

## PREDICTING RADIOACTIVE HEAVY METAL MOVEMENT THROUGH SOIL.

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### ABSTRACT

The rate of movement through soils of constituents in wastes depends on the nature of the disposal environment with respect to three major components: (a) the porous medium through which the fluid moves (soil), (b) the vehicle that transports the constituent (fluid), and (c) the potential pollutant constituent itself (heavy metal). A laboratory soil-column method was developed to provide data for predicting movement of potential pollutants through soils. The research describes the rate of movement of radionuclides  $^{32}\text{P}$ ,  $^{89}\text{Sr}$ ,  $^{90}\text{Sr}$  ( $^{90}\text{Y}$ ),  $^{45}\text{Ca}$ ,  $^{59}\text{Fe}$  in biological residues and metals As, Be, Cd, Cr, Cu, Fe, Hg, Ni, Pb, Se, V, and Zn in leachates. Attenuation of pollutants in soils was statistically compared to the measurable parameters of the components of the disposal environment. The application of the soil attenuation data to the Lapidus-Amundson and Error Function models for development of a simple universal equation, useful as a field oriented tool for predicting pollutant movement through soils is provided.

### BACKGROUND AND SCOPE

The most characteristic feature of soils, that must be fully taken into consideration in waste disposal, is the great variability that extends to all components.<sup>1,2</sup> Thus soils are not all alike, but differ just as plants and animals. The effectiveness of soil in a waste disposal system and a barrier to migration of hazardous waste pollutants should, therefore, begin with an understanding of the soil properties and the way they interact with wastes, their leachates, and specific pollutants such as radioactive elements.

There are three major components of the waste disposal environment that interact in any waste deposited on the land or in the soil that must be identified, described, and quantitatively evaluated. They are:

1. The porous medium through which the constituents are transported (e.g. soils),
2. The vehicle of transport that carries the polluting constituents or is itself the pollutant (e.g. aqueous leachates, organic solvents),
3. The specific polluting constituent itself (e.g. soluble heavy metal, radionuclide).

These three components interact and are important in management practices. All factors involved in attenuation of the polluting constituents change with time.

Predicting movement of hazardous waste constituents through soils has been approached in several quite different ways.<sup>3,4,5,6,7,8,9</sup> Each method has serious limitations in meeting the necessary criteria as a workable predictive tool. The laboratory soil-column concept remains as the most adaptable to provide data for predicting pollutant movement.<sup>4</sup> The soil-column technique involves the selection of soils representative of a suggested disposal site, packing PVC or glass columns to uniform soil densities similar to field conditions, and passing various solutions representative of the waste stream - solid waste leachates, solid wastes, or wastewaters - through the columns. Breakthrough curves (i.e.,  $C=C_0$  or  $C/C_0=1$ ; where C is concentration of soluble heavy

metal in the leachate effluent and  $C_0$  is the original influent solution) are developed. Data from the breakthrough curves and the soil characteristics may be used directly to predict radioactive metal attenuation or the factors of the disposal environment identified, sorted-out, and evaluated using statistics and computer techniques. Models may then be developed. Alternatively, the data may be used with a simulation model to regress metal movement rates with soil and waste characteristics and develop simple, user-oriented equations to predict metal movement for specific combinations of wastes and soils that have been studied.

### OBJECTIVES

The objectives of this presentation are: (a) to provide directions for conducting the soil-column test, (b) to interpret the results in terms of the movement and retention of waste constituents in soil, and (c) to apply the results to predict pollutant movement in soils and soil-clay liners.

### APPROACH

The soil-column technique has the advantage of screening a large number of soils of wide variability for pollutant attenuation while avoiding the multitude of problems associated with field conditions. The data can be used in two ways: (a) directly for prediction purposes and (b) indirectly through the development of rate equations. The soil-column method is adapted to generating a large volume of data at a relatively low cost. The second approach, therefore, is to use soil-column techniques in association with mathematics as finally applied to the concept of certain universal simulation models.<sup>10</sup> For example, the "Lapidus and Amundson"<sup>10</sup> and "Error Function" models have been adapted to develop user-oriented predictive equations of pollutant attenuation, provided that certain dominant characteristics of the components of the waste disposal environment have been determined.<sup>3</sup>

Predictive designs for land disposal of hazardous wastes therefore, are established on characteristics of the components of the disposal environment

affecting pollutant migration rates. These characteristics must be sorted out, identified, and quantified<sup>8,9,11</sup> through the soil-column techniques. Therefore, until a practical field-oriented method is developed to provide more reliable predictive information for a specific disposal site, the soil-column method is the most adequate method for predicting the movement of pollutants through soils.

## EXPERIMENTAL

### Materials

#### Soils

Twelve soils, representative of 7 major orders were collected throughout the USA at depths to avoid organic matter of surface layers. They ranged in pH from 4.2 for the Ultisol to 7.8 for the Aridisol and in clay from 1 to 52%, Table I. The two Mohave soils were included because one was calcareous and the other not. If others wish to characterize soils or soil-like material for their sites, they can compare soils with these reported here and estimate expected attenuation.

#### MSW Leachates

The municipal solid waste leachates (MSW) used are characterized elsewhere and in Table II.<sup>4,8,11</sup> Representative municipal solid waste was used to generate landfill leachate. The low concentration of heavy metal in the leachates required that enrichments be made of test elements on an equal molar basis (46-120 ppm) to assure that metals migrate through the soil column in sufficient concentration to be detected in a workable period of time. The elements were added

as As<sup>3+</sup>, Be<sup>2+</sup>, Cd<sup>2+</sup>, Cr<sup>2+</sup>, Cu<sup>2+</sup>, Hg<sup>2+</sup>, Ni<sup>2+</sup>, Pb<sup>2+</sup>, Se<sup>4+</sup>, V<sup>5+</sup> and Zn<sup>2+</sup>. The appropriate chloride was used except oxides were used for As, Cr, V, and Se, and nitrate for Pb.

