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Soil Clean-Up by Surfactant Washing. I. Laboratory Results and Mathematical Modeling

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Soil Clean-Up by Surfactant Washing. I. Laboratory Results and Mathematical Modeling

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Abstract

The removal of weathered-in PCBs from clayey soil by surfactant washing is demonstrated at bench scale. Spent surfactant solution was treated for recycle at bench scale by countercurrent liquid–liquid extraction for the removal of nonvolatile contaminants, and by thin film aeration in packed columns for removal of volatile organics. A correlation of micelle/water partition coefficients with octanol/water partition coefficients reported earlier by Valsaraj et al. is extended to several additional compounds. Mathematical models for batch–batch, batch–continuous flow, and countercurrent flow surfactant soil washing are described, and the effects of the model parameters are discussed.

I. INTRODUCTION

The costs of disposing of soils contaminated with hazardous wastes are now from \$600 to 1000 per cubic yard for incineration, and up to \$300 per cubic yard for disposal at an approved hazardous waste landfill. Wastes, including soils containing solvents, chlorinated dibenzofurans and dioxins, and more than 1000 mg/kg halogenated organics, are prohibited from land disposal. With more than 1200 sites on the National Priority (Superfund) List, it is apparent that improved technologies for the treatment of contaminated soils could result in massive savings to United States taxpayers and industries. Alternative methods of treating wastes which are banned from land disposal are badly needed. These should result in small volumes of concentrated wastes suitable for recycle and reuse or for incineration.

The removal of certain types of organic compounds from contaminated soils is handicapped by the very low solubilities of these compounds in water. These hydrophobic compounds include many common solvents (the chlorinated ethylenes and ethanes, carbon tetrachloride and chloroform, benzene, toluene, ethylbenzene, the xylenes, and the aliphatic hydrocarbons). They also include PCBs, polynuclear aromatic hydrocarbons, chlorinated pesticides, etc. The water solubilities of all of these compounds are greatly enhanced by micellar solubilization if the aqueous phase contains a surfactant at a concentration above its critical micelle concentration (cmc). The mechanism of the solubility enhancement is solution of the hydrophobic organic in the hydrocarbon phase which constitutes the interiors of the surfactant micelles. The effective solubilities of hydrophobic organics can be increased as much as a thousandfold by this process. Two early but still very useful references on solubilization are McBain and Hutchinson's book (*1*) and a review article by Klevins (*2*). The thermodynamics of solubilization (or mixed micelle formation) has been dicussed by Hall and Pethica (*3*) and Mukerjee (*4*). Vold and Vold (*5*) reviewed the theories of micelle formation, which provide the foundation on which any approach to solubilization must rest.

Early work on the use of surfactant solubilization for the decontamination of soils was carried out by Scholz and Milanowski (*6*), Ellis and his coworkers (*7, 8*), the Texas Research Institute (*9*), and Nash and associates (*10, 11*). Our work has dealt with *in-situ* surfactant flushing of contaminated soils by injection and recovery wells; much of it is relevant to aboveground soil washing with surfactant solutions. This includes mathematical modeling of *in-situ* surfactant flushing operations (*12*), development of a model for micellar solubilization (*13*), and laboratory-scale studies of micellar solubilization, surfactant flushing of contaminated soils in columns, and surfactant reclamation for recycle (*14, 15*).

This paper is organized as follows. After a discussion of analytical procedures, data are presented on the solubilization of PCBs adsorbed on clayey soils. This is followed by results on the removal of nonvolatile and volatile contaminants from surfactant solutions so that the surfactant can be recycled and the toxics concentrated into the smallest volume practicable. The next section deals with the correlation of octanol/water partition coefficients for several chemicals with their SDS/water partition coefficients. Then several mathematical models for soil surfactant washing are discussed. These include an equilibrium model for batch process surfactant soil washing, a diffusion-limited model for batch process surfactant soil washing, a diffusion-limited model for batch column operation with continuous-flow surfactant, and a diffusion-limited model for countercurrent surfactant soil washing. The last section summarizes the results and conclusions of the work.

