Bull Environ Contam Toxicol (2010) 85:525–529
DOI 10.1007/s00128-010-0151-5

Predicting the Accumulation of Organic Contaminants from Soil by Plants

Roger A. Cropp · Darryl W. Hawker · Maliwan Boonsaner

Received: 7 June 2010 / Accepted: 30 October 2010 / Published online: 11 November 2010

Abstract Analytic expressions for maximum chemical concentration attained in plants, and time this takes for uptake from surrounding soil were derived from a simple two-compartment soil/water–plant model. To illustrate, for the antibiotic norflxacin undergoing first order loss in the soil/water phase with a rate constant of 0.544 days^{-1}, maximum concentration in soybean P_{MAX} is predicted to occur after 2.79 days exposure and be independent of initial soil/water concentration SW_0 of 52.5 mg kg^{-1} dry weight. For soybean, the relationship between P_{MAX} and SW_0 is $P_{MAX} = 0.047SW_0$, resulting in predicted maximum levels of 2.20 mg kg^{-1} dry weight. Modelled plant concentrations agreed well with experimental data ($R^2 = 0.91$).

Keywords Soil/water–plant system · Maximum plant concentration · Time to maximum plant concentration · Analytic solutions · Antibiotics · Soybean

Plants are fundamental components of food webs and can accumulate organic contaminants from the soil and/or air (Fryer and Collins 2003). As well as possibly being detrimental to the plant itself, such contaminants can be accumulated or biomagnified by higher consumers in food webs (Paterson et al. 1991). Trapp and Mathies (1995) note that the uptake of chemicals into vegetation is a major pathway for the entrance of toxic substances into the food chain leading to humans. Despite this, the process of chemical movement from soil to vegetation remains poorly understood (McKone and Maddalena 2007).

Various empirical and process-based models have been developed in an attempt to understand and predict chemical fate and behaviour in soil/plant systems (McKone and Maddalena 2007). Dynamic models investigate the change in concentration in plants or plant tissues with time. 'PlantX', for example, is a four-compartment (roots, stems, leaves and fruit) dynamic model (Trapp 2004). As is typical of such complex models, analytic solutions are not available and the model must be solved numerically. While numerical solutions are useful for individual models, they often provide little indication of general underlying principles.

A one-compartment plant model with water as an ambient phase however has an analytic solution and is used in chemical risk assessment (Trapp and Matthies 1995). Assuming that the chemical concentration in an ambient water phase is constant, this solution has the following form.

$$P = \frac{b}{a} W(1 - e^{-at}). \quad (1)$$

In this expression, P is chemical concentration in the plant compartment, W the concentration in the water, a is a summation of first order loss rate constants from this compartment, b a plant and chemical-specific constant and t time. In this treatment, the steady-state (and maximum) plant concentration described by Eq. 1 is $\frac{b}{a}W$, and it strictly

Electronic supplementary material The online version of this article (doi:10.1007/s00128-010-0151-5) contains supplementary material, which is available to authorized users.

R. A. Cropp · D. W. Hawker (✉)
Atmospheric Environment Research Centre, School of Environment, Nathan Campus, Griffith University, Nathan, QLD 4111, Australia
e-mail: d.hawker@griffith.edu.au

M. Boonsaner
Department of Environmental Science, Faculty of Science, Silpakorn University, Nakhon Pathom 73000, Thailand

takes an infinite time to achieve. The time required to reach 95% of this steady-state value is however finite and is given by $-\ln\left(0.05/a\right)$ (McKone and Maddalena 2007). An analytic solution of the same form as that in Eq. 1, has also been found by Paterson et al. (1991). However, a significant problem with these approaches is that the plant concentration never decreases with time.

Concentrations of organic chemicals in adjacent soil or water phases are unlikely to always be constant. Rather, they may decrease due to various abiotic (e.g. hydrolysis) and biotic (e.g. microbial transformation) loss processes. The plant concentration should respond to this external forcing by also eventually decreasing. This has been observed experimentally in a number of instances (e.g. Boonsaner and Hawker 2010; Behrendt and Brüggeman 1993; Gao et al. 2005) and cannot be due to processes such as chemical transformation in the plant or loss of chemical to the atmosphere from the plant, as these can be accommodated by expressions such as Eq. 1. During this response, the concentration in the plant reaches a maximum value at a definite time.

