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Environ. Sci. Technol. 2002, 36, 2026–2032

Predicting the Fate of Sediment and Pollutants in River Floodplains

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Geological processes such as erosion and sedimentation redistribute toxic pollutants introduced to the landscape by mining, agriculture, weapons development, and other human activities. A significant portion of these contaminants is insoluble, adsorbing to soils and sediments after being released. Geologists have long understood that much of this sediment is stored in river floodplains, which are increasingly recognized as important nonpoint sources of pollution in rivers. However, the fate of contaminated sediment has generally been analyzed using hydrodynamic models of in-channel processes, ignoring particle exchange with the floodplain. Here, we present a stochastic theory of sediment redistribution in alluvial valley floors that tracks particle-bound pollutants and explicitly considers sediment storage within floodplains. We use the theory to model the future redistribution and radioactive decay of ^{137}Cs currently stored on sediment in floodplains at the Los Alamos National Laboratory (LANL) in New Mexico. Model results indicate that floodplain storage significantly reduces the rate of sediment delivery from upper Los Alamos Canyon, allowing 50% of the ^{137}Cs currently residing in the valley floor to decay radioactively before leaving LANL. A sensitivity analysis shows that the rate of sediment overturn in the valley (and hence, the total amount of radioactive ^{137}Cs predicted to leave LANL) is significantly controlled by the rate of sediment exchange with the floodplain. Our results emphasize that floodplain sedimentation and erosion processes can strongly influence the redistribution of anthropogenic pollutants in fluvial environments. We introduce a new theoretical framework for examining this interaction, which can provide a scientific basis for decision-making in a wide range of river basin management scenarios.

Introduction

Human activities such as mining, agriculture, and nuclear weapons development have loaded landscapes with a variety of environmental contaminants. Many of these substances, including heavy metals, agricultural pollutants, and radioactive elements, bind strongly to soils and sediments, which are delivered to rivers. For example, soluble cyanide from the recent tailings-dam spill into Hungary's Tisza River has mostly left the Tisza–Danube river system, but insoluble metals such as lead, copper, and zinc sequestered on river and floodplain sediment could be a more important and long-lasting ecological threat (*1*). Sediment in the upper Hudson River still contains polychlorinated biphenyls (PCBs) even though PCBs were banned by the Environmental Protection Agency over 20 years ago (*2*). Radioactively contaminated sediment resides in the floodplains of rivers draining nuclear facilities in the United States and the former Soviet Union, posing potential risks to human communities and ecosystems downstream (*3*, *4*). The recovery of these ecosystems will depend on the location and residence time of sediment in these fluvial environments and on any chemical alteration that the associated contaminants may undergo.

Sediment-bound contaminants preferentially adhere to fine-grained particles such as silt and clay, because of their large surface area-to-volume ratios and the high chemical activity of clay minerals (*5*). Fine-grained particles are generally transported through rivers in suspension and can be deposited on river bars and floodplain surfaces during overbank flooding. Thus, contaminated sediments tend to accumulate in floodplains adjacent to river channels, and these deposits become important nonpoint sources of downstream pollution as well as local sources for assimilation into plants and animals. Particles stored in floodplains generally have long residence times as compared with channel sediment because they are less accessible to erosion. Because many environmental contaminants break down through processes such as radioactive decay or bioprocessing, their long-term fate is controlled by the relative timescales of contaminant degradation and particle residence time in the valley floor.

The fate of contaminated sediment in rivers has commonly been evaluated using continuous models of hillslope and in-channel processes. Foster and Hakonson (*6*) used a landscape erosion model (the universal soil loss equation) to predict the delivery of fallout plutonium (which binds to sediment) from American rivers. Graf (*3*) modeled the movement of plutonium through the main channel of the Rio Grande in New Mexico using a hydraulically driven sediment transport model. Models of contaminant fate based on hydrodynamic theories of particle settling and resuspension have also been developed (e.g., refs *2*, *7*, and *8*), and such predictions are often used in evaluating natural recovery and in planning remediation. Such studies acknowledge the role of geological processes in redistributing sediment-bound contamination in watersheds, but they do not account for exchanges of sediment with the floodplain, which can be very large relative to the mean annual downstream flux (*9*). Sediment enters floodplains by settling onto point bars and floodplain surfaces and is remobilized as the channel banks erode. Such exchanges are crucial in pollutant problems because, in many valley floors, almost all of the pollutant inventory resides outside the active channel. The purpose of this paper is to present a new approach to predicting the fate of sediment and sediment-bound pollutants in river systems with floodplains. The next section presents the theoretical framework for the calculations. This is followed by an illustration of the technique with a relatively simple application from Los Alamos, NM, which is meant to demon-

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10.1021/es010509+ CCC: $22.00 © 2002 American Chemical Society
Published on Web 04/05/2002

strate the use of the model, the input data requirements, and convey some potential applications in a field setting.

