25	3.75	5	8	122

Note: where  $\theta_0$  is the initial volumetric water content of soil;  $i$  is average infiltration during the time of surface runoff, in case 7,  $i = 0.0119/0.0067$  mean that the average infiltration rate from the surface runoff star to the steady runoff is 0.0119, while from the steady runoff to the simulated rainfall end is 0.0067.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

⏪

⏩

◀

▶

Back

Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

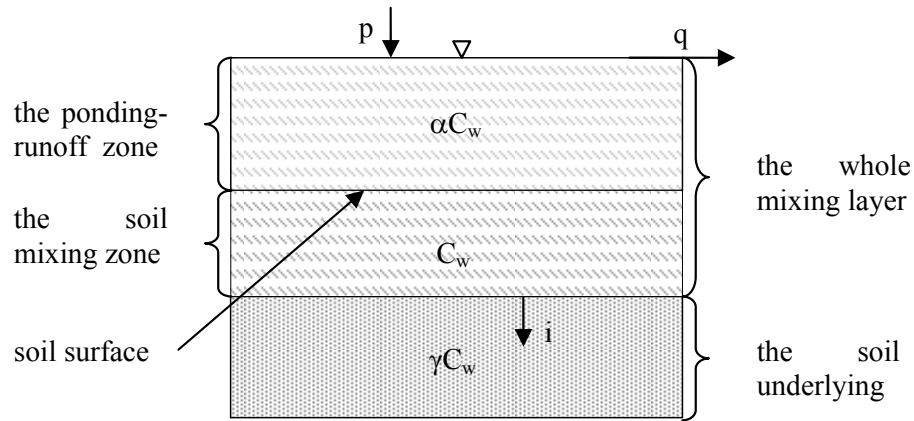
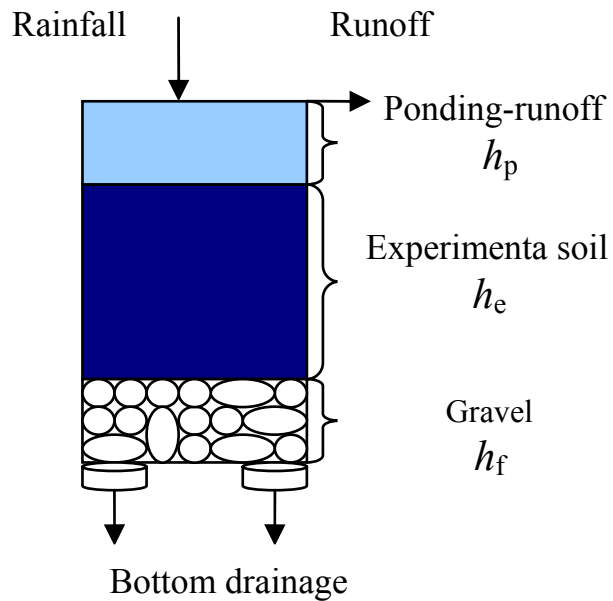


Fig. 1. Sketch of the simple two-layer model.

## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

<a href="#">Title Page</a>	
<a href="#">Abstract</a>	<a href="#">Introduction</a>
<a href="#">Conclusions</a>	<a href="#">References</a>
<a href="#">Tables</a>	<a href="#">Figures</a>
<a href="#">◀</a>	<a href="#">▶</a>
<a href="#">◀</a>	<a href="#">▶</a>
<a href="#">Back</a>	<a href="#">Close</a>
<a href="#">Full Screen / Esc</a>	
<a href="#">Printer-friendly Version</a>	
<a href="#">Interactive Discussion</a>	



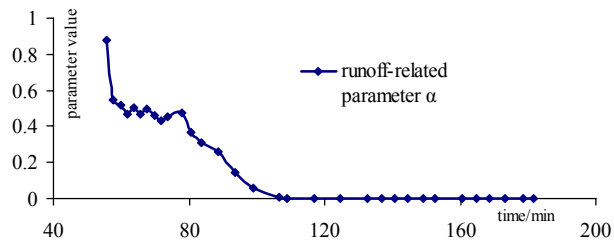
**Fig. 2.** Sketch of experimental frame (not to scale) of Tong et al. (2010).