From a risk management perspective, it is of considerable interest to know what maximum levels or concentrations of contaminants will be reached in plants, and how long this would take, given certain initial ambient conditions (Maia et al. 2009). Predicted concentrations could be compared with maximum residue limits of edible plants or other regulatory thresholds to see if and when they are exceeded. We wished therefore to develop a simple but informative model as a tool to help understand these aspects of the soil–plant system that have hitherto been little explored.

Recently, Boonsaner and Hawker (2010) investigated the uptake and accumulation of antibiotics by soybean (*Glycine max (L.) Merr.*) in Thailand. Here, changing economic conditions have led to the reuse of former aquaculture facilities for agricultural purposes. However, the soil is frequently contaminated with antibiotics and salt. Soybean was shown to be relatively salt tolerant and able to accumulate antibiotics including norfloxacin. These antibiotics, though essentially non-volatile, have been observed to undergo a number of loss processes in water and interstitial soil water (Boonsaner and Hawker 2010). Amongst the data from this work are norfloxacin concentrations in the external soil/water phase and plant with time (Table 1). Gaining insight into the plant-soil system and developing expressions for the maximum concentration in the plant and the time that this takes, these data can to used to illustrate the application of any derived model.

The purpose of this study was to develop analytic solutions for a two-compartment model of plant concentration as a function of time and an analytic solution for time to maximum concentration in the plant.

Table 1 Measured antibiotic (norfloxacin) concentrations in soybean and soil/water

Day	Plant (mg kg^{-1} dry weight)	Soil/Water (mg kg^{-1} dry weight)
0	0.00	52.5
2	2.26	16.9
4	2.34	5.36
6	2.59	1.70
8	1.38	0.62
10	0.57	nd[a]

From Boonsaner and Hawker (2010)

[a] Method detection limit for norfloxacin in plants and soil samples = 0.5 mg kg^{-1} dry weight. Plant and soil/water concentrations at 12, 20, 30 and 35 days below method detection limit

Materials and Methods

It is generally recognized that accumulation of contaminants from soil by plants takes place through an intermediate water phase (Paterson et al. 1991; Ryan et al. 1989). An obvious approach then would be a three-compartment (soil-interstitial water-plant) dynamic model. However, solutions to three-compartment models do not allow for the derivation of closed form analytic solutions for the time taken to reach maximum concentration. The inaccessibility of these solutions is demonstrated in the Electronic Supporting Information. A simpler two-compartment model with a single peripheral combined soil/water compartment in addition to that for the plant does allow the derivation of a closed form expression for the time to maximum concentration. While a less-realistic representation of the plant-water-soil system, the two-compartment model is the preferred approach to achieve our goal.

The two-compartment model involves only one peripheral compartment in addition to the compartment for the plant (Fig. 1). This peripheral compartment represents the soil and interstitial water phases, so a first order loss term from it is necessary. This term encompasses processes such as hydrolysis and other first order loss processes. Additionally, in this model, the plant and peripheral compartments are coupled via uptake and loss from the plant.

Contaminated soil was prepared using sterilized substrate taken from areas adjacent to aquaculture facilities in the area of Nakorn Pathom, central Thailand. The antibiotic, norfloxacin, was added to and mixed with the soil, along with water. The water was added to attain a 40% (w/w) water content, reflecting local field conditions. The nominal initial concentration of norfloxacin in this

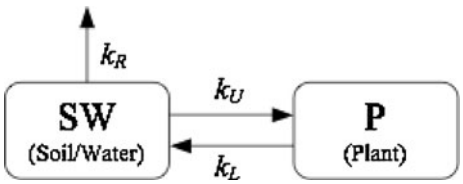

Fig. 1 Schematic of the two-compartment model of the plant-soil/water system

soil/water system was 55 mg kg^{-1} dry weight. All analyses were carried out in duplicate. Details of plant cultivation and characteristics together with plant and soil/water analysis are found in Boonsaner and Hawker (2010). Interstitial water concentrations by themselves were not directly measured. Raw data from this work (Table 1) suggests that maximum plant concentrations are reached in less than 5 days under the experimental conditions employed.