Theoretical Development

Our approach for predicting the fate of contaminated sediment in valleys with floodplains involves a probabilistic analysis of particle trajectories through the valley alluvium accounting for exchanges of sediment between the channel and floodplain. The analysis is based on the theory of discrete-time Markov chains (*10*) and requires an approximation that the valley floor is composed of n discrete sediment storage units. All of the particles within a given unit should be equally susceptible to future erosion, sediment transport, and deposition. The storage units must be delineated in such a way as to ensure that this is a reasonable approximation over some timescale of decades or longer. Examples of such storage elements include the channel bed, bars, floodplain surfaces, or geographical subsets of these deposits. Where sorting by particle size is a dominant mechanism determining the fate of particles (e.g., a gravel bed river where both the bed load and suspended load are of interest), the units may be further subdivided by size class. The current model assumes that these units are in steady state, in the sense that their masses do not change significantly over time. This assumption is valid in many places over timescales relevant to the contamination and recovery of floodplains. The possibility of adapting the approach to transient cases is discussed later.

Particle movement among the n temporary storage units is controlled by a set of transition probabilities, which are governed by the rates of geomorphic processes exchanging sediment among deposits in the valley floor. When a particle is in a unit i, there is a fixed probability p_{ij} that it will reside in unit j after a unit time. We derive these transition probabilities p_{ij} directly from the sediment budget of the valley floor. A sediment budget has been defined as a "quantitative statement of the rates of production, transport, and discharge of detritus" (*11*) for a system of interacting sediment storage elements in the landscape and includes measurements or calculations of the masses of each storage reservoir and the rates of the major processes exchanging sediment among them. Procedures for readily obtaining these data for watersheds at the appropriate temporal and spatial scales have been outlined (*12*). The use of Markov chains to analyze long-term sediment transfer in valley floors has been proposed before (*11, 13*), but no formalized theory has emerged from this work. Furthermore, these studies did not consider the physical mechanisms by which sediment is exchanged with the floodplain, nor did they analyze the fate of contaminants. Models of bank erosion, overbank sedimentation, and other processes involved in channel–floodplain sediment exchange already exist (e.g., refs *14–19*), but the interactions among these processes and their influence on the long-term disposition of sediment in valley floors has not been analyzed. Future applications, which emerge from this analysis, can incorporate these individual process models, to the extent that they can be parametrized for the appropriate environmental conditions.

The transition probabilities p_{ij} are determined for all i, j assuming that each transition consists of two distinct events: (1) the erosion event E_i that causes the particle to be mobilized from unit i and (2) the deposition event D_j that places the particle in unit j. In order for a particle to move from unit i to unit j, it is necessary that both events E_i and D_j occur. The transition probability per time p_{ij}, where $i \neq j$, is equal to the probability of the intersection of events E_i and D_j and can be computed using the definition of a conditional probability (*10*)

$$p_{ij} = P(E_i)P(D_j|E_i) \tag{1}$$

where $P(D_j|E_i)$ is the conditional probability that the particle is deposited in j, given it was first eroded from i during the same increment of time. A particle can remain in unit i either by not being mobilized (event E_i^c, the complement of E_i) or by being mobilized and then redeposited in i. The probability of the union of these two events is the transition probability p_{ii}

$$p_{ii} = P(E_i^c) + P(E_i)P(D_i|E_i) = (1 - P(E_i)) + P(E_i)P(D_i|E_i) \tag{2}$$

If a particle is mobilized within the valley floor and not redeposited in any of the n storage elements, it leaves the system at the downstream boundary. The probability that a particle starting in unit i is transported directly out of the model system at the downstream boundary, p_{ix}, is

$$p_{ix} = P(E_i)(1 - \sum_{j=1}^{n}(D_j|E_i)) \tag{3}$$

Using eqs 1–3, all of the transition probabilities can be computed directly from $P(E_i)$ and $P(D_j|E_i)$, which are determined using the sediment budget as follows.

The probability $P(E_i)$ of any particle in i being mobilized per unit time is the mass rate of erosion of unit i divided by the total mass of that deposit. This statement requires that all of the particles in each unit are equally susceptible to erosion, as discussed previously. To derive the deposition probabilities, we divide the model space (consisting of n discrete storage elements) into a finite number of longitudinally contiguous reaches. If a particle is eroded from unit i, which is in reach r, then the conditional probability that the particle will be deposited in unit j, which is also in reach r, is

$$P(D_j|E_i) = \frac{Q(D_j)}{\sum_{k \in R} Q(D_k) + Q(O(r))} \tag{4}$$

where $Q(D_j)$ is the deposition rate (mass per unit time) into unit j, $Q(O(r))$ is the sediment flux out of reach r at its downstream end (mass/time), and R denotes the set of storage units that are located in reach r. The summation $\sum_{k \in R} Q(D_k)$ is the total rate of sediment deposition into all the units located within reach r (mass/time). A particle which has been mobilized within reach r (whether it entered from upstream, from external sources, or was eroded from one of the units located in that reach) will either be deposited in one of the units within that reach or will exit the reach at its downstream boundary. The probability in eq 4 equals the mass fraction of all the sediment mobilized in reach r that is deposited in unit j. If the particle is not deposited in any of the units in reach r, it enters the downstream reach $r + 1$, the units in that reach become accessible, and the deposition probabilities for each of the downstream reaches are computed using the same logic as applied in eq 4.