Other displacing solutions used for evaluating the contribution of the soil to the pool of soluble potentially hazardous elements were (a) aqueous H<sub>2</sub>SO<sub>4</sub> adjusted to pH 3.0, (b) 0.025 M AlCl<sub>3</sub> plus 0.025 M FeCl<sub>2</sub> adjusted to pH 3.0, (c) deionized water, and (d) 0.01 and 0.25 M chelates EDTA, EGTA, DCyTA, HEEDTA, DTPA, and DTPA-TEA.

#### Biological Material

Plant materials (barley, wheat, lettuce, tomato) were grown in standard Hoagland's nutrient solutions containing 5 to 6.5 µg/l of the desired carrier-free radionuclides - <sup>32</sup>P, <sup>89</sup>Sr-<sup>90</sup>Sr(<sup>90</sup>Y), <sup>45</sup>Ca, <sup>59</sup>Fe - for one week of the 52 days of growth to tag the plant tissues. Algae (4 species) and fungi (6 species) were grown in Bristol's<sup>12</sup> and Czapek's<sup>12</sup> nutrient media, respectively, enriched with the appropriate carrier-free radionuclides. When suitable growth had occurred the fungal pads were removed, washed twice with 0.1N HNO<sub>3</sub> and twice with deionized water. The algae cells were concentrated by centrifugation, resuspended in 0.1N HNO<sub>3</sub> and washed twice with the acid and d-water. Dry weights were determined after lyophilization. After determining the radioactivity, all biological tissues were mixed with 300 g of the appropriate soil and placed on top of the columns of soil measuring 10x20 cm. The total weight of Mohave s 1 soil was 2700 g air dry, Fig. 1c.

Table I. Selected characteristics of soils used.

Soil Series	Soil Order	Clay	Silt	"Free" Iron Oxides	Soil Paste pH	Cation Exch. Capacity	Elec. Cond. of Extract	Column Bulk Density	Soil Surface Area	Predominant Clay Minerals
Davidson	Ultisol	52	23	17.1	6.4	9	168	1.40	159.3	Kaolinite
Molokai	Oxisol	52	25	23.2	6.2	14	1262	1.44	167.3	Kaolinite, gibbsite
Nicholson	Alfisol	49	47	5.6	6.7	37	176	1.53	120.5	Vermiculite
Fanno	Alfisol	46	19	3.7	7.0	33	392	1.48	122.1	Montmorillonite, mica
Mohave(Ca)	Aridisol	40	28	2.5	7.8	12	510	1.54	127.5	Mica, montmorillonite
Chalmers	Mollisol	31	52	3.1	6.6	22	288	1.60	95.6	Montmorillonite vermiculite
Ava	Alfisol	31	60	4.0	4.5	19	157	1.45	61.5	Vermiculite, kaolinite
Canelo	Alfisol	26	29	-	5.4	6	240	1.72	35.0	Kaolinite
Anthony	Entisol	15	14	1.8	7.8	10	328	1.87	49.8	Montmorillonite, mica
Mohave	Aridisol	11	37	1.7	7.3	10	615	1.78	38.3	Mica, Kaolinite
Kalkaska	Spodosol	5	4	1.8	4.7	6	237	1.53	8.9	Chlorite, kaolinite
Wagram	Ultisol	4	8	0.6	4.2	2	225	1.87	8.0	Kaolinite, chlorite
River sand	Entisol	1	2	0.5	7.2	2	210	1.73	3.6	Kaolinite, mica

Table II. Ranges of constituents detected in the natural leachate generated from municipal solid waste.

Constituent	Leachate I	Leachate II	Leachate III
	Range	Range	Range
	<----- mg/l ----->		
COD	100-200	100-550	100-635
TOC	200-900	700-10000	7800-10600
pH	3.4-6.8	3.2-5.4	5.0-5.4
EC(mmhos/cm)	2.6-3.5	9.0-11.5	8-13.0
TDS	1660-2240	5000-7000	8000-9000
Total P	2.0-4.0	12	63-102
NH <sub>4</sub> -N	125-150	110-162	101-139
Cl	≈3900	≈4000	≈3800
Ca	160-225	200-1000	600-700
Mg	25-60	60-360	130-140
Na	55-150	150-640	260-280
K	850-950	600-700	1140-1160
Si	20-25	32-33	39-41
Cd	<0.02	<0.02	<0.02
Co	<0.10	<0.05	<0.02
Cr	<0.05	<0.05	0.06
Cu	<0.05	<0.05	0.02-0.06
Fe	70-100	900-1000	650-730
Mn	0.6-1.8	12	10
Pb	<0.02	<0.05	<0.05
Ni	<0.05	0.05-0.25	0.21
Zn	0.10-2.10	9-13	4-7

The influence of the soil microflora activity on the movement of radiostrontium from contaminated fungal and algal materials was measured in soil columns leached with 150 ml of deionized H<sub>2</sub>O or aqueous HCHO (0.5%) 12 times at 48-hour intervals. The effect of DTPA on strontium movement was evaluated by leaching similar columns with 147 ml of deionized H<sub>2</sub>O and 3 ml of 15% NH<sub>4</sub>OH with and without 0.067 M DTPA. The leachates from the columns were collected and analyzed for radiostrontium by liquid scintillation. The movement of the radiostrontium through the variously treated soil columns also was evaluated by determining the <sup>89</sup>Sr extracted from each 5 cm-column section with 0.5N Sr(NO<sub>3</sub>)<sub>2</sub>. The extracts were made up to a specific volume, and assayed for radioactivity by the planchet-counting technique in a gas-flow detector having a detection efficiency of 0.40 for radiostrontium under the experimental conditions.

