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ScienceDirect
Ecotoxicology and Environmental Safety 67 (2007) 48–58
Ecotoxicology and Environmental Safety
www.elsevier.com/locate/ecoenv

Highlighted article

Assessing long-term environmental risks of trace elements in phosphate fertilizers

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Received 18 July 2006; received in revised form 25 November 2006; accepted 26 December 2006
Available online 12 February 2007

Abstract

The potential risks originating from arsenic and cadmium accumulations in cropland soils through the fertilizer applications have been public concern. A generalized trace element mass balance model was developed to evaluate the long-term fate and transport of arsenic and cadmium in cropland soils. Model simulation results showed that normal cropping practices do not have a significant effect on the total As content of the receiving soils, but the application of Cd-containing P fertilizers could, over time, cause Cd to accumulate in soil and therefore increases the risk of its transfer through the food chain. Regulations have been enacted in several states to set the maximum contaminant levels for arsenic and cadmium in fertilizers. The simulation outcomes indicated that some of the existing fertilizer regulations are not strict enough to prevent significant accumulation of Cd in cropland soils. Sensitivity analyses show the solid-solution partitioning coefficient, and the plant uptake factors are primary factors that affect the fate and transport of As and Cd in cropland soils. The uncertainty associated with assessing the fate of trace elements in cropland soils is due to the high variability of model parameters.

Keywords: Mass balance; Model; Cadmium; Arsenic; Fate and transport; Cropland soils; Monte Carlo simulation

1. Introduction

While naturally occurring and ubiquitous, trace elements such as As and Cd may be introduced into cropland soils by anthropogenic activities. Cultivation practices such as fertilization, irrigation, pesticide application, and organic waste disposal and atmospheric fallouts are potential sources (Chang and Page, 2000; Krage, 2002; Meeüs et al., 2002). Trace elements accumulating in the cropland soils may be transferred via the food chain to consumers of the crop harvests (Krishnamurti et al., 1999; Meeüs et al., 2002).

Phosphate fertilizer application is a significant contributor of trace element, especially for Cd accumulation in cropland soils (McLaughlin et al., 1996). The amount being added in a single application may be insignificant compared with the volume of receiving soil, its presence in soils may not be readily detectable by the routine field sampling and measurement protocols, but repeated application may lead to a gradual buildup of these elements in agricultural soils over time. In Europe, the proportion of Cd from P-fertilizers amounted to 74% of the total Cd load to arable soils (EUROSTAT, 1995), and cadmium from phosphate fertilizer constituted more than 50% of the total input in areas that were not heavily polluted or were not heavily industrialized (Meeüs et al., 2002). P fertilizer has been the major source of Cd found in pasture soils in Australia and New Zealand (Andrewes et al., 1996). Loganathan et al. (1995) showed a clear relationship between P fertilizer use and Cd accumulation in cropland soils.

In risk assessment, the food chain transfer of trace elements such as As and Cd is frequently described by solid-solution partition coefficient, K_d ($\mathrm{l\,kg^{-1}}$) that is given by the linear relation K_d = [Total concentration of soil ($\mathrm{mg\,kg^{-1}}$)]/[Concentration of soil solution ($\mathrm{mg\,l^{-1}}$)] and plant uptake factor (PUF) ($\mathrm{l\,kg^{-1}}$) which is given by PUF = [Concentration in plant tissue ($\mathrm{mg\,kg^{-1}}$)]/[Concentration in soil solution ($\mathrm{mg\,l^{-1}}$)]. The distribution and behavior of trace elements in cropland environments are a dynamic and interactive process and are affected by soil

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doi:10.1016/j.ecoenv.2006.12.013

properties. It may not be accurately estimated by the steady-state linear distribution constants of K_d and PUF. The fate and transport of trace elements in soils are determined by the dynamic equilibrium between those present in various soil components and are governed by interactive processes involving surface adsorption/desorption, precipitation/dissolution, plant uptake/residue, re-incorporation/mineralization, and solute transport. It is imperative that the fate and transport of trace elements in cropland soils be properly assessed. The mathematical modeling and simulations, with appropriate perspectives, are proficient in evaluating the long-term impacts.

