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Transport of bromide and pesticides through an undisturbed soil column: A modeling study with global optimization analysis

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ABSTRACT

The fate of pesticides in tropical soils is still not understood as well as it is for soils in temperate regions. In this study, water flow and transport of bromide tracer and five pesticides (atrazine, imazaquin, sulfometuron methyl, S-metolachlor, and imidacloprid) through an undisturbed soil column of tropical Oxisol were analyzed using a one-dimensional numerical model. The numerical model is based on Richards' equation for solving water flow, and the advection–dispersion equation for solving solute transport. Data from a laboratory column leaching experiment were used in the uncertainty analysis using a global optimization methodology to evaluate the model's sensitivity to transport parameters. All pesticides were found to be relatively mobile (sorption distribution coefficients lower than 2 $cm^3\ g^{-1}$). Experimental data indicated significant non-conservative behavior of bromide tracer. All pesticides, with the exception of imidacloprid, were found less persistent (degradation half-lives smaller than 45 days). Three of the five pesticides (atrazine, sulfometuron methyl, and S-metolachlor) were better described by the linear kinetic sorption model, while the breakthrough curves of imazaquin and imidacloprid were more appropriately approximated using nonlinear instantaneous sorption. Sensitivity analysis suggested that the model is most sensitive to sorption distribution coefficient. The prediction limits contained most of the measured points of the experimental breakthrough curves, indicating adequate model concept and model structure for the description of transport processes in the soil column under study. Uncertainty analysis using a physically-based Monte Carlo modeling of pesticide fate and transport provides useful information for the evaluation of chemical leaching in Hawaii soils.

1. Introduction

Reliable model predictions of contaminant fate and transport in soils depend on adequate parameterization of relevant flow and transport processes. Despite significant progress of the analytical and numerical procedures made in past decades, it remains difficult to obtain parameters governing fate and transport of reactive compounds (e.g., pesticides) from field leaching studies due to soil heterogeneity and complex boundary conditions (e.g., Dusek et al., 2011). Thus, laboratory column leaching experiments, also referred to as miscible displacement experiments, are frequently being performed since the experimental conditions (i.e., initial and boundary conditions) may be sufficiently monitored and controlled. The use of independently estimated input parameters for predictions should be the ultimate goal of modeling. However, the conditions of experiments from which the input parameters

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were estimated differ considerably from the flow and transport conditions on which the model predictions are made. This may therefore lead to modeling results with limited reliability (Vereecken et al., 2011). At present, observed information on solute transport (i.e., spatial or temporal variations of a given chemical in soil and/or soil water) is used to estimate transport parameters by means of inverse modeling.

Several studies suggested that both water flow and chemical transport data are needed for proper model description of transport processes in soils (e.g., Coppola et al., 2009). When transport of solutes is accounted for, different strategies can be followed to obtain soil hydraulic and transport parameters by inverse modeling (Šimůnek et al., 2002). A sequential procedure can be pursued, in which the soil hydraulic parameters are estimated first and then estimation of transport parameters follows (thus two independent optimizations are invoked). Alternatively, water flow data (e.g., soil water pressure, water content, and flux) and transport information (e.g., resident concentration and concentration in the effluent) can be used in a sequential manner. Eventually, combined optimization using water and solute information can be employed to simultaneously estimate both the soil hydraulic and solute transport parameters. Inoue et al. (2000) showed that combined optimization is the most robust approach as it yields smaller estimation errors than a sequential procedure.

Search algorithms based on the Levenberg–Marquardt method (e.g., Clausnitzer and Hopmans, 1995) were recently complemented by prediction uncertainty and parameter sensitivity analysis (Bates and Campbell, 2001; Beven and Binley, 1992) or replaced by so-called global optimization methods (Mertens et al., 2009; Pan and Wu, 1998; Takeshita, 1999). Vrugt et al. (2005) reported on an improved inverse modeling of subsurface flow and transport using a simultaneous optimization and data assimilation method. Beven et al. (2006) presented a method for estimating transport of atrazine at the field scale that accounts for parameter uncertainty by conditioning the parameter distributions and constraining the predictions with the results of laboratory breakthrough experiments. A review of recent developments in inverse modeling procedures relevant for unsaturated flow and transport processes was given by Vrugt et al. (2008). Nevertheless, systematic applications of these optimization methods for reactive transport studies are still scarce.