After extraction with 0.5N Sr(NO<sub>3</sub>)<sub>2</sub>, the soil was placed in 4N HCl on a hot bath at 70-80° C overnight and then filtered into a volumetric flask. The soil was returned to a beaker and washed with five 5-ml portions of 1N HCl. The extract was brought to volume and assayed for <sup>89</sup>Sr with a Packard Tri-Carb liquid scintillation spectrometer.

Further information on the displacement and availability to plants of algal- and fungal-bound <sup>89</sup>Sr was sought by growing barley, bean, lettuce, and tomato plants in soils from the different sections of the soil columns using the root-mat technique.

#### Methods

##### The Soil Column Method

Below is an abbreviated stepwise laboratory guide for convenience.

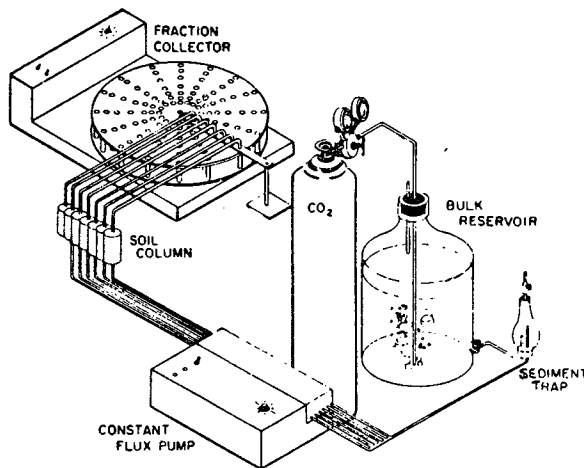
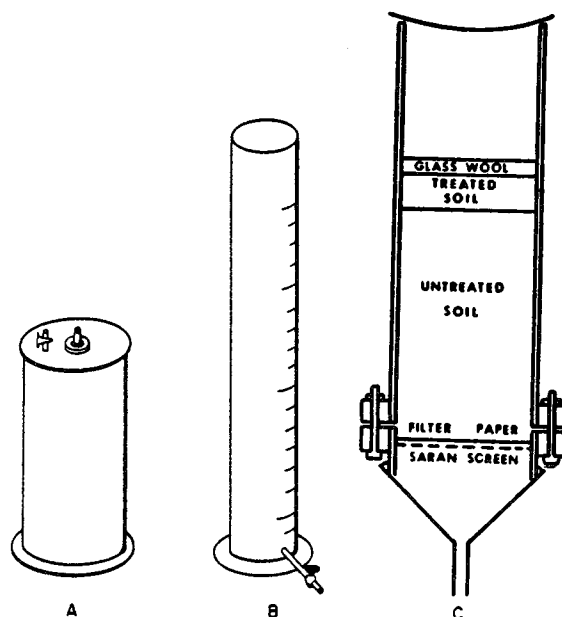


Fig. 1 Diagram of the soil column system using the peristaltic pump and fraction collector.

1. Collect representative soils taken from depth of expected waste stream penetration or until soil layers end and rock, gravel, or sand dominates.
2. Store part of each sample depth at field moisture for reference. If too wet to roll and screen (2mm), air dry until it can be screened but be careful not to allow the soil to dry completely.
3. Pack the soil into the soil column to a uniform density, equal to or slightly greater than, found under natural conditions. Determine the amount of soil (oven-dried basis) in the column by drying separate samples.

4. Save some soil for chemical and physical analyses such as moisture content and bulk density, porosity, sand, silt, and clay (<2 $\mu$ m).
5. Assemble the equipment according to the kind of waste fluid or solid waste tested according to Figs. 1.
6. Wet the soil column with deionized water or water containing gypsum (0.01N CaSO<sub>4</sub>·2H<sub>2</sub>O) by forcing water upward through the column against gravity. Allow to stand 7 days.
7. Meter the fluid waste stream or organic solvent containing the pollutant into the soil column from the bottom of the column upward against gravity using solution head or a peristaltic pump.
8. Collect the effluent from the soil column keeping accurate record of quantity discharge.
9. Analyze each one-half pore volume displacement for pollutant of concern using the AA spectrometric procedure recommended or other suitable analytical equipment.

#### Chemical and Physical Analyses.

Free iron oxides of the soils were determined by the method of Kilmer,<sup>13</sup> surface area by the method of Heilman, et al,<sup>14</sup> and manganese by modified procedure of Bernas.<sup>15</sup> For total analysis a sample size of 0.1g of finely ground soil, 1 ml of aqua regia and 6 ml of HF were used for digestion. Boric acid (2.0g) then was added and the sample diluted to a final volume of 50 ml.

The trace elements (As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn) and Al, Fe, and Mn of the enriched leachates (influent) and soil column effluents were measured by atomic absorption spectrophotometry using standard procedures except for As, Se, and Hg. Because of the relatively high concentrations of these elements, the more specialized techniques of analysis, such as cold vapor mercury analysis and hydride generation of As and Se were not required. Since these elements are subject to severe interference in atomic absorption analysis, chemical interferences were minimized by matrix adjustment. Lanthanum (1000 ppm) and K (100 ppm) were added to samples and standards alike to equalize the dissolution matrix for all samples. Non-atomic adsorption which was especially noticeable for Hg was measured with a H-continuum lamp (Varian Techntron), and subtracted from the sample reading.

Common ions (Ca, Mg, K, Na, Cl, NH<sub>4</sub>-N, P, and Si) were determined by the standard U.S. EPA recommended methods<sup>16</sup> and TOC by the conventional carbon analyzer method, using a Beckman 915A.

The pH values were measured using the glass electrode. Where pH, common ions, total dissolved solids were evaluated on water-saturated soils (soil-paste) and its extract, the method as recommended by the USDA<sup>2,11</sup> was used as was the total dissolved solids (TDS) and cation exchange capacity (CEC).<sup>2,11</sup>

Standard X-ray<sup>17</sup> and mechanical analysis procedures<sup>18</sup> were used to identify the <2 $\mu$ m clay minerals and the particle size distribution of the soils.

