Trace Metal Retention in the Incorporation Zone of Land-Applied Sludge

TAMMO S. STEENHUIS,*,†
MURRAY B. MCBRIDE,‡
BRIAN K. RICHARDS,† AND
ELLEN HARRISON§

*Department of Agricultural and Biological Engineering,
Department of Soil, Crop, and Atmospheric Sciences, and
Center for the Environment, Cornell Waste Management
Institute, Cornell University, Ithaca, New York 14853*

Recycling nutrients in wastewater sludge (biosolids) via land application is a desirable goal. However, potential movement of sludge-applied trace metals is of concern and an area of ongoing research. In this paper, we examine the first-order model used by the United States Environmental Protection Agency (U.S. EPA) for predicting losses from the zone of incorporation as part of the risk assessment that undergirded the development of Part 503 regulations (*1, 2*). We found that when empirical adsorption partition coefficients from the site are used as model inputs, the U.S. EPA model for the incorporation zone is similar to that derived from preferential flow theory and simulates well the loss of metal from the surface soil layer at an orchard site where sludge was applied 15 years earlier.

Introduction

Application of organic residuals such as municipal wastewater sludge to land is being widely promoted as a cost-effective disposal alternative, with agricultural, forest, and range lands as well as land reclamation sites increasingly used for land application. However, mass balances in a number of long-term studies on land application of sludge have been unable to account for up to half of the sludge-applied metals, challenging the concept of long-term metal immobilization in soil (*3−8*).

The loss of metals from fields that received sludge may possibly represent an environmental risk, and a better understanding of the factors governing metal mobility is necessary. In this paper, we will show that a model used by the U.S. EPA as a component of their risk assessment (*2*) is the same as a preferential flow model developed by Steenhuis et al. (*9*) and is able to predict the loss of metals from the zone of incorporation for a site to which sludge was applied 15 years prior to data collection.

Experimental Section

Model. Three separate model components were used by the U.S. EPA for assessing the risk of adverse human health effects resulting from metal ingestion via pathway 14 (sludge → soil → groundwater → human) (*1*) as a basis for the development of the Part 503 regulations (*2*). The soil was divided into the incorporation zone, the vadose zone, and a saturated

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* Corresponding author phone: (607) 255-2489; fax: (607) 255-4080; e-mail: tss1@cornell.edu.
† Department of Agricultural and Biological Engineering.
‡ Department of Soil, Crop, and Atmospheric Sciences.
§ Cornell Waste Management Institute.

("aquifer") zone (Figure 1), each with its own model component. The loss of metals from the zone of incorporation was based on a first-order model (*1*):

$$\frac{dM_{Me}}{dt} = -q\frac{M_{Me}}{D_l(\rho k_d + \theta)} \tag{1}$$

where M_{Me} = mass of metals in the zone of incorporation; q = flow rate (set equal to the U.S. EPA (*1*) recharge rate); D_l = depth of incorporation; ρ = bulk density; k_d = adsorption partition coefficient; θ = moisture content.

Integrating eq 1 gives:

$$M_{Me} = M_{Me0}\exp\frac{-Y}{D_l(\rho k_d + \theta)} \tag{2}$$

where Y = the cumulative amount of percolation since the application of the sludge and M_{Me0} = initial amount of metal applied.

Despite some different assumptions, the preferential flow model developed by Steenhuis et al. (*9*) has the same form as the U.S. EPA model expressed in eqs 1 and 2. The preferential flow model consists of a high conductivity surface layer (called distribution layer) overlaying a much lower conductivity soil with preferential flow paths (Figure 2). The distribution layer in the preferential flow model, which distributes water and solutes to the preferential flow paths (*9−11*), is comparable to the incorporation zone in the U.S. EPA model. The distribution layer has a higher conductivity than the remaining soil (especially shortly after application and plowing) and, therefore, is the same as the zone of incorporation. The flow in the distribution layer (all pores are taking place in the transport process) can be described with the linear reservoir theory (*9*). Gelhar and Wilson (*12*) showed that the equation describing the outflow of solutes from a linear reservoir is the same as eqs 1 and 2 where the depth of the incorporation zone, D_l, is replaced by the depth of the distribution zone, D_d. Steenhuis et al. (*9*) found that eq 2 could predict the loss of surface-applied chloride and blue dye in an undisturbed soil profile at 60 cm depth. Note, however, that although the models describe flow in the incorporation zone similarly, they are quite different in the remainder of the soil profile. Movement of metals below the incorporation zone was simulated by the U.S. EPA using conventional convective−dispersive type models, whereas preferential flow models would predict a much faster transport due to bypassing of a major portion of the soil matrix. In this paper, we discuss only the retention and loss of metals in the incorporation zone and in a subsequent paper we will investigate the transport through the saturated and unsaturated zones.