Analytic solutions to the model were used with a genetic algorithm (Holland 1975; Mitchell 1996) in an inverse modeling process to derive values for the rate parameters or constants k_R, k_U, and k_L (Fig. 1). The analytic solution derived for each parameter set was compared to the measured data for each model solution for each contaminant using an un-weighted least squares metric to determine the accuracy with which the model solution reflected the measured data. Parameter ranges were constrained to 0–1 for k_R, k_U and k_L, and were sampled at a resolution of 2^{-16}. A population of 100 individuals was bred for 100 generations with crossover rates of 0.50–0.75 and mutation rates of 0.005–0.01 to optimize the fit to the data.

Results and Discussion

Since the primary aim of this work was to develop simple yet useful modeling approaches, we wish to derive an analytic expression for the time (t_{MAX}) required to reach P_{MAX}, and hence obtain a useful analytic expression for P_{MAX}. The two-compartment model is described by the following differential equations.

$$\frac{dSW}{dt} = -(k_R + k_U)SW + k_L P, \tag{2}$$

$$\frac{dP}{dt} = k_U SW - k_L P. \tag{3}$$

Here SW and P represent contaminant concentrations in the soil/water and plant compartments respectively. The first order rate constant k_R describes transformation reactions in the interstitial water and k_U and k_L uptake and loss from the plant respectively. Equations 2 and 3 may be represented in matrix form as

$$\dot{U} = \begin{bmatrix} -(k_R + k_U) & k_L \\ k_U & -k_L \end{bmatrix} U = KU, \tag{4}$$

where $U = [SW, P]^T$.

The eigenvalues of this model are:

$$\lambda_1 = \frac{1}{2}\left\{-k_R - k_L - k_U + \sqrt{k_R^2 + k_L^2 + k_U^2 - 2k_L k_R + 2k_R k_U + 2k_L k_U}\right\} \tag{5}$$

$$\lambda_2 = \frac{1}{2}\left\{-k_R - k_L - k_U - \sqrt{k_R^2 + k_L^2 + k_U^2 - 2k_L k_R + 2k_R k_U + 2k_L k_U}\right\} \tag{6}$$

and the associated eigenvectors are

$$\xi_1 = \begin{bmatrix} \frac{k_L - k_U - k_R + \sqrt{k_L^2 + k_U^2 + k_R^2 + 2k_L k_U - 2k_L k_R + 2k_R k_U}}{2k_U} \\ 1 \end{bmatrix}, \tag{7}$$

$$\xi_2 = \begin{bmatrix} \frac{k_L - k_U - k_R - \sqrt{k_L^2 + k_U^2 + k_R^2 + 2k_L k_U - 2k_L k_R + 2k_R k_U}}{2k_U} \\ 1 \end{bmatrix}. \tag{8}$$

The solution for the plant concentration is simply:

$$P = C_1 e^{\lambda_1 t} + C_2 e^{\lambda_2 t}, \tag{9}$$

where

$$C_1 = \frac{k_U SW_0}{\sqrt{k_L^2 + k_U^2 + k_R^2 + 2k_L k_U - 2k_L k_R + 2k_R k_U}}, \tag{10}$$

and $C_2 = -C_1$.

Inspection of the eigenvalues for the model (λ_1 and λ_2) reveals that they are functions of the rate constants k_R, k_U and k_L only. As the eigenvalues control the time the system takes to reach its final state, this result indicates that the time to maximum plant concentration will be a function of the rate parameters only, and that t_{MAX} must therefore be independent of the initial chemical concentration in the soil/water matrix (SW_0). The maximum concentration in the plant occurs when:

$$\frac{dP}{dt} = \lambda_1 C_1 e^{\lambda_1 t} + \lambda_2 C_2 e^{\lambda_2 t} = 0, \tag{11}$$

and since $C_2 = -C_1$, it now possible to write an explicit expression for this time period. The solution to Eq. 11 reveals that the time to maximum concentration is given by:

$$t_{MAX} = \frac{1}{(\lambda_2 - \lambda_1)} \ln\left(\frac{\lambda_1}{\lambda_2}\right). \tag{12}$$