## Parameter identification and analysis of soluble chemical transfer

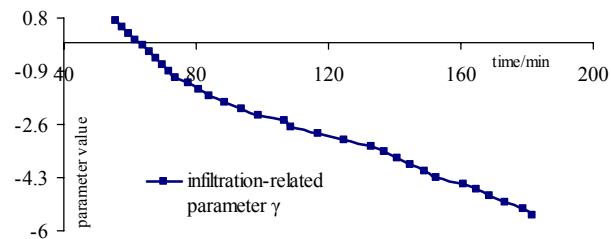
J. X. Tong et al.

<a href="#">Title Page</a>	
<a href="#">Abstract</a>	<a href="#">Introduction</a>
<a href="#">Conclusions</a>	<a href="#">References</a>
<a href="#">Tables</a>	<a href="#">Figures</a>
<a href="#">⏪</a>	<a href="#">⏩</a>
<a href="#">◀</a>	<a href="#">▶</a>
<a href="#">Back</a>	<a href="#">Close</a>
<a href="#">Full Screen / Esc</a>	
<a href="#">Printer-friendly Version</a>	
<a href="#">Interactive Discussion</a>	

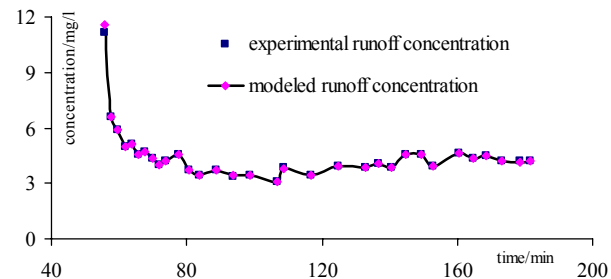




(a) identified incomplete runoff-related parameter  $\alpha$



(b) identified incomplete runoff-related parameter  $\gamma$



(c) comparison of experimental and modeled data

**Fig. 3.** Modeled data and parameters for case 1.

**Parameter identification and analysis of soluble chemical transfer**

J. X. Tong et al.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

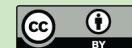
◀ ▶

Back Close

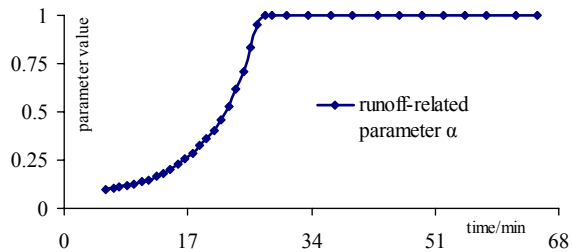
Full Screen / Esc

Printer-friendly Version

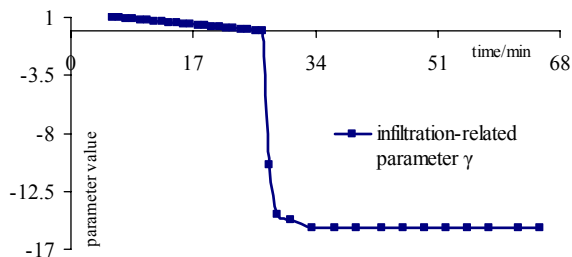
Interactive Discussion



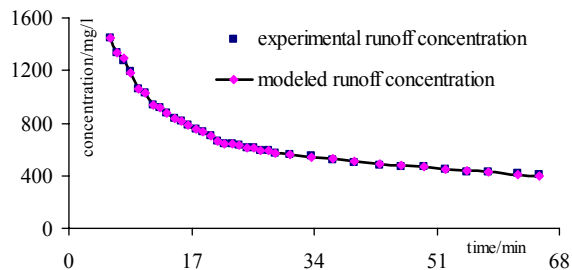




(a) identified incomplete runoff-related parameter  $\alpha$



(b) identified incomplete runoff-related parameter  $\gamma$



(c) comparison of experimental and modeled data

Fig. 5. Modeled data and parameters for case 3.

## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.

[Title Page](#)

[Abstract](#) | [Introduction](#)

[Conclusions](#) | [References](#)

[Tables](#) | [Figures](#)

[◀](#) | [▶](#)

[◀](#) | [▶](#)

[Back](#) | [Close](#)

[Full Screen / Esc](#)

[Printer-friendly Version](#)

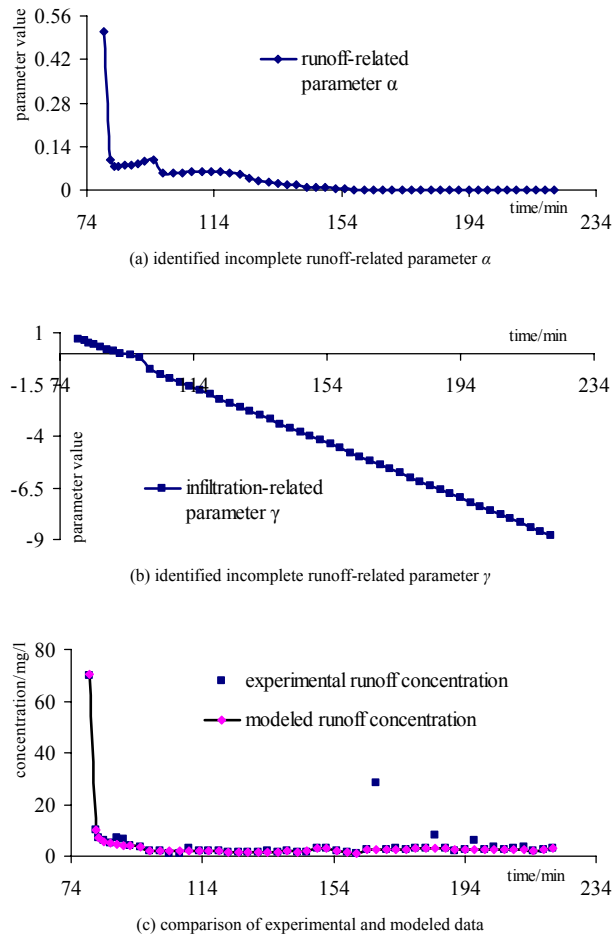
[Interactive Discussion](#)





## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.



**Fig. 6.** Modeled data and parameters for case 4.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

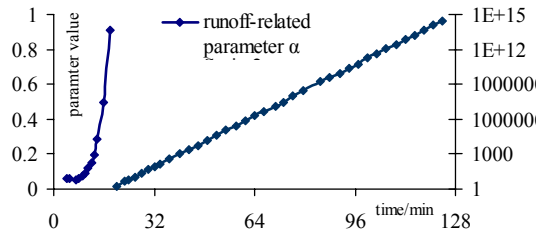
Interactive Discussion



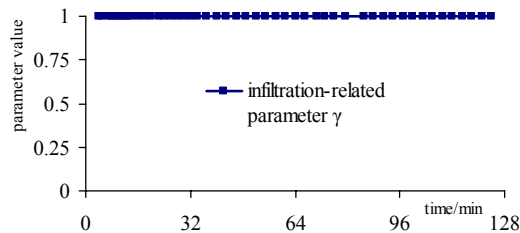


## Parameter identification and analysis of soluble chemical transfer

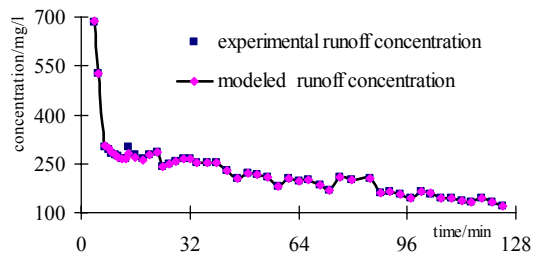
J. X. Tong et al.