Methods. *Sludge Application Site.* The data for retention of metals are obtained from the Cornell Orchard field-application site where a high calcium sludge (pH 6.5) was applied in 1978 (*7, 13*). The soil is a Hudson silty clay loam, classified as a fine, illitic, mesic Glossaquic Hapludalf. Sludge was applied in single heavy loadings to two sites within the orchard. At site I, (S1 in (*7*)), the profile consisted of a plow layer of approximately 15 cm depth. Approximately 10% of the soil volume was occupied by darkened "veins" of the applied sludge that could still be distinguished 18 years after application. The calcareous subsoil consists of a till layer with low conductivity 30 cm wide peds. The soil between the peds (the "old crack structure") consists of highly conductive soil with many preferential flow paths. From 1979 to 1983, the site was cropped, with the addition of some commercial
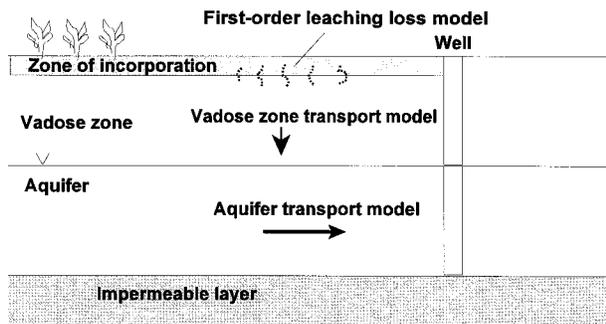
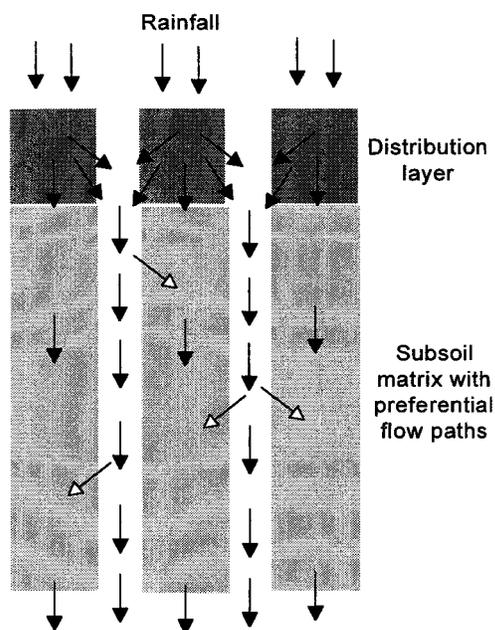FIGURE 1. Zones distinguished in modeling metal movement for risk assessment for pathway 14 by the U.S. EPA.

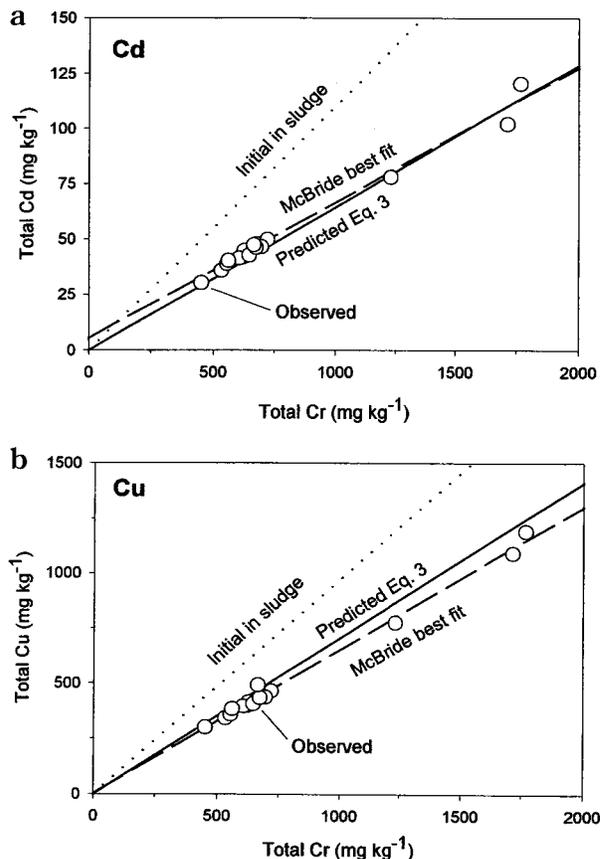FIGURE 2. Zones distinguished in the preferential flow model.

FIGURE 3. Plot of total metal vs total cadmium for the Cornell Orchard site. The open circles are discrete data points from orchard soil samples. Solid line depicts relationship predicted by eq 3. The dashed line is the best-fit line by McBride et al. (7). The dotted line is the ratio in the original sludge applied. (a) Cadmium vs chromium. (b) Copper vs chromium.

fertilizer, but remained fallow for much of the subsequent period and was planted with dwarf apple trees and permanent grass cover in 1986. At site II (S2 in ref 7), the topsoil was removed, replaced by the sludge, and used for vegetable growing experiments, and the site was later put into permanent grass.