The fate and transport of trace elements in soils have been investigated (Van der Zee et al., 1990; Boekhold and Van der Zee, 1990; Harmsen, 1992; Moolenaar and Lexmond, 1998; Pačes, 1998; Tiktak et al., 1998; Keller et al., 2001; Meeüs et al., 2002). The studies followed the basic principle of mass balance; that is, the net change of element in a soil layer is the balance between the input at the soil surface and the output through leaching, crop harvest and surface runoffs. Each of the input or output term in the mass balance equation is governed by a set of physical, chemical and biological processes that are interactive and simultaneous. For quantification, each reactive process included is represented by a mathematical equation and the equations must be solved simultaneously for the mass balance. The difference in the simulation models depends on the complexity of the model structure and the mathematical terms employed to describe them. While the computational capability has not been a limitation, realistic solutions may be obtained only when the parameters in the mathematical equations are properly defined and measured. In model development, one often needs to balance the representativeness of the mathematical expressions and the practicality of quantifying the parameters. Generally, a large amount of data is needed to derive the fate and transport parameters and to calibrate the models.

The purpose of this research was to evaluate the long-term fate and transport of As and Cd in cropland soils, based on simulation outcomes using a trace element mass balance mathematical model we developed. Monte Carlo simulations were employed to assess the uncertainty associated with model predictions and sensitivity analyses were carried out to identify the key factors that affect the fate and transport of As and Cd in the cropland soils. The model provides a basis for evaluating As and Cd accumulations in agricultural soils and plants that are grown on these soils and for assessing the potential for these trace elements to move into groundwater.

2. Approach

For a trace element in the root zone soils, the one-dimensional mass conservation equation may be written as

$$\frac{\partial C_T}{\partial t} + \frac{\partial \mathrm{Js}}{\partial z} + r_s = 0, \tag{1}$$

where C_T is the total soil trace element content, Js is the flux of trace element in the direction of water movement z, and r_s is a production term representing sources and sinks of the species.

In soils, most trace elements are not readily soluble and remain in solid phases. They may be adsorbed by clays and organic matter, may be associated with primary minerals, and may form inorganic precipitates. The behavior of trace elements in the soil–water–plant system is dependent on their chemical forms. Correspondingly, the trace element components of the soil may be divided among four phases, and the total trace element content of the soil, C_T (μmol l soil^{-1}), may be defined by

$$C_T = \theta C + \mathrm{Ad} + \mathrm{MP} + \mathrm{Org}, \tag{2}$$

where θ is the volumetric water content (cm^3 cm soil^{-3}), C is soil solution concentration (μM), and Ad, MP and Org refer to the element in the surface adsorbed phase, immobilized mineral phase, and organic matter phase (μmol l soil^{-1}), respectively.

Trace elements in the soil solution are of special interest as they are readily accessible to plants and are mobile through the vadose zone to reach underground waters. However, the concentrations are dependent on the kinetics between those in solution and solid phases. The surface adsorption and desorption reactions are rapid and reversible and are characterized by a thermodynamic equilibrium distribution:

$$\mathrm{Ad} = k_a C, \tag{3}$$

where k_a (l soil l^{-1} soil solution) is the linear adsorption constant. The dissolution and immobilization due to precipitation and co-precipitation with other solid minerals and intra-particle sites are characterized by a first-order kinetic equilibrium (Chen et al., 2006):

$$\frac{\partial \mathrm{MP}}{\partial t} = k_f(k_a + \theta)C - k_b\,\mathrm{MP}, \tag{4}$$

where k_f and k_b are the first-order forward (dissolution) and backward (immobilization) reaction rate constants (h^{-1}), respectively. In addition, a part of the trace element taken up by plants will return to the soil as crop residues. Mineralization of the crop residues in the soil may release the trace elements back into the solution and surface adsorbed phases, which may be described by a first-order kinetic as

$$\frac{\partial \mathrm{Org}}{\partial t} = -k_{im}\,\mathrm{Org}, \tag{5}$$

where k_{im} is the first-order organic mineralization rate constant (h^{-1}).

The solute transport through the root zone (Js in Eq. (2)) is generally described by the convective–dispersive transport equation. For trace elements such as As and Cd, the transport due to the concentration gradient-driven diffusion is not significant since the solution concentrations are relatively low and may be assumed uniform throughout the root zone. The solute transport through the homogeneous