(a) identified incomplete runoff-related parameter  $\alpha$



(b) identified incomplete runoff-related parameter  $\gamma$



(c) comparison of experimental and modeled data

**Fig. 8.** Modeled data and parameters for case 6.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

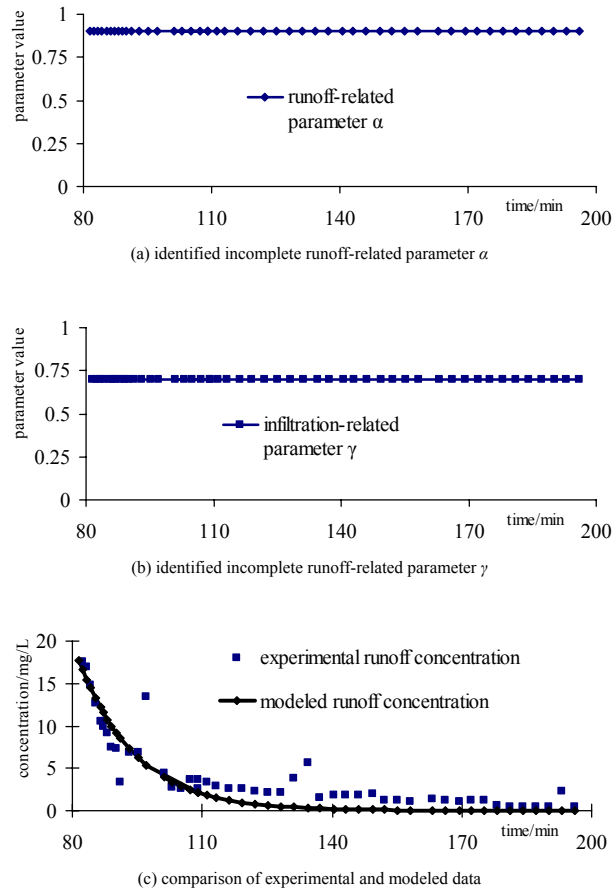
Printer-friendly Version

Interactive Discussion



**Parameter  
identification and  
analysis of soluble  
chemical transfer**

J. X. Tong et al.

**Fig. 9.** Modeled data and parameters for case 7.

Title Page

Abstract

Introduction

Conclusions

References

Tables

Figures

◀

▶

◀

▶

Back

Close

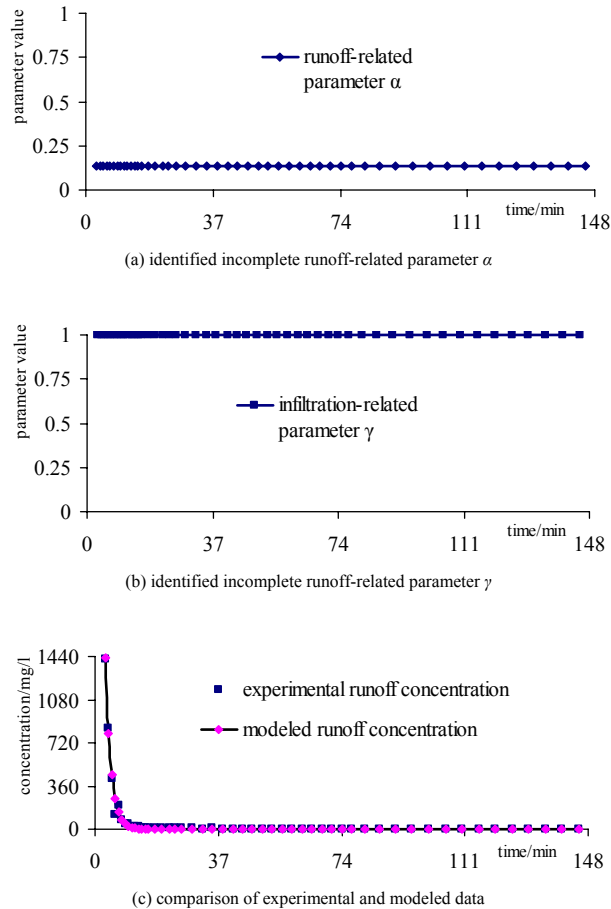
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.