### RESULTS AND DISCUSSION

#### Biologically-bound Metals

Radioactive isotope techniques have been helpful in distinguishing between heavy and trace nutrient

elements originating from natural sources as just discussed above and waste discharge sources. Biological systems have great capacity to absorb metals including radioactive elements. Plants and soil microorganisms are no exceptions. But this is not the end of the radioisotope metals journey. During the cycling and recycling of metals from dead to live tissue and back again there is a break in the cycle where soluble organometal complexes are formed that can leak into the soil environment. The organometal complexes may be chelates or behave like chelates and move readily through soils.<sup>19, 20</sup>

The results of tagging biological materials with radionuclides, returning them to the soil and leaching similar to rainfall under aerobic conditions, demonstrated the susceptibility of microbial degradation substances, microbial cells and cell debris to migration not shown by the metals in inorganic form<sup>21, 22, 23, 24, 25, 26.</sup>

#### Metal Movement from Soil Itself

The purpose of the investigation involving only water and dilute acid was to evaluate the contribution of soils to metal elution under natural and acidic leaching conditions (acid rain) and to relate these findings to measurable natural soil characteristics as an extension of earlier research reported from our laboratories.<sup>2,19,20</sup>

Water is the primary vehicle in which constituents move through soil. The most commonly encountered aqueous systems, (a) pure rainwater, (b) dilute acid (acid rainwater, pH 3.0), (c) dilute acid with oxidizing/reducing potential (with AlCl<sub>3</sub> and FeCl<sub>2</sub>), and (d) point source solid waste leachates, all cause various levels of K, Na, Ca, Mg, Cl, NH<sub>4</sub>, P and Si to solubilize and move. Some heavy metals also moved through the soil but to a much lesser extent. Pure water (deionized) resulted in the least heavy metal migration and the acid 0.025M AlCl<sub>3</sub> + 0.025M FeCl<sub>2</sub> adjusted to pH 3.0 resulted in the greatest solubilization and movement, Table III. Municipal solid waste landfill leachate did not add significantly to migration of heavy metals over deionized water during the 28 soil-pore-volume displacements. The mobility of heavy metals as well as common soil cations moved several times greater in the presence of AlCl<sub>3</sub> + FeCl<sub>2</sub> at the same pH 3.0 as the dilute acid alone. The implication of these four aqueous systems on the quality of our groundwater and food chain goes far beyond these experiments can predict at this time. The order of total amounts of trace elements solubilized and eluted from the 12 soils by the 0.025M AlCl<sub>3</sub> + FeCl<sub>2</sub> solution is Mn > Co > Ni > Cu > Cr > Pb > Cd the same as reported earlier.<sup>20</sup>

#### Metal Movement via Chelates

Using a wider variety of soils than reported earlier<sup>25</sup>, the influence of chelating agents on the movement of <sup>89</sup>Sr-<sup>90</sup>Sr(90Y) through soils with leaching was investigated. In the extended research the commercial chelates formed radionuclide-complexes in the soil which accelerated the rate of movement and depth of distribution of <sup>89</sup>Sr-<sup>90</sup>Sr(90Y) in the columns of soil. The displacement of the <sup>89</sup>Sr-complex in Mohave s 1 subsoil was 5, 12, 39, 46, 48, 75 and 86 percent for no commercial chelate < HEEDTA < DCyTA < EDTA < EGTA < DTPA and < DTPA-TEA, respectively. The small amount of organic matter in the subsoils did not appear to effect radiostrontium movement.

Table III. Maximum metal concentration in the solution displacement from representative soils receiving d-water, dilute H<sub>2</sub>SO<sub>4</sub>, dilute acid plus 0.025M AlCl<sub>3</sub> + 0.025M FeCl<sub>2</sub> and MSW leachate.<sup>1</sup>

SOIL	Al	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
-----> ug/g <----- Deionized Water (pH 7.0)										
Davidson c	<.5	<.005	<.05	<.1	<.05	0.10	0.20	<.05	<.5	<.005
Chalmers si c 1	<.5	<.005	<.05	<.1	<.05	0.10	0.10	<.05	<.5	<.005
Mohave s 1	<.5	<.005	<.05	<.1	<.05	0.20	2.00	<0.5	<.5	<.005
MSW Landfill Leachate (pH 5.4)										
Davidson c	<.5	0.010	<.05	<.1	<.05	0.10	0.80	<.05	<.5	0.5
Chalmers si c 1	<.5	<.005	<.05	<.1	<.05	0.10	0.20	<.05	<.5	0.9
Mohave s 1	<.5	<.005	<.05	<.1	<.05	0.20	3.00	<.05	<.5	0.1
Dilute Acid (H <sub>2</sub> SO <sub>4</sub> at pH 3.0)										
Davidson c	8.0	0.007	<.05	<.1	22	0.38	0.46	<.05	<.5	0.14
Chalmers si c 1	4.0	0.120	<.05	<.1	0.11	0.44	0.25	0.15	<.5	0.25
Mohave s 1	<.5	<.005	<.05	<.1	0.33	1.20	1.80	<.05	<.5	0.06
Dilute Acid (pH 3.0) plus 0.025 M AlCl <sub>3</sub> +FeCl <sub>2</sub>										
Davidson c	860	94	11	2.8	0.9	1,080	950	0.7	<.5	0.6
Chalmers si c 1	530	0.1	3.8	0.1	0.3	1,900	365	6.0	0.3	0.9
Mohave s 1	610	0.04	2.2	<.1	<.05	1,550	225	1.3	0.7	0.2

<sup>1</sup> During 20 pore-volume displacements bdl in ug/ml are Cd = 0.005; Cr = 0.1; Co = 0.05; Cu = 0.05; Pb = 0.5; Ni = 0.05; Mn = 0.05; Zn = 0.005; Al = 0.5, and Fe = 0.1.

and depth of distribution of <sup>89</sup>Sr-<sup>90</sup>Sr(<sup>90</sup>Y) in the columns of soil. The displacement of the <sup>89</sup>Sr-complex in Mohave s 1 subsoil was 5, 12, 39, 46, 48, 75 and 86 percent for no commercial chelate <HEEDTA<DCyTA<EDTA<EGTA<DTPA and <DTPA-TEA, respectively. The small amount of organic matter in the subsoils did not appear to effect radiostrontium movement.