As mentioned above, these eigenvalues are functions only of the relevant rate constants and not SW_0, so this time period is clearly independent of the initial concentration of the chemical contaminant in the soil/water compartment. The maximum concentration in the plant is obtained by

solving Eq. 11 using t_{MAX} as given by Eq. 12. An expression for P_{MAX} is then:

$$P_{MAX} = \frac{k_U}{\sqrt{k_L^2 + k_U^2 + k_R^2 + 2k_Lk_U - 2k_Lk_R + 2k_Rk_U}} \times \left[\left(\frac{\lambda_1}{\lambda_2}\right)^{\left(\frac{\lambda_1}{\lambda_2-\lambda_1}\right)} - \left(\frac{\lambda_1}{\lambda_2}\right)^{\left(\frac{\lambda_2}{\lambda_2-\lambda_1}\right)} \right] SW_0. \quad (13)$$

Equation 13 reveals that the maximum concentration attained in the plant is a linear function of SW_0 meaning, for example, that doubling SW_0 doubles P_{MAX}. A linear dependence of plant concentration on initial soil/water concentration has been noted previously by Kumar et al. (2005). However, this was an empirical observation. Here, we have obtained an analytic explanation for the linear relationship, and now illustrate its application to experimental data. The solutions presented here are not accessible from a three-compartment soil-interstitial water-plant model.

The values of the three rate constants (k_R, k_U and k_L) that gave the best un-weighted least squares fit to the norfloxacin data set when simultaneously derived by the genetic algorithm are shown in Table 2. Evaluation of Eq. 12 using the values in Table 2 indicates that the maximum concentration in soybean is reached at $t_{MAX} = 2.79$ days.

The relationship between P_{MAX} and SW_0, confirmed by numerical techniques, was

$$P_{MAX} = 0.047SW_0. \quad (14)$$

Using Eq. 14, the initial experimental soil concentrations result in predicted maximum levels in soybean of 2.20 mg kg^{-1} dry weight. Overall, modelled plant concentrations agree well with the experimental data plotted in Fig. 2 ($R^2 = 0.91$ from weighted nonlinear regression).

Dolliver et al. (2007) found concentrations of the sulfonamide antibiotic sulfamethazine of 0.1–1.2 mg kg^{-1} dry weight in corn (*Zea mays* L.), lettuce (*Lactuca sativa* L.) and potato (*Solanum tuberosum* L.) but only sampled after 45 days exposure. In view of the results from the present study, levels could conceivably been higher prior to this and highlight the need for modelling studies that enable temporal trends to be predicted. Although the response of the soybean plant in the illustrative data is relatively rapid, with other plants and other chemical

Table 2 Values for rate constants derived by a genetic algorithm to give best unweighted fit to the measured norfloxacin data in both plant and soil/water simultaneously

Rate constant	GA Range	Value (days^{-1})
k_R	0–1	0.544
k_U	0–1	0.049
k_L	0–1	0.210

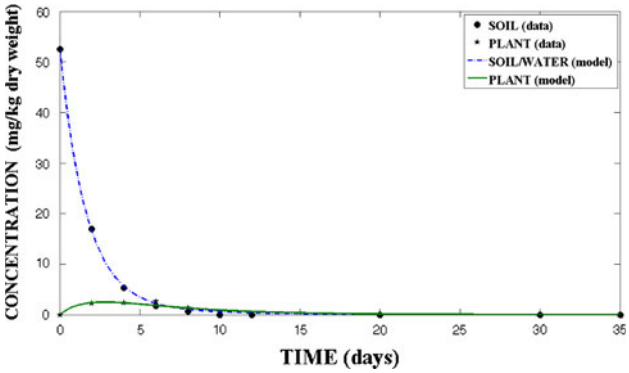

Fig. 2 Experimental data (*points*) and model solution (*lines*) for norfloxacin. The model solution uses the rate constants given in Table 2

contaminants this may not be the case. In some instances growth dilution may have to be taken into account. One way in which this is often done is to represent growth dilution as a first order loss process (Steyaert et al. 2009). This may be incorporated within the modelling approach employed in this work.