The transition probabilities are arranged in a transition matrix $\mathbf{P} = \{p_{ij}\}$

$$\mathbf{P} = \begin{pmatrix} p_{11} & \cdots & p_{1n} & p_{1x} \\ \vdots & \ddots & & \\ p_{n1} & & p_{m} & p_{nx} \\ 0 & 0 & \cdots & 1 \end{pmatrix} \tag{5}$$

The final row indicates that particles transported out of the system remain out of the system with probability one. The entries p_{ij} must be less than or equal to one, and the row sums in $\mathbf{P}$ must all equal one.

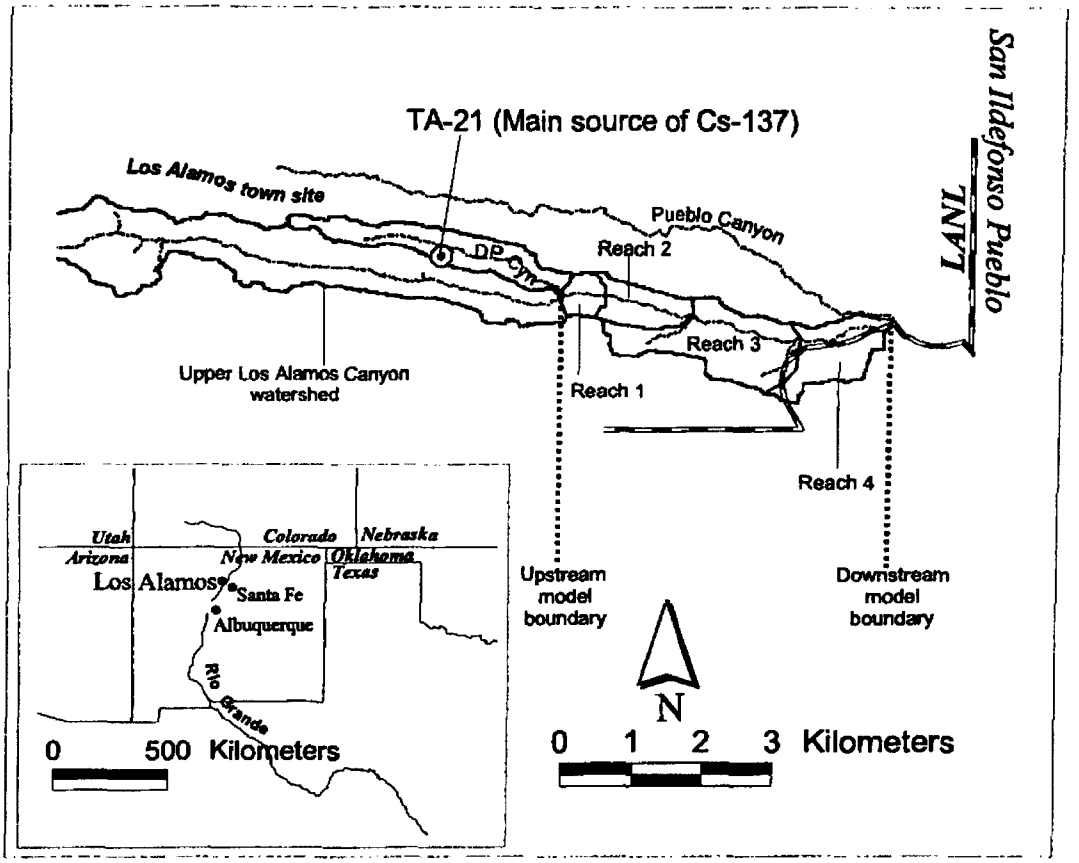

FIGURE 1. Upper Los Alamos Canyon, NM. Map shows the watershed boundary, the four reaches in the model, and the location of the principal source of ^{137}Cs. The model described in this paper represents the movement of particles initially stored in the channel and floodplain of each reach (a total of eight potential storage elements), and predicts future sediment and contaminant delivery at reach boundaries. The downstream boundary of the lowermost reach is the confluence with Pueblo Canyon, near the LANL–San Ildefonso Pueblo property boundary.

The particle transit time is the time a particle takes to reach the downstream boundary, starting from some initial deposit i. Some particles will exit the system rapidly, whereas others will be stored repeatedly within various storage units before leaving the valley. The probability distribution of particle transit times for sediment initially residing within unit i can be computed using the Chapman–Kolmogorov equations (*10*). The proportion of particles originating in a particular deposit which are transported past the downstream boundary in t years is equivalent to the probability that any particular particle reaches the boundary in t years. This probability can be computed from

$$g_i(t) = \mathbf{P}^t_{ix} - \mathbf{P}^{t-1}_{ix} \tag{6}$$

where $g_i(t)$ is transit time probability density at time t for a particle starting in unit i at $t = 0$, and $\mathbf{P}^t_{ix}$ denotes the entry from the ith row and last column of the matrix $\mathbf{P}$ raised to the t th power. The temporally varying delivery of sediment which originated in unit i at time 0 can be computed by multiplying eq 6 by the mass of unit i.

