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THE ROLE OF THE WATER/SOIL DISTRIBUTION COEFFICIENT IN THE WATERSHED TRANSPORT OF ENVIRONMENTAL RADIONUCLIDES

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Management Perspective

Drainage basin runoff is a major source of numerous chemical contaminants reaching aquatic systems. A knowledge of the residence times of such pollutants is often required to predict their removal from a given watershed. This residence time is usually inferred using the assumption that the removal rate via rivers is proportional to the pollutant inventory in the soils. In many a situation, however, good estimates of watershed residence times for atmospherically-delivered pollutants cannot be obtained since realistic estimates of their inventories are not available.

Recently, it has been suggested that certain natural as well as nuclear fallout radionuclides may be used to derive more precise estimates of residence times. However, differing removal rates were obtained using different radionuclides in the same watershed. In the present work we show that these differences arise as a result of previous models' inability to distinguish between radionuclide removal rate and soil erosion rate. We demonstrate that when the partitioning of a radionuclide between water and solids is taken into account, virtually similar results are obtained irrespective of the nature of the radionuclide under consideration. We also give a complete mathematical description of our approach.

The results obtained using radionuclides may be directly

applicable to other pollutants with similar water/solid partitioning behaviour. For example, estimate obtained by using lead-210 may be directly used to infer the residence time of stable lead in a given watershed. The described technique may also be used to derive estimates of soil erosion. However, additional laboratory work will be required to derive such estimates.

Perspectives de la direction

L'écoulement de surface d'un bassin hydrographique est une source majeure de nombreux contaminants chimiques qui atteignent les systèmes aquatiques. Il est souvent nécessaire de connaître les temps de séjour de ces polluants pour prévoir leur élimination d'un bassin donné. Le temps de séjour est généralement déterminé à partir de l'hypothèse selon laquelle le taux d'élimination par les cours d'eau est proportionnel aux quantités de polluants dans les sols. Dans bien des cas, toutefois, il est impossible d'obtenir de bonnes estimations des temps de séjour des polluants d'origine atmosphérique dans un bassin hydrographique étant donné l'absence d'estimations réalistes de leurs quantités.

Récemment, il a été proposé que certains radionucléides naturels de même que des radionucléides de retombées nucléaires puissent servir à établir des estimations plus précises des temps de séjour. Toutefois, on a obtenu différents taux d'élimination à l'aide de différents radionucléides dans un même bassin. Dans l'étude actuelle, nous montrons que ces différences découlent de l'inaptitude des modèles antérieurs à distinguer entre le taux d'élimination du radioinucléide et le taux d'érosion du sol. Nous démontrons que, lorsque l'on tient compte du partage d'un radionucléide entre la phase aqueuse et la phase solide, on obtient pratiquement les mêmes résultats, indépendamment de la nature du radionucléide considéré. Nous donnons également une description mathématique complète de notre approche.

Les résultats obtenus à l'aide des radionucléides peuvent s'appliquer directement à d'autres polluants caractérisés par un comportement semblable de partage eau/solides. Par exemple, l'estimation obtenue à l'aide du plomb-210 peut servir directement à établir le temps de séjour du plomb stable dans un bassin donné. La technique décrite peut également s'appliquer à des estimations de l'érosion du sol. Toutefois, d'autres travaux en laboratoire seront requis pour pouvoir établir ces estimations.

Abstract

The concept of the distribution coefficient is invoked to rationalize the observed dependence of the watershed residence time of a radionuclide on its nature. A mathematical model is presented to show that this residence time is proportional to the dimensionless field distribution coefficient of the radionuclide. The proportionality constant, β, is defined as the ratio of the volume of rain-impacted soil in the watershed and the annual volume of rainfall in the watershed or expressed as the ratio between the water penetration depth in soil and the annual thickness of water above the soil surface. An empirical evaluation of β supports our assumption of its constancy in a given watershed. The described model may be very useful in deciphering the impact of atmospherically-delivered pollutants on watershed quality. Expressions are also derived to estimate the value of soil erosion constant using naturally-occurring radionuclides.

