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Modelling cadmium contamination in paddy soils under long-term remediation measures: Model development and stochastic simulations☆

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ABSTRACT

A pollutant accumulation model (PAM) based on the mass balance theory was developed to simulate long-term changes of heavy metal concentrations in soil. When combined with Monte Carlo simulation, the model can predict the probability distributions of heavy metals in a soil–water–plant system with fluctuating environmental parameters and inputs from multiple pathways. The model was used for evaluating different remediation measures to deal with Cd contamination of paddy soils in Youxian county (Hunan province), China, under five scenarios, namely the default scenario (A), not returning paddy straw to the soil (B), reducing the deposition of Cd (C), liming (D), and integrating several remediation measures (E). The model predicted that the Cd contents of soil can lowered significantly by (B) and those of the plants by (D). However, in the long run, (D) will increase soil Cd. The concentrations of Cd in both soils and rice grains can be effectively reduced by (E), although it will take decades of effort. The history of Cd pollution and the major causes of Cd accumulation in soil were studied by means of sensitivity analysis and retrospective simulation.

1. Introduction

Levels of heavy metals in cultivated soils can go up over time as a consequence of farming practices (irrigation and fertilizer application, for example) as well as that of atmospheric deposition in the face of increasing urbanization and industrialization (Cai et al., 2015). Accumulation of heavy metals in cultivated soils threatens human health because the metals can end up in food (Chary et al., 2008). Paddy fields in southern China are being polluted with Cd, a metal readily taken up by the rice plant, as has been seen in the rice grown in Youxian county in China's Hunan province (CBSNEWS, 2013; Wang et al., 2016). Large-scale Cd contamination of paddy soils and of rice products poses a tough challenge to local authorities (Du et al., 2013).

Soil remediation measures are taken place to decrease metal concentrations in paddy soil or to reduce plant uptake. For a large contaminated areas, applying soil amendments to stabilize metals in soil presents a more realistic solution than digging out thousands of tonnes of contaminated soils and replacing with clean soil (Kumpiene, 2010). Liming compounds, Mn and Si oxides, zeolites, biochar, natural clay minerals and phosphates are widely used as soil amendments that are able to adsorb, complex or precipitate metals in soil or competitively inhibit uptake by crops (Chaney, 2015; Kumpiene, 2010; Li and Xu, 2015; Sasaki et al., 2012). To assist decision making, evaluating the long-term efficacy of soil amendments and other management practices in reducing Cd contamination is essential. However, little is known about long-term *in situ* dynamics of Cd accumulation in soil because even soil surveys – let alone laboratory and field experiments – are labour intensive and time consuming. A mathematical model that can simulate the mass flows of Cd in a soil–water–plant system under different remediation measures in the long term, therefore, offers an attractive alternative.

Environmental models are designed for various purposes such as modelling the distribution of chemicals among different media (soil, water, and air, for example), the movement of chemicals through river flows, the relative distribution among soil layers at varying depths, and the transfer of chemicals from the soil to plants (Peng et al., 2015). These models are generally field- or subject-specific: a model developed for application in one field or subject

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often proves less effective when used in another. Generally, mechanism models that describe the nature of environmental processes are better at simulating the behaviour of the contaminants in such short-term processes as dispersion, leaching, and uptake by plants (Schoups and Hopmans, 2006). On the other hand, empirical models, which require less data, are better at predicting the general trends of contaminant accumulation over larger spatial or time scales (Posch and de Vries, 2009). In soil, detectable changes in heavy metal concentrations may require years of accumulation (Sun et al., 2011). Therefore, empirical models are generally used for modelling long-term changes in the concentrations of heavy metals in soil (Chen et al., 2013; Hu et al., 2013).

The path and destination of heavy metals in a soil–water–plant system are determined by complex and interactive processes including adsorption and desorption related to soil particles, diffusion and percolation with soil solution, and absorption and mineralization by organisms (Chen et al., 2007). Typically, the empirical models designed for simulating long-term accumulation of metals in soil are based on the mass balance theory and focus on major environmental processes (Posch and de Vries, 2009). Chen et al. (2007) developed a Windows-based soil trace element model (STEM) to evaluate the accumulation of Cd in cultivated soils following long-term application of Cd-containing phosphatic fertilizers. This model tracked 100 years of mass balance of Cd between external inputs added to the surface of the soil, outputs through leaching and plant uptake, and the accumulation of Cd in different chemical forms. de Vries and McLaughlin (2013) developed a mass-balance-based model and simulated Cd concentrations in soils and crops in Australian agricultural systems over two centuries (1900–2100). In this model, fertilizer application, atmospheric deposition, bio-solids, and irrigation were considered separately, that is as different paths through which Cd is added to soil. Similarly, Six and Smolders (2014) predicted the mass balance of Cd in European agricultural soils under five regional scenarios through a set of empirical models. These models were able to quantify the relationship between input loads and metal concentrations in soils and to evaluate the impacts of environmental parameters on the rate at which the metals accumulated in the soils.