If the average concentration of a particular contaminant in each of the n storage elements is known and the contaminant concentration is reduced at a rate proportional to the concentration (as in the case of radioactive decay discussed in the following section), the flux of contaminant across the downstream boundary which originated in unit i at time 0 will be

$$f_i(t) = M_i\, g_i(t) C_i(0) e^{-\lambda t} \tag{7}$$

where M_i is the mass of sediment in unit i, $C_i(0)$ is the initial contaminant concentration in sediment in unit i at time 0, and λ is the decay constant. Other contaminants will have other decay functions, depending on the nature of the processes by which they degrade, and they can be incorporated into this theoretical framework by replacing eq 7 with an appropriate contaminant decay function.

Field Application

We illustrate the theory and some of its uses as a practical tool by applying it to a section of upper Los Alamos Canyon, NM (Figure 1), an alluvial valley draining portions of Los Alamos National Laboratory (LANL). Radioactive contaminants are present in floodplain sediment on LANL property upstream of the San Ildefonso Indian Reservation. The study area is the 5.3-km section of the valley between DP Canyon and Pueblo Canyon. DP Canyon drains Technical Area (TA-21, the LANL facility which was the primary source of contamination to upper Los Alamos Canyon. The confluence with Pueblo Canyon is located near the LANL–San Ildefonso property boundary (Figure 1), so modeled rates of contaminant transport past this point approximate fluxes off LANL property. The main contaminant of concern is ^{137}Cs, which has a half-life of 30.2 years and has accumulated in floodplain deposits downstream of the confluence with DP Canyon. Reneau et al. (*20*) determined the distribution of ^{137}Cs in channel and floodplain deposits in the study area in 1997, based on geomorphic mapping and an extensive sampling program. We retain their use of curies (English units instead of metric units of bequerels) as a measure of radioactivity,

TABLE 1. Sediment and ^{137}Cs Distribution in Upper Los Alamos Canyon, Geomorphic Process Rates, and Mean Transit Times

reach	length (km)	geomorphic unit	mass[a] (T)	initial ^{137}Cs inventory[b] (mCi)	rate of channel bed scour/fill[a] (T/year)	rate of floodplain sedimentation/bank erosion[a] (T/year)	rate of sediment transport from reach[a] (T/year)	modeled mean particle transit time[c] (year)
1	0.68				2500	40	2300	
		channel	3100	12				18
		floodplain	2000	29				67
2	1.50				5600	130	2300	
		channel	9400	16				17
		floodplain	6500	39				65
3	1.62				6100	70	2300	
		channel	6200	18				9
		floodplain	3600	42				58
4	1.54				5800	50	2300	
		channel	5000	6				4
		floodplain	2700	14				53
entire valley floor	5.3		38500	176				

[a] Calculation of the elements in the sediment budget summarized in Supporting Information appendix. [b] Contaminant inventories as of 1997, from ref *20*. [c] Average length of time particle starting in a given deposit will take to reach the downstream boundary, computed using eq 6.

TABLE 2. 9 × 9 Transition Probability Matrix[a] Used in the Model Application to Upper Los Alamos Canyon, NM

	location at time $t+1$								
location at time t	reach 1 channel	reach 1 floodplain	reach 2 channel	reach 2 floodplain	reach 3 channel	reach 3 floodplain	reach 4 channel	reach 4 floodplain	past downstream boundary
reach 1 channel	0.616	0.007	0.265	0.006	0.077	0.001	0.020	0.0002	0.008
reach 1 floodplain	0.011	0.980	0.007	0.0002	0.002	2.3×10^{-5}	0.0005	4.8×10^{-6}	2.0×10^{-4}
reach 2 channel	0	0	0.822	0.010	0.121	0.001	0.032	3.0×10^{-4}	0.013
reach 2 floodplain	0	0	0.014	0.980	0.004	4.9×10^{-5}	0.001	1.0×10^{-5}	4.2×10^{-4}
reach 3 channel	0	0	0	0	0.728	0.008	0.188	0.002	0.074
reach 3 floodplain	0	0	0	0	0.015	0.980	0.004	3.6×10^{-5}	0.002
reach 4 channel	0	0	0	0	0	0	0.672	0.008	0.320
reach 4 floodplain	0	0	0	0	0	0	0.014	0.980	0.006
past downstream boundary	0	0	0	0	0	0	0	0	1

[a] This matrix contains our estimates of the annual probabilities of a particle moving among the nine sediment storage reservoirs, computed from the sediment budget in Table 1 and eqs 1–5 in the text. The values along the main diagonal contain probabilities of a particle starting and ending a year in the same reservoir. Note that all the rows sum to one, accounting for all possible outcomes for a particle starting in each deposit. All model results presented in Table 1, Figures 2–5, and in the text are computed directly from this matrix of probabilities.

because it is the standard unit of measurement used in environmental applications at Los Alamos. One curie (Ci) is the quantity of radioactive material that has 3.7×10^{10} disintegrations per second, which is equivalent to the amount of radiation emitted by 1 g of the element radium. Reneau et al. (*20*) estimated a total inventory of 176 mCi (0.176 Ci) of ^{137}Cs in the study area in 1997. Most of this inventory resides in floodplain deposits adjacent to the channel (Table 1), and concentrations generally decrease with distance from DP Canyon (*20*).