In 1993, soil samples collected from the surface (0−15 cm) at different locations within the sludge treated area were analyzed for total metals following nitric acid digestion (4 M HNO_3 for 16 h at 80 °C), followed by ICP emission analysis of digests. For each soil sample from the surface 15 cm, McBride et al. (7) plotted the concentration of total Cr vs the concentration of each of the metals for which the sludge addition had substantially increased the soil concentration. The plots for most metals were surprisingly linear, despite the fact that 15 years had passed since the sludge was applied. Examples shown in Figure 3 include total Cr vs total Cd (Figure 3a) and total Cu (Figure 3b). Because of a high background concentration of Pb as a result of the Pb-based sprays, chromium was selected as the metal against which other metal concentrations were plotted. Cr is generally accepted to be a relatively insoluble and immobile metal in soils. The relatively high adsorption partition coefficient in Table 1 confirms this.

Sludge/Soil Characteristics. To check the validity of the first-order equation, we need to know both the initial sludge metals concentrations and the metal adsorption partition coefficients. Adsorption coefficients for the metals were determined by mixing orchard soil (collected near the sludge

TABLE 1. Observed Trace Metal Related Parameters in Applied Sludge and in Application Site Soil

element	sludge M_{Me0}/M_{Cr0}	k_d (cm^3 g^{-1})	observed site I M_{Me}/M_{Cr}	R^2	observed site II $M_{Me}/M_{Cr}{}^a$	av retained
Cr	1	1229	1		1	1
Zn	3.78	283	2.74	89	3.15	0.78
Cu	0.97	216	0.65	99	0.65	0.67
Cd	0.11	138	0.066	98	0.066	0.58
Sr^b	0.62	72	0.187	99		0.27
S	13.0	33	1.96	95		0.15
Ca	62.8	5.6	19.5	98		0.31
Na	1.07	5.2	0.11	75		0.10

^{a} Only two values. R^2 values are, therefore, meaningless. ^{b} Sr content of sludge from Furr et al. (14).

site) with air-dried sludge (archived from the original 1978 sludge application experiment). Replicate mixtures of 5 g sludge with 5 g soil (1:1 ratio) were prepared, 20 mL of distilled water was added, and the suspensions were shaken gently on a rotary shaker for 24 h. After centrifugation and filtering through 0.2 μm polycarbonate filters, the solutions were analyzed for dissolved metals by ICP-emission spectrophotometry. Total metal concentrations in the solid phase were calculated from analyses of the orchard soil and sludge after nitric−perchloric wet ash digestion. Table 1 gives the average k_d values of these sludge/soil mixtures.

Various analyses are available for the metals in the sludge (7, 13, 14). The analyses performed in the 1980s involved

several dry ashing and wet digestion techniques in addition to neutron activation analysis. The McBride et al. (7) analysis of the archived sludge samples used nitric−perchloric wet ash digestion. For consistency, we will, therefore, use only the archived sludge metal concentrations reported by McBride et al. (7). Table 1 shows the ratios of the various metals to total Cr in the archived sludge.

Results and Discussion

Testing the Equation. Let us now examine if the theory (as expressed in eq 2) can reproduce the observed linear relation between the total amount of Cr (M_{Cr}) and total amount of a second metal in the incorporation zone, M_{Me}. The quotient of M_{Me} and M_{Cr} (the ratio of metal to Cr) can be expressed with eq 2 by ignoring the background metals in the original soil, noting that θ is small compared to k_{Me}, and assuming that D_l and D_d have the same depth, D:

$$\frac{M_{Me}}{M_{Cr}} = \frac{M_{Me0}}{M_{Cr0}} \exp\left[-\frac{Y}{\rho D}\left(\frac{1}{k_{Me}} - \frac{1}{k_{Cr}}\right)\right] \quad (3)$$

Equation 3 shows that for a given cumulative percolation, Y, all of the parameters on the right-hand side are constant and, thus, the ratio M_{Me}/M_{Cr} is constant, predicting the linear relationship observed by McBride et al. (7). As a further test of the validity of eq 3, we plot in Figure 3a the amount of Cd in the incorporation zone (M_{Cd}) vs M_{Cr} 15 years after application using a 15 cm incorporation zone, 90 cm annual rainfall, a bulk density of 1.2 kg/L and, from Table 1, the original sludge metal ratio (M_{Cd0}/M_{Cr0}) and measured adsorption partition coefficients, k_{Cr} and k_{Cd}. Because of the shallowness of the top layer, we assumed that the cumulative percolation was equal to the cumulative amount of precipitation. A similar plot for Cu is shown in Figure 3b. The heavy solid line in both cases is close to the observed data points and very similar to the best fit (thin solid line) obtained earlier by McBride et al. (7). Thus, eq 3 can simulate well the observed soil concentrations of Cu and Cd. As we will see next, soil concentrations of other metals were also well simulated.

