Journal of Contaminant Hydrology 158 (2014) 14–22

Contents lists available at ScienceDirect

Journal of Contaminant Hydrology

journal homepage: www.elsevier.com/locate/jconhyd

Predicting release and transport of pesticides from a granular formulation during unsaturated diffusion in porous media

Marcos Paradelo [a,b,*], Diego Soto-Gómez [a], Paula Pérez-Rodríguez [a],
Eva Pose-Juan [c], J. Eugenio López-Periago [a]

[a] Soil Science and Agricultural Chemistry Group, Department of Plant Biology and Soil Science, Faculty of Sciences, University of Vigo, E-32004 Ourense, Spain
[b] Department od Agroecology, Faculty of Science and Technology, Aarhus University, Blichers Allé 20, P.O. Box 50, DK-8830 Tjele, Denmark
[c] Institute of Natural Resources and Agrobiology of Salamanca (IRNASA-CSIC), 37008 Salamanca, Spain

ARTICLE INFO

Article history:
Received 5 February 2013
Received in revised form 20 July 2013
Accepted 28 October 2013
Available online 16 December 2013

Keywords:
Soil pesticide transport
Diffusion
Controlled release
Formulation
Soil
Agrochemicals

ABSTRACT

The release and transport of active ingredients (AIs) from controlled-release formulations (CRFs) have potential to reduce groundwater pesticide pollution. These formulations have a major effect on the release rate and subsequent transport to groundwater. Therefore the influence of CRFs should be included in modeling non-point source pollution by pesticides. We propose a simplified approach that uses a phase transition equation coupled to the diffusion equation that describes the release rate of AIs from commercial CRFs in porous media; the parameters are as follows: a release coefficient, the solubility of the AI, and diffusion transport with decay. The model gives acceptable predictions of the pesticides release from commercial CRFs in diffusion cells filled with quartz sand. This approach can be used to study the dynamics of the CRF-porous media interaction. It also could be implemented in fate of agricultural chemical models to include the effect of CRFs.

1. Introduction

Controlled-release formulations (CRFs) are mixtures of one or more active ingredients (AIs) with a carrier. CRFs are designed to enhance the application of the pesticide to crops and the effectiveness of the pesticide (Collins et al., 1973). Granulates are a very common type of CRF used to regulate the release of AIs into the soil and to control soil-borne diseases within the natural variability of both the soil and rainfall. Therefore, studies examining the mechanisms that control the release of an AI and its transport in soil are of particular interest. The ability to model the coupled release and transport of AIs would facilitate the development of new CRFs, provide new methods to validate their effectiveness and improve existing methods for environmental risk assessments of pesticide usage.

A variety of studies on the release of agricultural chemicals from CRFs have been published. These include field-scale studies that have shown that commercial starch-encapsulated formulations of atrazine decrease pesticide losses in leachates and increase its persistence in soil (Gish et al., 1994). The behavior of different types of formulations has also been described. For example, commercial formulations of alachlor, atrazine and fenamiphos affect the potential of these pesticides to become water pollutants under severe rainfall conditions (Davis et al., 1996). A sepiolite-gel matrix CRF has been found to significantly decrease the leaching of metribuzin in soil column tests (Maqueda et al., 2008). Atrazine release from alginate-based CRFs in soil columns decreased regarding application of water suspension of herbicide (Malyszka and Jankowski, 2004). A decrease in the rate of the release of an alginate-based CRF of alachlor into the soil has been observed with a decrease in the soil water potential, suggesting a diffusion-controlled release rate (Nasser et al., 2008). The use of a pillared clay-controlled release formulation of alachlor can increase the persistence of alachlor in the soil (Gerstl et al., 1998). More recently, the use of modified montmorillonites as carriers has been shown to decrease the potential losses of simazine (Cornejo et al., 2008), fluometuron (Gámiz et al., 2010) and other anionic herbicides (Undabeytia et al., 2003).

---

[*] Corresponding author.
E-mail address: mparadelo@uvigo.es (M. Paradelo).

0169-7722/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jconhyd.2013.10.009

The influence of CRFs on pesticide losses by leaching has been studied using field-deployed lysimeters together with rainfall simulations (Potter et al., 2010); these authors reported that the use of a CRF with a clay-alginate polymer can decrease metolachlor leaching. Organo-clay formulations influence the bioavailability of AIs via their adsorption of AIs (Sánchez-Verdejo et al., 2008; Trigo et al., 2009). Lignin-based CRFs can decrease the leaching losses of isoproturon, imidacloprid and cyromazine (Garrido-Herrera et al., 2009). A physically based model to describe release of AIs from membrane coated CRFs in free water was reported (Shaviv et al., 2003a; Shaviv et al., 2003b).