We divided the canyon into the four reaches, depicted in Figure 1. Each of the four reaches was subdivided into a channel and floodplain (see Figure SI-1, Supporting Information), so we consider the fate of sediment currently residing within eight discrete sediment storage units (i.e., $n = 8$). The theory is parametrized using an estimated sediment budget of the valley floor, which includes measurements or calculations of the rates of sediment transfer processes and the masses of the sediment reservoirs on which these processes act. Sediment budgets are commonly estimated for geomorphic systems such as river valleys, and the procedures for estimating the sediment budget vary based on field conditions and the level of accuracy desired for a given application. Malmon (*21*) presents a detailed analysis of the sediment budget of upper Los Alamos Canyon. This analysis is summarized in the Supporting Information appendix and in Table 1. We used the resulting sediment budget (Table 1) to derive the entries in the transition probability matrix (Table 2) as outlined in eqs 1–5.

Results and Discussion

This section demonstrates some of the computations that can be made using the model presented in the previous section and the sediment budget from upper Los Alamos Canyon. The current analysis models the fate of active sediment stored in the valley floor after 1997, which contains ^{137}Cs from LANL operations. In the discussion which follows, "valley-derived" sediment refers to those particles which were stored in the channels and floodplains along the study reaches in 1997 ($t = 0$), when the ^{137}Cs inventories were measured (*20*). While the model can compute the redistribution of sediment entering the system from upstream, hillslope, or tributary sources over time (*21*), this section does not consider sediment which enters the valley after 1997.

Using the transition probability matrix in Table 2 and the masses of sediment reservoirs in Table 1, application of eq 6 leads to the prediction that half of the ~38 500 metric tons of active sediment currently stored in the valley floor will be evacuated and replaced with new sediment in the next 12 years, 90% in 87 years, and 99% in 211 years. Modeled mean particle transit times to the confluence with Pueblo Canyon vary from 4 years for sediment initially in the reach 4 channel to 67 years for the reach 1 floodplain (Table 1).

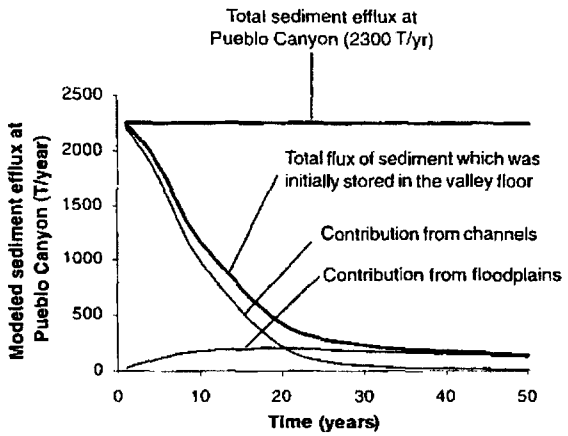

FIGURE 2. Modeled sediment efflux at the confluence with Pueblo Canyon. Sediment "initially stored in the valley floor" refers to the flux of sediment across the downstream boundary that was stored in one of the eight storage units at time 0. Channel and floodplain contributions are the sums of sediment originating (at time 0) in the four channel units and the four floodplain units, respectively. Total sediment flux at the upstream and downstream boundaries are constant (2,300 T/year; Table 1), but the relative contributions of channel, floodplain, and external sediment sources vary over time.

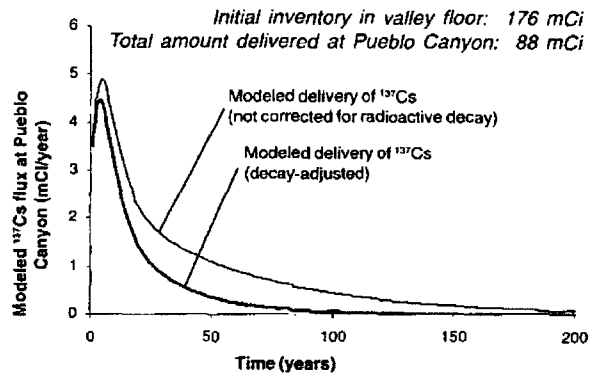

FIGURE 3. Modeled ^{137}Cs flux at the confluence with Pueblo Canyon. The heavy black line is the predicted flux of ^{137}Cs at the downstream boundary, corrected for radioactive decay. To show the effect of radioactive decay versus geomorphic processes in reducing future contaminant fluxes, the lighter line depicts the modeled flux of ^{137}Cs computed without accounting for radioactive decay. According to the model, 50% of the ^{137}Cs currently residing in the valley floor will decay radioactively before leaving the system. Note that the predicted flux only accounts for future delivery of the contaminant inventory currently residing in the valley floor and assumes that sediment entering the study area in the future will carry negligible amounts of ^{137}Cs.

While the total sediment efflux at Pueblo Canyon is constant (in keeping with the steady-state assumption), the source area of that sediment changes over time. According to the model, in the first year, nearly all of the sediment transported past the Pueblo Canyon confluence derives from the eight valley floor storage elements (Figure 2). This implies that much of the sediment entering the system from external sources in a given year goes into some form of temporary storage in the valley floor (primarily into channel units), rather than immediately exiting the system. Initially, the modeled sediment efflux is dominated by sediment currently stored in the four channel units, but as this sediment is depleted, the dominant source of valley-derived sediment (i.e., sediment which is stored within the eight geomorphic units at time 0) becomes the floodplain (Figure 2). After 30 years, nearly all of the valley-derived portion of the sediment efflux consists of sediment that was stored in the floodplain at time 0.