Acetic acid forms readily in municipal organic solid wastes, food processing wastes, animal manures and in many other organic residues (that are not highly toxic to soil microorganisms) when anaerobic conditions exist. Calcium acetate has been identified in soils receiving acetic acid<sup>19</sup>. Thus, one of our objectives was to compare the effect of soil surface treatment with Sr(Ac)<sub>2</sub> and Ca(Ac)<sub>2</sub>, followed by pulse-application of water, for moving <sup>89</sup>Sr-<sup>90</sup>Sr(<sup>90</sup>Y) and <sup>45</sup>Ca through various soils. The acetates, just as the chelates, substantially enhanced the mobility of the radioisotopes. The rate of movement through the different soils was inversely related to the clay and organic matter content as reflected by the cation exchange capacity. The Sr(Ac)<sub>2</sub> treatment resulted in a greater percentage movement of the contaminant <sup>89</sup>Sr, than Ca(Ac)<sub>2</sub>. Although there was no statistical significant difference between the effects of Ca(Ac)<sub>2</sub> and Sr(Ac)<sub>2</sub> on the rate <sup>45</sup>Ca-contaminant moved through the soil.

#### Metal Movement from Soil Microorganisms

The adsorbed and metabolized radioisotopes in the cells of soil microorganisms which upon decaying release particulates and presumably metallorganic chelates<sup>19, 24, 25, 26</sup> to the soil solution. Despite the extensiveness of this earlier research there remains a need to further evaluate and quantify movement of radio-activity through soils via organic

channels in view of recent problems of groundwater pollution. As a continuation of earlier research<sup>26</sup>, our efforts centered on the uptake, transformation and movement of radiostrontium (<sup>89</sup>Sr-<sup>90</sup>Sr(<sup>90</sup>Y)) through soils as related to the time allowed for decomposition of contaminated fungi and algae to occur. Data in Table IV reports the relative movement of <sup>89</sup>Sr-<sup>90</sup>Sr(<sup>90</sup>Y) from algal and fungal tissues through Mohave sandy loam as related to biodegradation of tissues with time. The sodium acetate-extractable <sup>89</sup>Sr-<sup>90</sup>Sr(<sup>90</sup>Y) moved more rapidly from the algal than fungal tissue of the organisms involved. The differences, however, were not apparent until after about 168 days of incubation. There also was a significant difference between the mobility of the radiostrontium in the applied inorganic and the biologically-bound forms. The organic source moved to greater depths in the soil than the inorganic source.

#### Metal Movement from Plant Materials

Relatively little attention has been directed toward the behavior of organic complexes of elements, as compared to inorganic, with respect to soil attenuation and transport. Phosphorus is a good example and fission products of uranium as represented by Sr, Cs are others. Yet, much of the small volume of soil-transport literature points to the possible greater mobility of organically-bound metals than inorganic ions.<sup>19,24,26,27</sup>

Data in Table V illustrate this point. Using the radioisotope techniques, elements well known to plant nutritionists - Ca, Fe, and P - and a biologically active fission element, Sr, were found to migrate more rapidly through soils when originating from organic residues than as simple soluble inorganic ions. Moreover, the effluents from soil columns

Table IV. Relative movement of radiostrontium contained in contaminated algal and fungal tissues through Mohave sandy loam as related to biodegradation of tissues in soil with time.

Material Applied	Pulsing Solution	Soil Column Depth	Sodium Acetate - extractable $^{89}\text{Sr}$ - $^{90}\text{Sr}$ ( $^{90}\gamma$ )		
			Leached 12 times at 2-day intervals	Leached 12 times at 1-week intervals	Leached 12 times at 2-week intervals
		cm	%	%	%
$^{89}\text{Sr}(\text{Cl})_2$	d-water	0-5	88.9 <sup>1</sup>	80.2	80.1
		5-10	8.3	14.0	12.7
		10-15	2.2	3.0	4.0
		15-20	0.5	2.8	3.2
$^{89}\text{Sr}(\text{Cl})_2$	HCHO-0.5%	0-5	96.2	85.6	80.3
		5-20	2.1	11.2	15.1
		10-15	0.9	3.0	3.0
		15-20	0.8	0.2	1.6
Algal material ( <i>Chlorococcum</i> Ap.)	d-water	0-5	96.4	81.5	50.1
		5-10	3.5	10.8	27.3
		10-15	0.1	5.2	12.3
		15-20	0.1	2.6	10.3
Algal material ( <i>Oscillatoria</i> <i>bijuga</i> )	HCHO-0.5%	0-5	92.4	80.1	55.6
		5-10	7.6	10.3	32.1
		10-15	0.1	7.3	9.2
		15-20	bd <sup>1</sup>	2.3	3.1
Fungal material ( <i>Rhizopus</i> <i>arrhizus</i> )	d-water	0-5	95.2	86.2	68.5
		5-10	3.1	5.7	20.2
		10-15	1.3	5.1	9.0
		15-20	0.4	3.0	2.3
Fungal material ( <i>Aspergillus</i> <i>niger</i> )	HCHO-0.5%	0-5	96.9	87.0	65.0
		5-10	1.7	12.8	22.7
		10-15	1.0	1.1	8.2
		15-20	0.4	0.1	4.1

<sup>1</sup>Data in this column derived from Fuller and L'Annunziata (1969); all other data unpublished. Water pulses of 250 ml H<sub>2</sub>O represent approx. normal field-holding-capacity at ~ 0.3 bar tension.