Résumé

Le concept du coefficient de distribution permet de rationaliser la dépendance observée du temps de séjour d'un radionucléide dans un bassin hydrographique à l'égard de sa nature. Un modèle mathématique est présenté en vue de montrer que ce temps de séjour est proportionnel au coefficient sans dimension de distribution du radionucléide sur le terrain. La constante de proportionnalité, ß, est définie comme étant le rapport du volume du sol exposé aux précipitations dans le bassin hydrographique et le volume annuel des précipitations dans le bassin versant, ou bien, elle est exprimée par le rapport entre la profondeur de pénétration de l'eau dans le sol et l'épaisseur annuelle de l'eau au-dessus de la surface du sol. Une évaluation empirique de ß corrobore notre hypothèse de sa constance dans un bassin donné. Le modèle décrit peut être très utile pour déterminer l'impact des polluants d'origine atmosphérique sur la qualité du bassin versant. Des expressions sont également déterminées pour estimer la valeur de la constante de l'érosion du sol à partir de radionucléides présents dans la nature.

1. Introduction

Numerous studies in the past have relied on the 'particle reactive' nature of both naturally-occurring ^{210}Pb or ^{7}Be and fallout ^{137}Cs, $^{239,240}Pu$ or ^{241}Am to derive estimates of soil erosion [1,2] or to construct input-output budgets based on atmospheric deposition and fluvial removal of these radionuclides [3-8]. All such studies follow the reasonable assumption that removal rate is proportional to the radionuclide inventory in the watershed. If this were the sole assumption necessary to adequately describe the particle related transport in a watershed, similar residence times should be obtained irrespective of the nature of the radionuclide used as tracer. The results from more recent studies [5,6,8] clearly show that the inferred residence times are dependent on the nature of the radionuclide under consideration.

Since water plays an integral role in the soil erosion and fluvial transport processes, part of the radioactivity associated with soil particles is removed to the water. Therefore, a consideration of K_d, the field distribution coefficient expressed as a quotient of the activity in the particulate phase (mBq g^{-1}) and in solution (mBq cm^{-3}), is one possible way to rationalize the dependence of watershed residence time on the nature of radionuclide. Though widely recognized, the influence of K_d on radionuclide migration in the watershed has not been explicitly embodied in the existing models. The present communication thus reports our attempt to formulate the role of K_d in the watershed transport of environmental radionuclides.

2. Radionuclide transport model

In the simplest model, the fluvial removal F_{ir} (mBq cm^{-2} y^{-1}) of the ith radionuclide is considered to be a first-order type process with the removal constant k_i (y^{-1}) being proportional to the radionuclide inventory I_i (mBq cm^{-2}) in the watershed:

$$F_{ir} = k_i I_i \tag{1}$$

Alternatively, if F_{ic} (mBq cm^{-2} y^{-1}) is the constant flux of the radionuclide and λ_i (y^{-1}) its decay constant, k_i and mean residence time ($\tau_i = 1/k_i$) can also be obtained from the well-known [8] input-output equation

$$F_{ic} - I_i (\lambda_i + k_i) = 0 \tag{2}$$

For time-dependent flux, $F_i(t)$, the change in the radionuclide inventory in the watershed is described [8] as

$$\frac{dI_i(t)}{dt} = F_i(t) - I_i(t) [\lambda_i + k_i] \tag{3}$$

The unit area (1 cm^2) of the watershed receiving the radionuclide flux $F_i(t)$ is also impacted by a certain annual volume (cm^3 y^{-1}) of rainfall at a rate V_{wi} given by cm^3 y^{-1}/ cm^2 or cm y^{-1}. Note that V_{wi} essentially represents the annual thickness of water above the soil surface (Fig. 1a). This rainfall, in turn, impacts a certain volume (cm^3) of soil particles per cm^2 beneath the soil/water interface given as V_{si}, where V_{si}(cm) represents the water penetration depth