McBride et al. (7) also calculated the retention of several other sludge-applied metals in the top 15 cm of the field site. We can test if the losses calculated by McBride et al. (7) can be predicted with the model. McBride et al. (7) argued that the ratio of (M_{Me}/M_{Cr}) to (M_{Me0}/M_{Cr0}) represents the portion of the metal retained in the root zone relative to Cr. For example, if no depletion of a metal M_{Me} in the incorporation zone relative to Cr has occurred, then obviously $M_{Me}/M_{Cr} = M_{Me0}/M_{Cr0}$ and the retention ratio = 1. The metal/Cr ratio changes only if the loss of one metal is faster than the other. By rewriting eq 3 slightly, the loss of metals relative to Cr can then be written as:

$$\frac{M_{Me}/M_{Cr}}{M_{Me0}/M_{Cr0}} = \exp\left[-\frac{Y}{\rho D}\left(\frac{1}{k_{Me}} - \frac{1}{k_{Cr}}\right)\right] \quad (4)$$

In eq 4, the left-hand side, which is the retention of the metal relative to Cr, is calculated on the basis of observed soil data in McBride et al. (7), and the right-hand side can be calculated independently with parameters in Table 1 as mentioned above.

To calculate the left-hand side of eq 4 (the M_{Me}/M_{Cr} ratio), McBride et al. (7) obtained the best-fit line through the data. This line may have a small intercept with the y axis (Figure 3a). Given the small background levels of the metals in soils relative to metals added in sludge, the present theory implies that the line should go through the origin. Therefore, we refitted the earlier data with a zero intercept. The calculated amounts of metals retained, adjusted for the zero intercept,
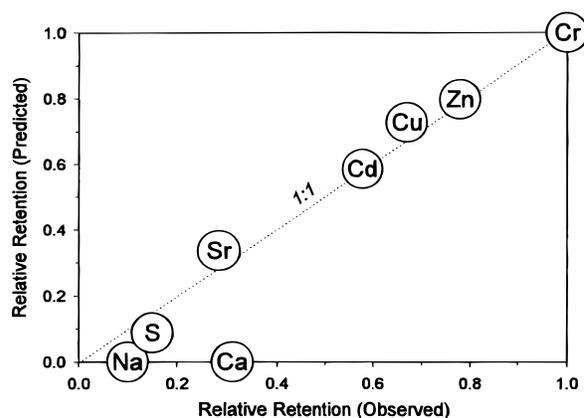

FIGURE 4. Predicted (right-hand side of eq 4) vs observed retained portion of metals (left-hand side of eq 4) in the 15 cm surface layer of the Cornell Orchard site.

are shown in Table 1 for sites I and II. These values are similar to those in ref 7 from where the sludge M_{Me}/M_{Cr} ratios were taken (13, 14). Because the K_d values were obtained from the archived sludge, we used the ratios of the archived sludge for consistency. The percentage retained for sites I and II are the same except for Zn which is more bound at site II because of the calcareous nature of the subsoil.

In Figure 4, the value of the left-hand side of eq 4 (McBride's et al. (7) observed relative retention) is plotted on the x axis and the right-hand side (calculated retention) is plotted on the y axis. The same values as above were used. Considering the simplicity of the approach, a reasonable prediction is obtained. The only element for which the measured relative retention is much higher than that predicted is calcium. Records show that the field was limed in 1985, thus violating the assumption that the only significant input of metals was via sludge additions. The Ca added in lime, while measured as an increased retention from the higher content in the soil, could, thus, not be predicted from eq 4.

In summary, we have found that the first-order loss model of the U.S. EPA (1) for the incorporation zone has the same mathematical form as a preferential flow model for the distribution zone and can predict the loss and retention of metals in the surface zone of application using experimentally determined k_d values. The use of k_d implies an equilibrium between adsorbed and dissolved fractions in the distribution zone. This metal dissolution is enhanced by the dissolved organic matter. We found that, given sufficient time and rainfall, a substantial portion of less strongly adsorbed metals can leach out of the zone of incorporation.

What this paper does not answer is the ultimate fate of the metals below the zone of incorporation. Preferential flow transport in the subsoil facilitates relatively rapid movement in the subsoil in contrast to the U.S. EPA convective−dispersive approach, which predicts a much slower leaching process. This rapid transport under preferential flow can be contributed to the inhibiting effect of metal−organo complexes on adsorption as well as the tendency to bypass in the subsoil. The convective−dispersive equation assumes that there is an equilibrium between the adsorbed and dissolved phases, and this procedure would result in average heavy metal velocities of millimeters per year.

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