(20 cm deep) contained these four elements much more abundantly in organic forms and organic debris, such as fragmented microbial cells and tissues, than in inorganic solution. The similarity among four elements in the percentage movement of total added was unexpected during the first 84 days of incubation. Differences began to appear after 168 days of incubation. Also, the total amount of Ca that moved through the soil was much greater than the other elements even though the percentage of the total added that moved was less. Calcium and Sr moved more in the cationic than organic form. Iron from most residues appeared to be less mobile than P or Sr, despite the fact the amount of Fe in the original residues was less than Ca, Sr, and P. The data for Ca and P movement was similar to that of earlier research.<sup>19,24,27</sup> The data for total, organic, and inorganic P reveals that those treatments which result in an increase in the total P movement over the control do so by increasing the movement in the organic rather than inorganic form. Plant residues, however, result in all four elements moving through soil more rapidly than when they were applied as inorganic salts. The organic forms originate largely from microbial synthesis and degradation products of the organic materials added, as demonstrated by the increase in movement with length of time of incubation. The chemical separation between organic and inorganic Ca, Fe and Sr was not considered to be sufficiently quantitative to permit recording the data in Table V. Qualitatively, the bulk of

these elements appeared to move in the inorganic form, much of which was absorbed to colloidal size particulates, such as clay.

#### PREDICTION OF POLLUTANT MOVEMENT

The single goal in the disposal of waste is to insure the containment of potential environmental polluting constituents at the site. There are few guidelines and no standardized methods for estimating movement of pollutants through the soil. Our ability to provide managers of land disposal operations with even the crudest quantitative procedure has not emerged to date.

The soil-column technique, therefore, was developed to provide a more quantitative basis for estimating pollutant movement through soils. The data generated for the breakthrough curves can be used for this purpose in at least two ways: (a) directly for predictive purposes and (b) indirectly to develop a universal user-oriented predictive tool in the form of a simple expression readily solvable by simple mathematics.

#### Direct Application of Breakthrough Data

When the soils are known, and available, and the transporting fluid is known, a series of soil columns may be established and breakthrough curves plotted

Table V. Comparative movement of P, Ca, Sr, and Fe contained in inorganic salts and plant residues applied to Mohave s 1 and incubated for different lengths of time.

Material added	Amount added tons/acre	Cumulative element displaced after*					
		7 Days		84 Days		168 Days	
		Total	Organic	Total	Organic	Total	Org.
		----- % of total applied ----->					
Phosphorus - <sup>32</sup> P							
H <sub>3</sub> PO <sub>4</sub> + <sup>32</sup> P	P ⇄ of 10t barley residue	0.10	0.09	0.51	0.40	1.82	1.40
*Barley residue	10	1.12	0.92	3.62	2.51	5.47	4.52
*Wheat residue	10	1.13	0.87	5.37	5.50	6.36	5.31
*Bean residue	5	0.62	0.51	6.55	5.92	7.23	6.16
*Lettuce residue	5	1.31	1.09	8.83	8.-01	9.41	7.92
*Tomato residue	5	0.75	0.85	5.92	5.03	7.93	7.01
Calcium - <sup>45</sup> Ca							
<sup>45</sup> CaCl <sub>2</sub>	Ca ⇄ 10 t barley residue	0.09	nr	0.17	nr	0.16	nr
Barley	10	1.61	nr	2.31	nr	3.32	nr
Bean	5	2.83	nr	2.92	nr	3.21	nr
Lettuce	5	3.14	nr	3.65	nr	5.32	nr
Strontium - <sup>89</sup> Sr							
<sup>89</sup> SrCl <sub>2</sub>	Ca ⇄ 10 t barley residue	0.08	nr	0.12	nr	0.80	nr
Barley	10	1.38	nr	3.28	nr	7.22	nr
Bean	5	2.44	nr	4.63	nr	9.61	nr
Lettuce	5	1.42	nr	2.34	nr	9.58	nr
Iron - <sup>59</sup> Fe							
<sup>59</sup> FeCl <sub>3</sub>	Fe ⇄ 10 t barley residue	<0.05	nr	0.22	nr	1.35	nr
Barley	10	<0.05	nr	3.41	nr	4.22	nr
Bean	5	<0.05	nr	5.00	nr	5.36	nr
Lettuce	5	<0.05	nr	6.93	nr	5.59	nr

<sup>1</sup> Unpublished data from Fuller (1966). U. S. Atomic Energy Commission Research Report 1. Contract No. AT(11-1)947. Oakridge Nat'l Lab., Oakridge, TN

\* A total of 15 aqueous pore volume displacements after incubation of 7, 84, and 168 days at 30C. nr means determined but not reported.

from C/C<sub>0</sub> data and pore volume displacements. The plotted migration rates then may be applied directly for prediction of rates of pollutant movement. By knowing the depth of soil to the watertable, rainfall, and water infiltration rate, translocation of pollutants may be estimated directly from the breakthrough curves at the concentration sought for containment.