(Fig. 1b). The soil volume contains a homogeneously distributed radionuclide at a concentration given as C_{is}(mBq cm^{-3}). If C_{iw}(mBq cm^{-3}) denotes the concentration of this radionuclide in water in equilibrium with this soil volume, then within this conceptual framework the material balance equation for the accumulation of activity in the watershed can be written as

$$\frac{d}{dt}(C_{is} \cdot V_{is}) = F_i(t) - \lambda_i (C_{is} \cdot V_{si}) - C_{iw}(t) \cdot V_{wi}(t) \qquad (4)$$

$$\text{Setting } C_{is} \cdot V_{si} = I_i(t) \qquad (5)$$

equation (4) can be rewritten as

$$\frac{dI_i(t)}{dt} = F_i(t) - \lambda_i I_i(t) - C_{iw}(t) \cdot V_{wi}(t) \qquad (6)$$

Integration of equation (6) with the boundary condition $I_i(t) = 0$ at $t = 0$ yields

$$I_i(t) = e^{-\lambda_i t} \int_0^t e^{\lambda_i t} [F_i(t) - C_{iw}(t) \cdot V_{wi}(t)] dt \qquad (7)$$

and if $F_i(t)$ is constant ($= F_{ic}$)

$$I_i(t) = \frac{F_{ic}}{\lambda_i} [1 - e^{-\lambda_i t}] - e^{-\lambda_i t} \int_0^t C_{iw}(t) \cdot V_{wi}(t) \cdot dt \qquad (8)$$

By comparing equations (3) and (4), we find that

$$F_{ir} = C_{iw}(t) \cdot V_{wi}(t) \tag{9}$$

Equations (1), (8) and (9) clearly show that k_i is not a constant but depends on $C_{iw}(t)$ and $V_{wi}(t)$. From equations (5) and (9) and assuming radionuclide distribution equilibrium is established immediately after water comes in contact with soil, we obtain

$$\frac{I_i(t)}{F_{ir}(t)} = \frac{V_{si}(t)}{V_{wi}(t)} \cdot K'_{di} , \tag{10}$$

where

$$K'_{di} = \frac{C_{is}}{C_{iw}} \tag{11}$$

is the dimensionless distribution coefficient given as $K'_{di} = \rho K_d$ with ρ being the density of soil particles (g cm^{-3}). Equation (6) can be rewritten, following equations (5) and (11), in terms of K'_{di} as

$$\frac{dI_i(t)}{dt} = F_i(t) - I_i(t) \left[\lambda_i + \frac{V_{wi}(t)}{V_{si}(t) \quad K'_{di}}\right] \tag{12}$$

From equations (3) and (12), it follows that

$$k_i = \frac{V_{wi}(t)}{V_{si}(t) \cdot K'_{di}} \tag{13}$$

Thus $k_i \to 0$ if $V_{wi}(t) \to 0$ or if $V_{si}(t) \cdot K'_{di}$ is very high.

If $$\frac{V_{si}(t)}{V_{wi}(t)} = \beta \tag{14}$$

then

$$\tau_i = \beta \cdot K'_{di} \tag{15}$$

Assuming $\beta(y)$ is constant and is independent of the nature of the radionuclide, it may be inferred that the magnitude of τ_i is proportional to K'_{di}. We shall examine the validity of these assumptions later in the text.