Over large spatial or temporal scales, environmental processes are best described in quantitative terms as ranges of values of the relevant parameters instead of as fixed values. Keller et al. (2001) developed PROTERRA-S, an empirical stochastic balance model, to estimate heavy metal contents of agricultural soils on a regional scale by considering the spatial variability of different forms or paths through which heavy metals are added to the soils – through manures and fertilizers and as atmospheric deposition, for example – and of other relevant factors such as soil pH, and the crops that were grown. Oporto et al. (2012) predicted the spatial variability of Cd accumulation in a mining area by including parameter uncertainty in a mass balance model. By and large, stochastic models coupled with the Monte Carlo method can calculate the cumulative distributions of heavy metals in the soil and predict the probable risks from heavy metal concentrations that exceed the stipulated maximum permissible limits at present or in the future (Chen et al., 2007).

However, the existing mass balance models need to be improved so that they can take into account the effects of different management practices or time-dependent scenarios. Firstly, an independent model that has a user-friendly interface and can display the results in the form of charts and tables is needed if the model is to be widely accepted, especially in economically underdeveloped regions without experts in model application. Secondly, the model should accept a variety of data as inputs, including time-dependent values of pollutants from various sources and those of a range of environmental parameters. A wide range of inputs means that the model can be used widely. Thirdly, some environmental processes can be described by various equations that have different input parameters. Allowing the user to select from a range of such equations expands application scope of the model by increasing the number of optional parameters. Lastly, it should be possible to control the precision of the model's solutions and the cycles of Monte Carlo simulation independently.

In the present study, we developed PAM-HMs, a Windows-based **p**ollutant **a**ccumulation **m**odel to simulate the mass balance of **h**eavy **m**etals in soil, by integrating the main input and output fluxes and Monte Carlo simulation. The PAM-HMs is composed of many optional sub-models and parameters to describe the environmental processes of heavy metals in soil-plant system. These sub-models are freely selected according to data accessibility of the model user. Therefore, the data acquisition of the PAM-HMs model is flexible and one can conduct simulation based on limited data from field survey and literature review. As a case study, we applied the model in Youxian county, Hunan province, China, in order to predict the long-term trends in Cd concentrations in paddy soils and in rice grains grown under different remediation measures. The objectives were to illustrate the capability and feasibility of the model and to evaluate the efficacy of the remediation measures in the long term.

2. Model development

2.1. Model framework

Accumulation of heavy metals in a surface soil pool can be described by several mass-balanced processes involving the movement of metals among soil, water, and plants. The PAM-HMs model summarizes the major input fluxes and output processes of heavy metals in the soil pool as well as their partitioning between soil solution and the solid phase. Fig. S1 shows the framework of the PAM-HMs model. Each of these processes can be described by several empirical or mechanism equations. Therefore, dynamic changes in metal concentrations in the soil pool can be solved by choosing appropriate combinations of equations adapted to different purposes and available data sets.

2.2. Model equations

2.2.1. Governing equation

For a trace metal such as Cd completely mixed in the root-zone soil pool, horizontal diffusion is insignificant (Chen et al., 2007; Keller et al., 2001), and dynamic changes in the total metal content can be written as a one-dimensional mass conservation equation (de Vries and McLaughlin, 2013; Oporto et al., 2012):

$$\frac{\partial C_t}{\partial t} = \frac{I_t}{\partial t} - \frac{\partial U}{\partial t} - \frac{\partial L}{\partial t} \tag{1}$$

where C_t is the total metal content in soil (mg dm^{-3}); t is the time step (an hour or a day); $\frac{I_t}{\partial t}$ is the total metal input flux (mg dm^{-3} t^{-1}); $\frac{\partial U}{\partial t}$ denotes the metal flux through plant uptake (mg dm^{-3} t^{-1}); and $\frac{\partial L}{\partial t}$ denotes the metal flux through the vertical movement of soil water (mg dm^{-3} t^{-1}).

2.2.2. Metal adsorption equations

In soil, heavy metals are adsorbed to the surface of soil particles or bound to the primary minerals and organic matter or dissolved in the solution phase. The behaviour of heavy metals in the soil–water–plant system depends on their amounts in the dissolved form. For a long-term simulation, the sorption and desorption of heavy metals in soil can be considered as instant processes