Another means of predicting pollutant migration rate is to rank the pollutants according to soil interactions. Although this method is more quantitative than the conceptual "model" of personal judgment, it too is a highly qualitative procedure though actual research data are used. Heavy metal-soil interactions are ranked using prominent toxic waste elements, As, Be, Cd, Cr, Cu, Hg, Ni, Pb, Se, V, and Zn, with soils representing major soil orders of the world. Cations and anions are ranked separately because of differences in migration behavior in different soils. The soil environment may be strictly anaerobic and the leachate flow saturated, like that of conditions under a landfill operation or set up aerobically for surface pollutants. Predicted relationships for similar soils and any situation can be found by using published figures and typical attenuation curves as presented for each soil and a given element.3,4,28,29

Soil-column data can provide yet another means of predicting pollutant retention by soils. An example of this is illustrated by heavy metal attenuation to develop breakthrough curves (e.g. C/C<sub>0</sub> at increasing pore volume displacements) for different soils with a single metal, e.g. Ni x 4 soils, Fig. 2 and different metals with a single soil, e.g. Ava si c l x Ni, Be, Se (Fig. 3). These curves are then used to construct a set of typical breakthrough curves, Fig. 4. The different types of breakthrough curves for each soil and a given element are given an identification letter, A to E, (Fig. 4). The values of C/C<sub>0</sub> obtained from any one soil column correspond to one of the generalized curves in Fig. 4. Weakly retained elements are represented by curves A and B. Complete breakthrough where C/C<sub>0</sub> = 1 occurs rapidly. The rise in pollutant concentration in the effluent of A begins earlier than B and breaks through earlier. In turn, B is more rapid than C, and so on. Curves C and D represent more of a steady-state condition. Curve E is an example of an extreme situation of soil (clay) that did not permit the pollutant (metal) to reach C/C<sub>0</sub> = 0.1 in the number of pore volume displacements taken place.

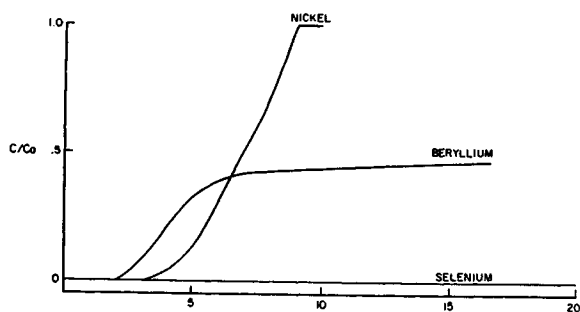


Fig. 2. Relative Migration of Nickel, Beryllium, and Selenium Through AVA Silty Clay.

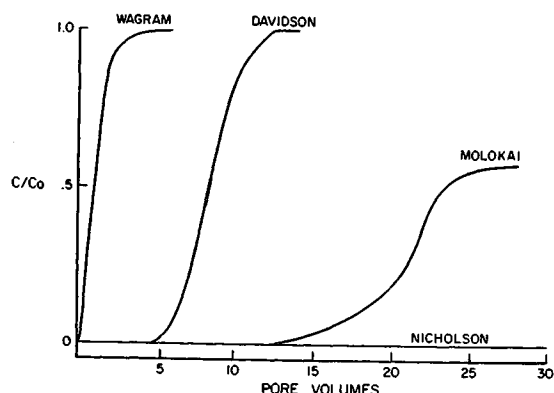


Fig. 3. Relative Migration of Nickel Through 4 Diverse Soils.

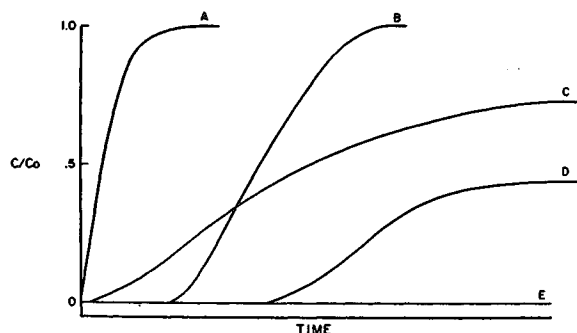


Fig. 4. Types of Breakthrough Curves Generated in This Study.

To better understand this, elution curves obtained from each soil column are coded in Table VI. Sandy soils (Wagram, Kalkaska, Anthony) are identified most often with sharp breakthroughs. Clay soils (Nicholson, Molokai) demonstrate slow leakage and high retention. Mohave (Ca) cl is an exception for Cr (VI) but it contains free CaCO<sub>3</sub> (lime) and has a relatively high pH of 7.8, both of which decrease migration. Again, if others characterize a soil or soil-like material at some other location or depth, for example, they can compare the characteristics of the most similar soil material used in this study and estimate the attenuation characteristics of their material for disposals.

Table VI. Designation Showing Type of Curve Generated From Each Column.

Soil	As	Be	Cd	Cr	Cu	Hg	Ni	Pb	Se	V	Zn
Davidson c	C	D	C	E	E	C	B	E	E	E	D
Molokai c	E	E	E	E	E	D	D	E	E	E	E
Nicholson si c	E	E	E	D	E	B-C	E	E	E	E	D
Fanno c	C	E	E	C	E	C	E	E	E	D	C
Mohave <sub>Ca</sub> c	E	E	E	A	E	D	E	E	C	E	E
Chalmers si c l	C	D	D	C	E	D	D-E	E	E	C	D
Ava Si c l	C	D	A	C	D	B-C	A	D	E	B	A-B
Anthony s l	A	D	A	A	D	A	A	D	C	A	B
Mohave s l	B	D	D	A	E	R	C	E	C	B	B
Kalkaska s l	C	D	C	C	E	C	B	E	C	D	B
Wagram s l	A	C	A	A	E	A	A	B	D	A	A

### Development of Models for Prediction

If a universal mathematical expression is to be developed for predicting pollutant migration, one must involve a concept of a model. "A model provides a simplified analogy for a natural phenomenon."<sup>30</sup> For our purpose, a model can be defined as a simplified representation of an actual waste disposal system. Briefly, three kinds of models relate to prediction of pollutant movement: (a) a conceptual model, which is the oldest and is strictly based on personal judgment, (b) a physical model, which is a scaled-down version of the actual system, and (c) a mathematical model.