The stochastic model presented here can identify the origin of particles reaching the basin outlet (using eq 6). This capability offers considerable benefits for improving quantitative estimates of contaminant transport downstream, for identifying the sources of sediment-bound contamination in watersheds, and for anticipating the potential impacts of various remediation alternatives. In upper Los Alamos Canyon, floodplain-stored sediment initially (i.e., in 1997) contains 70% of the contaminant inventory (Table 1), and contaminant concentrations generally decrease in the downstream direction (*20*). Equations 6 and 7 can be used to model the future delivery of the ^{137}Cs inventory currently residing in the valley floor of upper Los Alamos Canyon (Figure 3). The modeled flux in Figure 3 is equivalent to the flux of the contaminant at the basin outlet if no more ^{137}Cs were to enter the system from upstream or from lateral sources (e.g., if all sediment entering the system in the future were uncontaminated). This is a reasonable approximation for upper Los Alamos Canyon, where contaminant concentrations on sediment entering the study area peaked in the 1950s and have since dropped to relatively low levels (*20, 21*). It is straightforward to account for time-varying contaminant concentrations on sediment entering the model space by partitioning the contaminant influx among the sediment reservoirs using the deposition probabilities (*21*); however, for simplicity in this application, we make the assumption that all of the ^{137}Cs already resides in the valley floor at time 0.

The predicted contaminant flux at Pueblo Canyon rises slightly over the first few years as the contribution of the floodplain sediment from upstream (i.e., more contaminated reaches) increases but then drops rapidly as the channel-stored ^{137}Cs is depleted and the remaining floodplain-stored ^{137}Cs decays (Figure 3). The modeled fluxes in Figure 3 do not account for contributions of ^{137}Cs from sources outside the study reaches, and the initial increase in ^{137}Cs flux did not occur in model runs which incorporated anticipated future contributions of the contaminant from DP Canyon (*21*). To highlight the effect of radioactive decay of ^{137}Cs on reducing future contaminant fluxes, we plotted the equivalent contaminant flux computed without correcting for decay (Figure 3, lighter line). According to model predictions, 50% of the original ^{137}Cs inventory (as of 1997) will decay radioactively before being transported across the property boundary, and the total modeled delivery of ^{137}Cs amounts to 88 mCi.

The probabilistic approach can be used to compare the relative importance of different source areas on the downstream contaminant flux. For example, Figure 4A compares the relative contributions of the four reaches to the future flux of ^{137}Cs at the LANL/San Ildefonso property boundary. It is also possible to compare the relative contributions of different geomorphic units. Figure 4B shows the aggregated contributions of the channel versus the floodplain over time, indicating that channel-stored sediment should only contribute significantly to the contaminant flux over the next 20–30 years. The capacity to compare the influence of different contaminant sources along a river could provide a quantitative basis for cost–benefit analyses, risk analyses, and for choosing among a variety of proposed remediation alternatives.

Using the sediment budget in Table 1 to derive the transition probabilities, the model predicts that 88 mCi of ^{137}Cs will reach the confluence with Pueblo Canyon in the future, while the remainder is expected to decay radioactively before reaching the property boundary. The total amount of ^{137}Cs that is eventually delivered to the downstream model boundary reflects the rate at which sediment is turned over

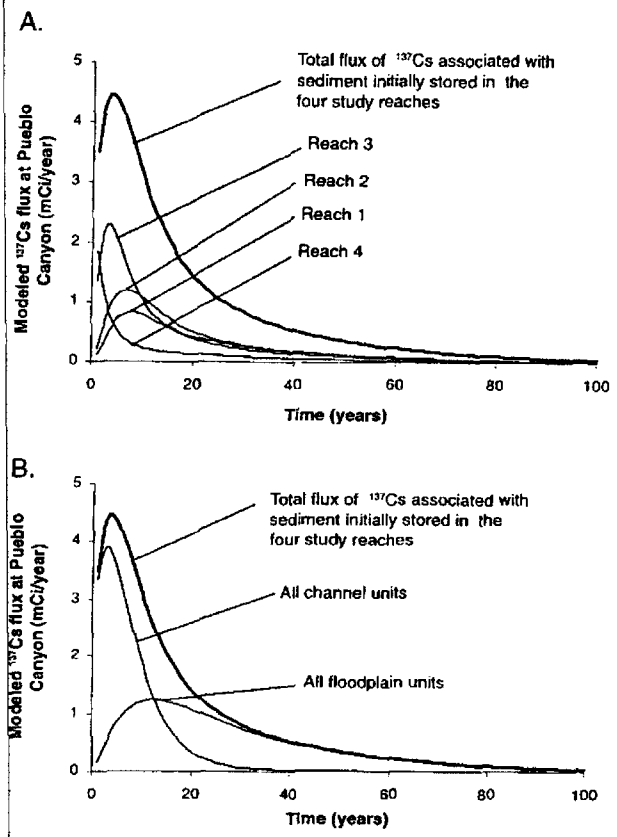

FIGURE 4. Modeled ^{137}Cs flux at the confluence with Pueblo Canyon, by reach and by geomorphic unit: (A) ^{137}Ce flux by reach, showing the combined contributions of the channel and floodplain for each reach; (B) combined ^{137}Cs flux for channel and floodplain units in all reaches.