Treating the plant as a single compartment, and therefore plant concentrations as homogenous, is a common simplification (Steyaert et al. 2009). This will neglect likely processes such as translocation however. Considering the plant as comprising compartments such as root stem and leaf can accommodate this (Gent et al. 2007; Hung and Mackay 1997; Behrendt and Brüggeman 1993). Unfortunately, this approach incurs a heavy penalty, with the additional mathematical complexity generally prohibiting the obtaining of analytic solutions, and is therefore not helpful in view of the objectives of this work to derive a simple but useful heuristic model.

Our simple two-compartment model approximates the important processes in the plant-soil/water interactions and allows analytic solutions for the maximum plant concentration and the time to maximum concentration to be derived. This information is of significant practical use and can act as a general template for accumulation of organic contaminants from soil by plants where those contaminants are undergoing concomitant first order loss processes in the environment external to the plant.

Acknowledgments This study was supported by the National Research Fund of Thailand and the Silpakorn University Research and Development Institutue. The authors would like to thank A. Boonsaner and S. Jaipan for their plant and soil preparations and O. Kaewnun for her laboratory assistance.

References

Behrendt H, Brüggeman R (1993) Modeling the fate of organic chemicals in the soil plant environment. Chemosphere 27: 2325–2332

Boonsaner M, Hawker DW (2010) Accumulation of oxytetracycline and norfloxacin from saline soil by soybean. Sci Total Environ 408:1731–1737

Dolliver H, Kumar K, Gupta SC (2007) Sulfamethazine uptake by plants from manure-amended soil. J Environ Qual 36:1224–1230

Fryer ME, Collins CD (2003) Model intercomparison for the uptake of organic chemicals by plants. Environ Sci Technol 37: 1617–1624

Gao Y, Zhu L, Ling W (2005) Application of the partition-limited model for plant uptake of organic chemicals from soil and water. Sci Total Environ 336:171–182

Gent MPN, White JC, Eitzer BD, Mattina MJI (2007) Modeling the difference among Curcubita in uptake and translocation of p, p′-dichlorophenyl-1, 1-dichloroethylene. Environ Toxicol Chem 26:2476–2485

Holland JH (1975) Adaptation in natural and artificial systems. University of Michigan Press, Ann Arbour

Hung H, Mackay D (1997) A novel and simple model of the uptake of organic chemicals by vegetation from air and soil. Chemosphere 35:959–977

Kumar K, Gupta SC, Baidoo SK, Chander Y, Rosen CJ (2005) Antibiotic uptake by plants from soil fertilized with animal manure. J Environ Qual 34:2082–2085

Maia PP, da Silva EC, Rath S, Reyes FGR (2009) Residue content of oxytetracycline applied on tomatoes grown in open field and greenhouse. Food Control 20:11–16

McKone TE, Maddalena RL (2007) Plant uptake of organic pollutants from soil: Bioconcentration estimates based on models and experiments. Environ Toxicol Chem 26:2494–2504

Mitchell M (1996) An introduction to genetic algorithms. MIT Press, Cambridge, Mass

Paterson S, Mackay D, Gladman A (1991) A fugacity model of chemical uptake by plants from soil and air. Chemosphere 23:539–565

Ryan JA, Bell RM, Davidson JM, O'Connor GA (1989) Plant uptake of non-ionic chemicals from soils. Chemosphere 17:2299–2323

Steyaert NLL, Hauck M, van Hulle SWH, Hendriks AJ (2009) Modelling bioaccumulation of semi-volatile organic compounds (SOCs) from air in plants using allometric principles. Chemosphere 77:727–732

Trapp S (2004) Plant uptake and transport models for neutral and ionic chemicals. Environ Sci Pollut Res 11:33–39

Trapp S, Matthies M (1995) Generic one-compartment model for uptake of organic chemicals by foliar vegetation. Environ Sci Technol 29:2333–2338