**Fig. 10.** Modeled data and parameters for case 8.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

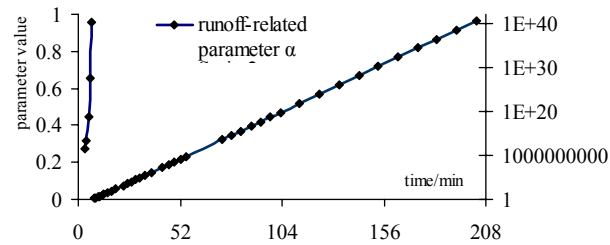
Printer-friendly Version

Interactive Discussion

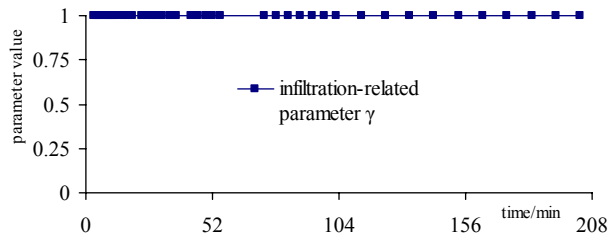


## Parameter identification and analysis of soluble chemical transfer

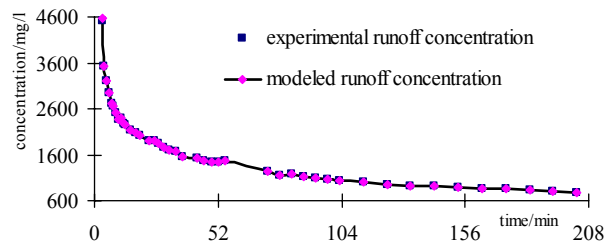
J. X. Tong et al.



(a) identified incomplete runoff-related parameter  $\alpha$



(b) identified incomplete runoff-related parameter  $\gamma$



(c) comparison of experimental and modeled data

**Fig. 11.** Modeled data and parameters for case 9.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

◀ ▶

◀ ▶

Back Close

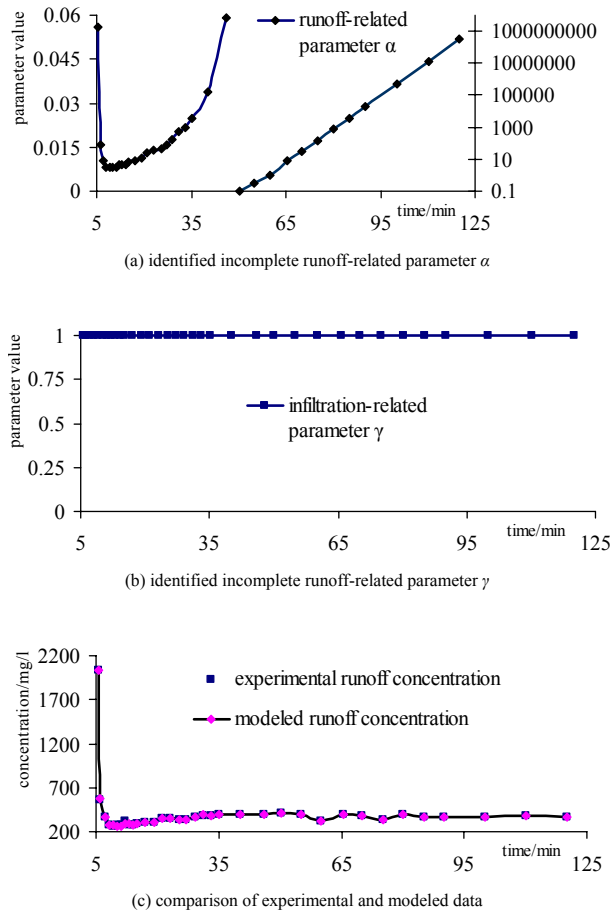
Full Screen / Esc

Printer-friendly Version

Interactive Discussion

## Parameter identification and analysis of soluble chemical transfer

J. X. Tong et al.



**Fig. 12.** Modeled data and parameters for case 10.

Title Page

Abstract Introduction

Conclusions References

Tables Figures

⏪ ⏩

◀ ▶

Back Close

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