Experimental breakthrough curves (time series of concentration in the effluent from a soil column) are used to characterize flow and solute processes in soils, e.g., physical and chemical nonequilibrium, biochemical degradation and production, and sorption kinetics. For instance, Fortin et al. (1997) performed an experiment involving flow interruptions on a soil column under saturated conditions and revealed the sorption kinetics of simazine. Bedmar et al. (2004) conducted laboratory leaching experiments on packed soil columns with the herbicides atrazine and metribuzin. In principle, the values of sorption distribution and degradation parameters can be estimated from batch sorption and degradation (incubation) experiments (e.g., Dusek et al., 2010a; Kulluru et al., 2010). However, the use of the coefficients estimated from these independent experiments often leads to discrepancies in prediction of fate and transport under both laboratory and field conditions (see the review from Vereecken et al. (2011)). Hence, the transport parameters can be also estimated directly using data from laboratory (Altfelder et al., 2001; Beigel and Di Pietro, 1999; Gaber et al., 1995) and field leaching studies (Dusek et al., 2011; Kasteel et al., 2010; Roulier and Jarvis, 2003).

Spatial variability of model input parameters as well as uncertainty in their adequate determination propagate through modeling systems in a largely unknown way. Deterministic models coupled with a Monte Carlo framework (e.g., Dubus and Brown, 2002; Lindahl et al., 2005) and stochastic approaches (e.g., Hu and Huang, 2002; Vanderborght et al., 2006) have been used to account for uncertainty analysis in pesticide fate and transport modeling. For pesticides, sorption distribution and degradation parameters have received the greatest attention (Dubus et al., 2003a, 2004; Roulier et al., 2006). Nevertheless, a significant influence of soil properties on pesticide leaching was also noted in several studies (e.g., Vereecken and Dust, 1998; Stenemo and Jarvis, 2007). Dubus et al. (2004) showed that optimized transport parameters depend on the initial values used in their optimization. Dubus et al. (2004) also demonstrated that the sorption distribution and degradation parameters could be both positively and negatively correlated.

Weathered tropical soils are not well understood in respect to transport parameters since the majority of studies have been undertaken in temperate regions (e.g., D'Alessio et al., 2014; Laabs and Amelung, 2005; Racke et al., 1997). Tropical soils often contain aggregates and large portion of fine micropores. Preferential flow effects in aggregated Oxisols have been reported in the literature (Loague et al., 1995, 1996). Besides differences in physical soil properties, soil chemical properties play an important role in controlling pesticide fate. Although the clay content in Oxisols is often high, the cation exchange capacity is low due to weathering of primary minerals. The effect of tropical climates on pesticide fate and transport includes increased volatility and enhanced chemical and microbial degradation rates (Racke et al., 1997). In comparison with temperate regions, field dissipation of pesticides under tropical climate was found to be 5 to 10 times faster (Laabs et al., 2002). Similarly, Laabs et al. (2000) reported short (<14 days) dissipation half-lives of pesticides in a Brazilian Oxisol topsoil. Nevertheless, the presence of pesticides in lysimeter percolate demonstrated that these compounds possess a leaching potential in spite of their fast dissipation in tropical climate (Laabs et al., 2000).

Our previous studies reported on ongoing research aiming to verify the leachability of new pesticides in tropical soils: Dusek et al. (2010a, 2011) summarized the results of a field leaching experiment complemented with modeling of water flow and pesticide transport; Sobotkova et al. (2011) estimated soil hydraulic properties of a laboratory column used for pesticide transport experiments. These studies examined new pesticides under consideration either for new licensing or for license renewal by the Hawaii Department of Agriculture for use in Hawaii. For leaching studies in Hawaii, atrazine is frequently used as the reference pesticide because it has been extensively used in Hawaii and its leaching behavior is well understood in Hawaiian conditions. Based on the fact that atrazine has been found in groundwater in Hawaii, it is a known leacher under Hawaii conditions. Although atrazine has low sorption distribution coefficient, field leaching study conducted on different tropical soils in Hawaii indicated that