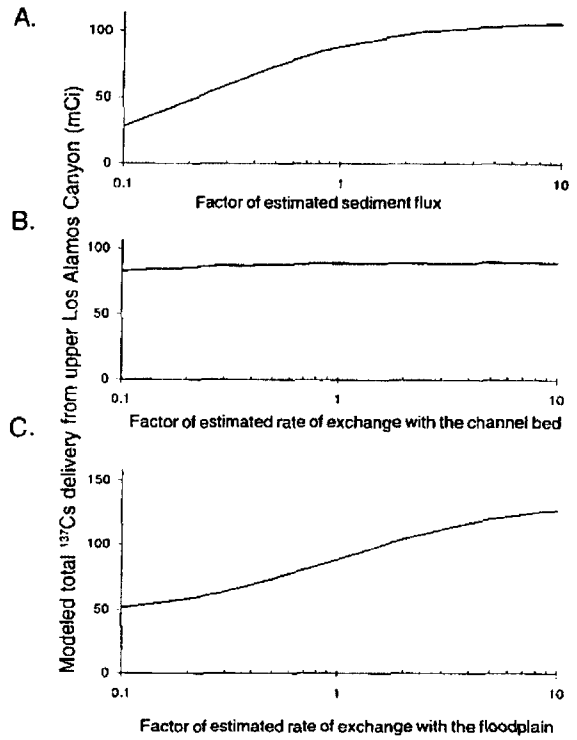

FIGURE 5. Sensitivity of modeled ^{137}Cs delivery at Pueblo Canyon to the components of the sediment budget: (A) sensitivity of modeled ^{137}Cs delivery to downstream sediment flux; (B) sensitivity of modeled ^{137}Cs delivery to the rate of sediment exchange with the channel bed (scour and fill); (C) sensitivity of modeled ^{137}Cs delivery to the rate of sediment exchange with the floodplain (floodplain sedimentation and bank erosion). Estimated rates of each of the geomorphic processes are summarized in the sediment budget in Table 1.

in the valley floor. We use this value as a metric for analyzing the sensitivity of the model to the sediment budget parameters. The modeled total ^{137}Cs delivery was computed as the three geomorphic process rates were varied over 2 full orders of magnitude. Increasing the sediment flux (while holding the rates of sediment exchange with the channel and floodplain constant) reduces the probability that any particle will be deposited in the valley floor (eq 4). Thus, the rate of sediment overturn and the total amount of ^{137}Cs delivery from the valley floor both increase with increasing sediment flux, from 27 to 106 mCi as sediment flux increases over 2 orders of magnitude (Figure 5A). The model is relatively insensitive to the rate of sediment exchange with the channel bed (Figure 5B), because increasing the probability of particle erosion from the bed is balanced by an increasing probability of redeposition, according to the steady-state assumption. In the Los Alamos example, the model is more sensitive to changes in the rate of sediment exchange with the floodplain (i.e., to rates of bank erosion and to the frequency and magnitude of sedimentation from overbank flows) (Figure 5C). Total modeled ^{137}Cs delivery varies from 51 to 127 mCi as floodplain deposition/erosion rates increase from 0.1 to 10 times the original value of 1 cm/year. However, the sedimentation rate is the best-constrained value in the sediment budget (*21*) and is probably within a factor of 2 of the true value. Nevertheless, this sensitivity analysis further emphasizes the importance of sediment exchange with the floodplain as a primary mechanism of moderating contaminant delivery from watersheds.

The current version of the model assumes that the valley is in steady state and that the historical sediment budget is a good approximation of future conditions. Watershed perturbations such as climate change, fire, or anthropogenic disturbances can create transient conditions which cause the transition probabilities (eqs 1−4) to change over time. The Cerro Grande fire in May 2000 burned part of the headwaters of Los Alamos Canyon, which may now impose transient conditions on the hydrology and sediment transport regimes of the reaches we have studied (e.g., refs *22*−*25*). The transient case can be modeled by changing the entries in the transition matrix according to observed or predicted changes in the sediment budget. The Chapman−Kolmogorov equation does not apply in this case, but the same results can be achieved numerically using a time-varying transition probability matrix. However, the method outlined in the previous section remains applicable to other floodplain reaches for which steady-state conditions can be identified.

Alluvial valley storage strongly modulates downstream sediment flux and water quality in many river systems (*26*). The residence time of sediment in a valley depends on the rates of channel−floodplain sediment exchange processes, the rate of downstream sediment transport, and the masses of the sediment reservoirs on which these geomorphic processes operate. As particles move intermittently down valleys following random trajectories, sediment-bound contaminants may degrade at a contaminant-specific rate. The long-term fate of sediment-stored pollutants depends on the relative timescales of particle migration and contaminant degradation. The current study presents a theoretical framework for analyzing this interaction and a potential platform for designing long-term management responses to an increasingly important class of environmental problems.