Following equations (12) and (14), the steady-state inventory of a naturally-delivered radionuclide such as ^{7}Be or ^{210}Pb is given as

$$I_i = \frac{F_{ic}}{\left(\lambda_i + \frac{1}{\beta \cdot K'_{di}}\right)} \tag{16}$$

For nuclear fallout radionuclides such as ^{137}Cs or $^{239,240}Pu$, the inventory can be calculated by numerical integration of equation (12) as

$$I_i(t) = e^{-\gamma_i t} \int_0^t e^{\gamma_i t} \cdot F_i(t) \cdot dt \tag{17}$$

where $\gamma_i = \left(\lambda_i + \frac{1}{\beta \cdot K'_{di}}\right)$.

3. Results and discussion

In broad terms, equation (15) describes the role of both the physical and chemical parameters involved in the transport of environmental radionuclides in the watershed. Thus the physical characteristics of the watershed are described by β, while the chemical interactions influencing the distribution of a radionuclide between the solid and solution phases of the system are given by K'_{di}. The major implication of equation (15) is that since β is deemed to be constant and independent of the nature of the radionuclide, the residence time of a radionuclide in a watershed is primarily determined by its K'_{di} obtainable in the system.

The assumption of a constant β for a given watershed can be independently evaluated only by equation (14). In absence of a knowledge of $V_{si}(t)$, the value of β may be derived following equation (15) for the purpose of the present investigation. It should however be noted that such an evaluation of the constancy of β requires residence time as well as the water/soil partitioning data for more than one radionuclide in the same watershed. Due to the non-availability of measurements meeting both these requirements, we have relied on radionuclide residence time data from three different watersheds [5,6,8] in our empirical evaluation of the assumption of watershed constancy of β. A $K_d(cm^3\ g^{-1})$ value of 3.3×10^5 was used for the transuranics. This value has been reported by Wahlgren and Nelson [9] for fallout $^{239,240}Pu$ in Lake Michigan. For the remaining radionuclides we used the following K_d values derived from our field measurements [10] on Ottawa River waters and suspended sediments: ^{7}Be, 6.5×10^3; ^{137}Cs,

1.8×10^5; and ^{210}Pb, 1.9×10^5. This watershed lies in close proximity to the Saguenay River watershed [5], one of the locations chosen for the evaluation. The value of ρ was set at 2.5 g cm^{-3} in each case to obtain K'_{di}.

The results given in Table 1 show less than twofold variation in the values of β obtained by using different radionuclides in a given watershed. Taken together, the values for the three watersheds vary at most by a factor of about 5, though generally higher values for the Columbia River watershed likely result from extensive dam construction which serves to slow downstream transport of sediment [6]. These variations may be accounted for by the fivefold to tenfold fluctuations in K_d values attributable to particle size differences alone in sediments [11] though other factors such as suspended solid concentrations and overall chemical characteristics of the system are also likely operative [12-14]. Thus the small range in values of β obtainable in a given watershed, when considered in relation to the nature of K_d, strongly suggests that our assumption of watershed constancy of β is reasonable.

The dependence of residence time on K'_{di} given by equation (15) also underscores the realization that substances with similar K'_{di} values will be removed from the watershed at similar rates, irrespective of the fact whether they are radioactive or not. Setting aside the issue of the pollutant nature of anthropogenic radionuclides, the use of natural or fallout radionuclides as tracers in watershed studies is also based on the fact that reasonably accurate estimates of their soil inventories can be readily obtained.

As noted earlier, in writing the activity balance equation (4) it is assumed that particulate activity is not removed by the volume of water, V_{wi}. In reality, of course, V_{wi} carries both the soluble and particulate activity. A consideration of the latter component is necessary to formulate the role of β in deriving an estimate of the land erosional constant, E_c (cm y^{-1}). Assuming that the volume of soil corresponding to E_c does not affect V_{wi}, equation (4) may be written as

$$\begin{aligned} \frac{dI_i}{dt} &= F_i(t) - \lambda_i C_{is} V_{si} - C_{iw} \cdot V_{wi} - E_c \cdot C_{is} \\ &= F_i(t) - I_i\left(\lambda_i + \frac{1}{\beta \cdot K''_{di}} + \frac{E_c}{\beta \cdot V_{wi}}\right) \end{aligned} \tag{18}$$