II. EXPERIMENTAL WORK

Analyses

The surfactant used throughout this work was sodium dodecylsulfate (SDS), 99+% pure, from Fluka. Analyses of SDS solutions for toluene, xylene, and 1,2-dichlorobenzene were done by UV spectrophotometry. A Varian Cary Model 2300 recording spectrophotometer was used, and spectra were taken between 300 and 220 nm; samples which were too concentrated were volumetrically diluted with SDS solution of the same concentration as the sample, and SDS solution was used in the comparison cell of the double beam instrument. Calibration curves were prepared by using solutions containing known concentrations of the hydrophobic organic dissolved in 50 m*M* SDS. UV spectrophotometry was also used for analyzing PCBs in oil.

Other compounds (trichloroethylene; dieldrin; heptachlor; PCBs in soil, water, and surfactant solution) were determined by gas chromatography using EPA's Method 8080 or (for trichloroethylene) Method 8010. Analysis of the surfactant solutions required preliminary treatment of the samples. To a 150-mL sample of the surfactant solution was added 150 mL pesticide grade hexane, a stirring bar was added, and the beaker was covered tightly with aluminum foil. The beaker was put on a magnetic stirrer and the stirrer speed was adjusted so that a small vortex was visible at the hexane–water interface; the vortex did not pull any hexane droplets down into the water layer. This mixing was continued for 24 h. Then portions of the hexane layer were withdrawn for gas chromatographic analysis. This rather time-consuming procedure is necessary to avoid the formation of extremely persistent water–hexane emulsions. Extractions of the compounds of interest were quantitative within the limits of experimental error.

Solubilization of PCBs

Soil containing aged PCBs (Aroclor 1260) and of relatively high clay content was available from a hazardous waste site. It was felt that this material would provide a more stringent test of surfactant soil washing than soils spiked in the laboratory, inasmuch as the PCBs have had ample opportunity to weather in.

The contaminated soil was thoroughly mixed, after which three samples were taken for determination of PCBs. The remaining soil was divided into four 100-g portions and placed in amber 1-L glass jars. 800 mL of 50 m*M* SDS solution was added to three of the jars, and deionized water was added to the fourth. (The cmc of SDS at room temperature is 8 m*M*.) The contents of the jars were then mixed with magnetic stirrers for 24 h at room temperature. The suspensions were allowed to settle for 24 h, and the surfactant solutions were decanted and filtered through a 0.45 μm filter. The filtered SDS solutions were then analyzed for PCBs. Three jars were refilled with 800 mL of fresh SDS solution, the fourth was refilled with 800 mL deionized water, the mixing and settling processes were repeated, and samples were taken for analysis. In the third cycle of washing, the mixing was carried out for 5 days. In the fourth, mixing was carried out for 7 days.

The results were as follows. The concentrations of Aroclor 1260 in the three samples analyzed initially were 1260, 1150, and 1050 mg/kg, averaging 1150 mg/kg. The results of the batch soil washing experiments are given in Table 1.

The batch washing experiments yielded an average of 99.7% removal of the PCBs in the 2-week period, with residuals well below the 50 mg/kg level which is the current maximum concentration for which land disposal in a "non-PCB" landfill is permitted.

Surfactant Recovery Studies

For soil surfactant washing and *in-situ* surfactant flushing to be economical, a treatment method for the contaminant-laden surfactant solution which permits its reuse is necessary. Also, concentration of the contaminant(s) in a small volume of highly concentrated material would facilitate their recycling, if possible, or their destruction by incineration or other methods.

TABLE 1

Results of Batch Soil Washing for the Removal of Aroclor 1260 with 50 m*M* SDS[a]

Sample	1	2	3	4 (deionized water)
Solution after 7 days (3rd extraction)	16,600 μg/L	8,520	14,600	ND
Solution after 14 days (4th extraction)	1,630	3,420	431	ND
Residual Aroclor 1260 in the washed soil, mg/kg	4.93	3.11	2.26	1,531

[a] ND = not detected at a detection limit of 5 μg/L.