Mathematical models offer a promising method of assessing waste disposal system.<sup>31</sup> The mathematical model of a system is a logical model which is usually developed by considering the physical-chemical characteristics of the whole system. Through simulation, the model can describe the system in its present state or be used to evaluate its future behavior or status. Simulation can be defined as a numerical technique for conducting experiments on a digital computer using mathematical and logical models that describe the biological, chemical, and/or physical characteristics of the system over a period of time.<sup>30</sup> The availability of high-speed computers and the development of scientific and simulation programming languages have made mathematical modeling more attractive and popular than ever.

### Universal Equations for Prediction of Pollutant Movement

The development of mathematical models, Lapidus and Amundson,<sup>10</sup> and Error Function, are being published in detail (Amoozegar, Fuller, and Warrick, in press)<sup>31,32</sup> and will appear in a U. S. Environmental Protection Agency report (Fuller and Amoozegar, in press), therefore, only an example is given here. The velocity of relative concentration  $C/C_0 = 0.5$  for Cd movement through the soil Chalmers si c l, with the characteristics of;

clay = 31.0 %  
silt = 52.0 %  
FeO = 3.1%

and MSW leachate with;

total organic carbon (TOC) = 0.11%, and  
total soluble salts (SALTS) = 0.15%

for pore water velocity,  $v = 1.3$  cm/day is calculated. The velocity equation for the Cd relative concentration of 0.5 obtained from the Lapidus and Amundson<sup>10</sup> model is:



$$V.5 = v [29.9085/\text{CLAY} + (0.10846 \times 10^{-2}) \times (\text{CLAY} + \text{SILT})^2 + 8.5322/\text{FeO} + (0.10148 \times 10^{-1}) \times \text{FeO}^2 + 84.1320 \times \text{SALTS} - 205.1267 \times \text{SALTS}^2 + 0.4422 \times \text{TOC} - 12.6058]/25$$

By substituting the soil and leachate properties into the equation the solution is:

$$V.5 = 1.3 [29.91/31.0 + .00108 (31. + 52)^2 + 8.53/3.1 + .01015 \times 3.1^2 + 84.13 \times .15 - 205.1 \times .15^2 + 0.442 \times .11 - 12.606]/25 = 0.35 \text{ cm/day, the migration rate of Cd.}$$

#### LIMITATIONS AND ADVANTAGES OF THE SOIL-COLUMN METHOD

The column method, an "input/output" system, is represented by soil which is (a) disturbed from its natural habitat, (b) mixed until homogeneous, (c) packed to densities equivalent to or greater than those found under its natural conditions, and (d) percolated with waste streams containing soluble potential pollutants. No attempt is made to identify the numerous chemical, physical, and biological reactions taking place between the three major components of the specific environment (porous medium, transport vehicle, and pollutant(s)). Because the soil is disturbed, certain numerous gross natural variations of the soil habitat (such as cracks, clay pans, texture stratifications, excessively compacted layers, root and rodent channels, pipings, etc.) are not known and therefore are not included in the interpretation of the column results. Some natural heterogeneities in the physical character of the soil area, such as those listed above, can exert a dominant influence on pollutant movement making predictions from the soil column method, or any other soil method which involves disturbed soil samples, unrealistic. As many of the natural soil and land characteristics as possible should be identified and evaluated independently from the soil-column test. In many instances field conditions are so variable there is no realistic way to assess their impact on attenuation of pollutants.

Homogeneity can be achieved by mixing the soil at the disposal site or by removing the soil from the site, mixing it, replacing it, and compacting it into a barrier. Where soils are highly heterogeneous and cannot be mixed to homogeneity, homogeneous soil should be found, tested by the soil-column method, and brought onto the site. Briefly, the soil-column limitations and advantages are:

#### Limitations

- ° The method evaluates only the soils capacity to attenuate or retain pollutants and may not reflect actual field conditions where the many natural soil variations are not or cannot be identified. In fact, it should be kept in mind that the method was not designed to characterize the natural landscape variabilities. This must be done independently.
- ° The actual transport system (e.g. leachate, solvent, waste stream) should be identified and used in the soil column to obtain the most quantitative evaluation of pollutant movement. Sometimes this is not possible prior to first disposal.

- ° The method over predicts, i.e. it predicts a greater rate of movement than occurs under natural conditions. Many natural unknown phenomena such as dehydration, aging, co-precipitation reactions, and biological fixation occur at the disposal site that cannot be fully identified or evaluated.

#### Advantages

- ° This method is less complicated than many other methods.
- ° It does not require infinite information of attenuation mechanisms which need many years to discover and evaluate. It is a simple input/output system.
- ° It is responsive to changes in the fluid concentrations as the fluid undergoes alteration during percolation through the soil. As new products are formed and reformed during percolation of the waste stream through the column, a great number of reactions take place chemically, physically, and biologically that are only characteristic of this type of transport through soil as both soil and waste stream undergo changes resulting from interactions of contact. Unlike batch methods, therefore, the original transport fluid does not contact the whole soil except that at the column surface, just as under natural field conditions.
- ° Soil structure, pore space distribution, the tortuous capillaries, and diffusion phenomena all become a part of the column method that gives the technique a more field-realistic representation than a batch-type method.
- ° Compared with field studies that can be confounded by a great number of uncontrollable variables the method evaluates the soil alone free of unmeasurable natural field anomalies that shift and change from location to location, often within short distances.
- ° The length of the soil column is such that the data generated can be projected while approaching a steady state; therefore, predictions can be applied to any depth of soil or distance or time of travel of the pollutant.
- ° Actual soils from the proposed or selected site are used and if possible, the actual leachate or waste stream is involved.
- ° The soil-column method is ideally adapted for disposal site soil liner evaluation.
- ° Several different pollutant attenuations such as several metals (Cd, Zn, Ni) can be evaluated at one time in a single transport system.
- ° The method is easily adapted to mathematical modeling for the ready establishment of universal prediction equations simplified enough for field use with a minimum of mathematical computation.

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