Acknowledgments

This work is supported by a grant from the Collaborative UC-Los Alamos Research (CULAR) program, by the Environmental Restoration Project at LANL, and by a Horton Research Grant from the American Geophysical Union. We thank J. Lyman, C. Salazar, and M. Van Eeckhout for field assistance, S. Bozkurt and A. Teo for help in the laboratory, and P. Beeson for providing GIS data. D. Alsdorf, D. Broxton, M. Gabet, and two anonymous reviewers provided insightful comments on the manuscript.

Supporting Information Available

A description and schematic diagram of the geomorphology of upper Los Alamos Canyon, and a summary of the calculations and data used to parametrize the model. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

(1) Koenig, R. *Science* **2000**, *287*, 1737.
(2) Connolly, J. P.; Zahakos, J. A.; Benaman, J.; Ziegler, C. K.; Rhea, J. R.; Russel, K. *Environ. Sci. Technol.* **2000**, *34*, 4076.
(3) Graf, W. L. *Plutonium in the Rio Grande: Environmental Change and Contamination in the Nuclear Age*; Oxford University Press: New York, 1994.
(4) Van der Perk, M.; Burrough, P. A.; Culling, A. S. C.; Laptev, G. V.; Prister, B.; Sansone, U.; Voiteskhovitch, O. V. In *Floodplains: Interdisciplinary Approaches*; Marriott, S. B., Alexander, J., Eds.; Geological Society London, Special Publication 163; Geological Society of London: London, U.K., 1999; pp 61−67.
(5) Eisenbud, M. *Environmental Radioactivity*; Academic Press: Orlando, FL, 1987.
(6) Foster, G. R.; Hakonson, T. E. *J. Environ. Qual.* **1984**, *13*, 595.
(7) Gailani, J.; Ziegler, C. K.; Lick, W. *J. Great Lakes Res.* **1991**, *17*, 479.
(8) Thomann, R. V.; Mueller, J. A.; Winfield, R. P.; Huang, C. R. *J. Environ. Eng.* **1991**, *117*, 161.
(9) Dunne, T.; Mertes, L. A. K.; Meade, R. H.; Richey, J. E.; Forsberg, B. R. *Geol. Soc. Am. Bull.* **1998**, *110*, 450.
(10) Ross, S. M. *Introduction to Probability Models*. 6th ed.; Academic Press: San Diego, CA, 1997.
(11) Dietrich, W. E.; Dunne, T.; Humphrey, N. F.; Reid, L. M. In *Sediment Budgets and Routing in Forested Drainage Basins*; Swanson, F. J., Janda, R. J., Dunne, T., Swanston, D. N., Eds.; USDA Forest Service General Technical Report PNW-141; U.S. Department of Agriculture: Portland, OR, 1982; pp 5−23.
(12) Reid, L. M.; Dunne, T. *Rapid Evaluation of Sediment Budgets*; Catena Verlag: Reiskirchen, Germany, 1996.
(13) Kelsey, H. M.; Lamberson, R.; Madej, M. A. *Water Resour. Res.* **1987**, *23*, 1738.
(14) Begin, Z. B. *J. Geol.* **1981**, *89*, 497.
(15) Thorne, C. R.; Tovey, N. K. *Earth Surf. Processes Landforms* **1981**, *6*, 469.
(16) Parker, G.; Sawai, K.; Ikeda, S. *J. Fluid Mech.* **1982**, *115*, 303.
(17) James, C. S. *J. Hydraul. Res.* **1985**, *23*, 435.
(18) Pizzuto, J. *Sedimentology* **1987**, *34*, 301.
(19) Howard, A. D. In *Lowland Floodplain Rivers: Geomorphological Perspectives*; Carling, P. A., Petts, G. E., Eds.; J. Wiley and Sons Ltd.: Chichester, U.K., 1992; pp 1−39.
(20) Reneau, S. L.; Ryti, R. T.; Tardiff, M.; Linn, J. Evaluation of sediment contamination in Upper Los Alamos Canyon (Reaches LA-1, LA-2, and LA-3); Los Alamos National Laboratory Report LA-UR-98-3974; Los Alamos National Laboratory: Los Alamos, NM, 1998.
(21) Malmon, D. V. Ph.D. Dissertation, University of California, Santa Barbara, CA, 2002.
(22) Beeson, P. C.; Martens, S. N.; Breshears, D. D. *Hydrol. Proc.* **2001**, *15*, 2917.
(23) Johansen, M. P.; Hakonson, T. E.; Breshears, D. D. *Hydrol. Proc.* **2001**, *15*, 2953.
(24) McLin, S. G.; Springer, E. P.; Lane, L. J. *Hydrol. Proc.* **2001**, *15*, 2967.
(25) Wilson, C. J.; Carey, J. W.; Beeson, P. C.; Gard, M. O.; Lane, L. J. *Hydrol. Proc.* **2001**, *15*, 2995.
(26) Trimble, S. W. *Science* **1999**, *285*, 1244.

Received for review January 5, 2001. Revised manuscript received February 5, 2002. Accepted February 14, 2002.

ES010509+