It should be noted that K'_d and K''_d refer to two different dimensionless distribution coefficients. It is important to note that E_c is a characteristic of the land and does not depend upon any radionuclide. It is also clear that V_{wi} in reality describes only annual rainfall activity and does not depend on any radionuclide; therefore, it may simply be denoted as V_w. Comparing equations (3) and (18), we obtain

$$\frac{1}{\beta \cdot K''_{di}} + \frac{E_c}{\beta \cdot V_w} = k_i \tag{19}$$

or

$$\frac{1}{K''_{di}} + \frac{E_c}{V_w} = k_i \cdot \beta \tag{20}$$

Equation (20) explicitly states the role of β in describing the erosion of radionuclide-bearing particles and enables determination of E_c when K''_{di}, V_w, β and k_i are known. Since k_i is 'constant' and β is assumed to be constant, a positive value for E_c will be obtained only if $K''_{di} > K'_{di}$. This is possible only if the solution phase corresponding to K''_{di} measurements is devoid of particulates; in other words, K''_{di} pertains to the "true" partitioning of the radionuclide between the solution and solid phases. Further evaluation of equation (20) must await the availablility of such K''_{di} values.

Since β is deemed to be constant, it may be eliminated by writing an equation similar to equation (20) for the jth radionuclide:

$$\frac{1}{K''_{dj}} + \frac{E_c}{V_w} = k_j \cdot \beta \qquad (21)$$

From equations (20) and (21), we obtain

$$E_c = V_w \left(\frac{k_i}{K''_{dj}} - \frac{k_j}{K''_{di}}\right) / \left(k_j - k_i\right) \qquad (22)$$

Thus, E_c may be estimated in absence of a knowledge of β provided two different radionuclides are considered.

4. Conclusion

The results from the present investigation strongly suggest that the watershed residence time of a given

radionuclide depends on its field K'_{di} and that equation (15) adequately describes this proportional dependence. An empirical testing of β, the assumed proportionality constant, does suggest its 'constancy' within the range of variations obtainable in K'_{di} values for the same radionuclide. Since β is independent of the nature of the radionuclide and is deemed to be constant, a knowledge of β and the field K'_{di} value of a radionuclide (or other chemical) are the only parameters required to derive the residence time of a radionuclide (or other chemical) uniformly dispersed in a given watershed. In the absence of a knowledge of β, the value of E_c may be inferred using equation [22] provided other pertinent data on two different radionuclides are considered. Essentially, all relevant studies reported thus far [15] have relied on the use of only one radionuclide, usually ^{137}Cs, to estimate E_c, so a direct comparison between the reported values of E_c and those obtainable using equation [22] cannot as yet be made.

Equation (20) clearly shows the dependence of soil erosional constant on β and K''_{di}, the distribution coefficient based on the 'true' partitioning of radionuclide between solution and solid phases. Taken together, these results present a clear distinction between two important parameters involved in the fluvial transport of pollutants.

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TABLE 1

Estimated values of β for various radionuclides in different watersheds

Radionuclide	τ_i (y)	β (y)
Rhône River, Switzerland [8]		
^{7}Be	37	2.3×10^{-3}
^{210}Pb	1400	2.9×10^{-3}
^{137}Cs	800	1.8×10^{-3}
Columbia River, Canada/U.S.A. [6]		
^{137}Cs	4100	9.1×10^{-3}
$^{239,240}Pu$	5700	6.9×10^{-3}
^{241}Am	5000	6.1×10^{-3}
Saguenay River, Canada [5]		
^{210}Pb	3000	6.3×10^{-3}
^{137}Cs	1500	3.3×10^{-3}
$^{239,240}Pu$	3000	3.6×10^{-3}