The classical description of controlled release process is the Higuchi's model (Higuchi, 1961) which defines three stages: i) a lag period during which water penetrates and dissolve the AI, ii) a linear release when water penetration and AI release occur together and, iii) a decaying release due to the depletion of the AI into the granule.

Since a complete implementation of the Higuchi's model can be cumbersome for practical purposes, simplifications to model controlled release of agrochemicals are often used in several fields. A simplification assuming that release can be as a pseudo-first order kinetics was used to test experimental CRFs of carbofuran in soil (Choudhary et al., 2006). Another approach assumes that release is controlled by a solubilization-limited process and decay of the AI (Collins et al., 1973). This is only valid if transport is negligible regarding the flux rate; such in the case of granules submerged in water, but may not be valid for unsaturated soil. Empirical release models and closed forms of physically based release equations have been developed (Ritger and Peppas, 1987), but these cannot reproduce the influence of varying soil moisture conditions in the field. In addition, changes in the pore water velocity have influence on the time course of the release rate of AI from CRFs (Paradelo et al., 2012). A full mathematical description of the release process should reproduce all the environmental effects described above, but this approach is very demanding in terms of computation. Therefore, it is desirable to provide an efficient approach to model the pesticide release from CRF in varying moisture conditions.

The objective of this paper is to propose a simpler approach as a tool to simulate the controlled release of pesticides buried in soil. This paper focuses on modeling the release of pesticides from uncoated granulated CRFs in porous media. The model was compared with diffusion experiments of carbofuran and fenamiphos CRFs embedded in sand diffusion cells under unsaturated moisture conditions.

2. Materials and methods

2.1. Release kinetics model

The solubilization kinetics was modeled by a phase transition kinetics equation that was proposed by other authors to model the solubilization kinetics of minerals (Parkhurst and Appelo, 1999). The rate of the phase transition during the solubilization takes the form:

$$\frac{dm}{dt} = -k_1 \frac{A}{V} \left(\frac{m}{m_0}\right)^b \left(1-10^{SI}\right) \tag{1}$$

where k_1 is the specific rate, and *SI* is the saturation index of the pesticide, $A\,V^{-1}$ is the relationship between the area of surface contact (A) and the volume (V) of the solid per unit of mass. The values of m_0 and m are the initial and actual (at time t) mass of the solid phase of the AI in the granules, respectively, and b is a shape factor of the granule.

2.2. Transport model

If the pesticides react with the porous matrix, the expression for diffusion with linear adsorption model and first order decay in the liquid phase takes the form:

$$\left(1 + \frac{\rho_b\ K_D}{\theta}\right)\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) + \frac{\partial c_s}{\partial t} \tag{2}$$

where ρ_b is the bulk density of the porous matrix, θ is the water content on a volume basis; K_D is the linear coefficient partition, c is the resident concentration in the liquid phase; t is time; x is the distance; D is the effective diffusion coefficient in the pores porous matrix, given by $D = \theta\,\tau\,D_0$, where D_0 is the molecular diffusion coefficient for infinite volume dissolution and τ is the tortuosity factor calculated by the Millington and Quirk formula (Millington and Quirk, 1961), that is valid for an isotropic porous medium granular matrix (Radcliffe, 2010):

$$\tau = \frac{\theta^{7/3}}{\theta_s^2} \tag{3}$$

where θ_s is the saturated water content. For our diffusion cells $\tau = 0.17$ (Table 2). If the pesticide is linearly adsorbed the solid/liquid equilibrium partition coefficient K_D can be used to calculate the linear retardation term in the left hand of Eq. (2) $\left(1 + \frac{\rho_b\ K_D}{\theta}\right)$. The $\partial c_s/\partial t$ is the sink rate to account the removal rate of the pesticide from pore water by degradation, the subscript $_s$ indicates the concentration depleted in the liquid phase. Using the appropriate initial and boundary conditions that meet the conditions imposed in the diffusion experiments, numerical solutions of Eq. (2) can be obtained.

Modeling of the redistribution of unreactive Br^- is better done by using analytical solutions of the non-reactive diffusion (Crank, 1975):

$$\frac{\delta c}{\delta t} = D\frac{\delta^2 c}{\delta x^2}. \tag{4}$$

If the domain is defined by the impermeable boundaries at $x = 0$ and $x = L$, being L the length of the cell, Eq. (4) can be solved for diffusion cells with the initial conditions:

$$c(0 \le x < L/2, t = 0) = c_0$$

and

$$c(L \ge x \ge L/2, t = 0) = 0.$$

If diffusion does not reach the ends of the cell the boundary conditions are

$$c(x = 0, t > 0) = c_0$$