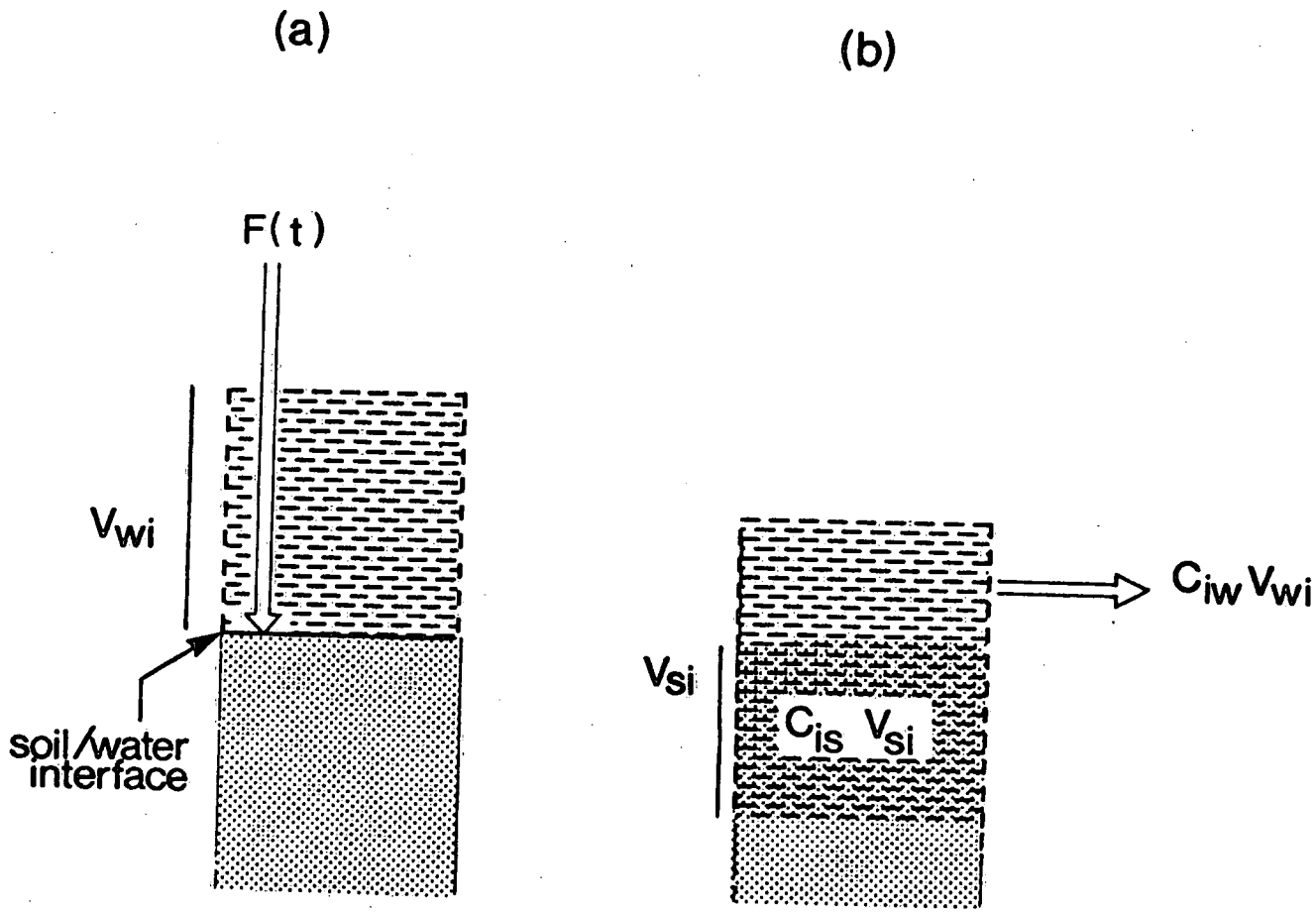

Fig. 1. Depiction of model parameters.

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