Nonvolatile Contaminants

Countercurrent extraction with hexane, modified to prevent emulsion formation, was used to remove PCBs and dieldrin from 50 m*M* SDS solutions. Underwood's column, described previously (*14*), was used; a diagram of the apparatus is shown in Fig. 1. The column is 90 cm long by 4 cm inside diameter. A plastic scouring pad was placed at the interface between the surfactant solution and the overlaying hexane layer to facilitate hexane droplet coalescence. A dispersion head at the bottom of the column produced hexane droplets about 0.5 cm in diameter. A Masterflex pump was used to circulate the hexane up through the column, and the hexane was replaced about every 30 min. A second Masterflex pump introduced

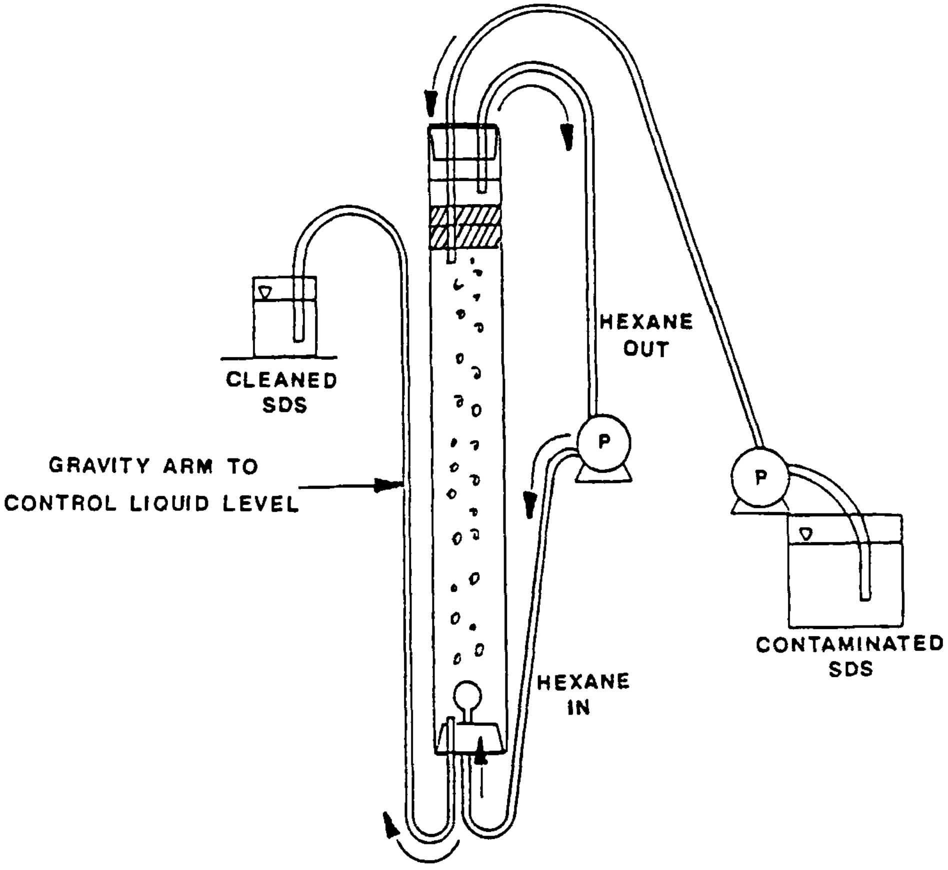


FIG. 1. Countercurrent extraction apparatus for removal of nonvolatile organics from surfactant solution.

TABLE 2
Surfactant Reclamation by Countercurrent Extraction with Hexane

Compound	Initial concentration[a]	Final concentration	Percent removal	Treatment time (h)
Dieldrin	87 mg/L	2.4 mg/L	97	2.0
PCBs (in oil)	Saturated[b]	—	82[c]	1.5

[a] In 50 mM SDS solution.

[b] Oil sample contained 41.8% by weight Aroclor 1260.

[c] Based upon linear response calibration curve of spectrophotometer.

the contaminated SDS solution at the top of the column. SDS solution samples were taken from the gravity discharge for analysis for the contaminant. PCB analysis of the aqueous phase was done by UV absorption (230–300 nm, 1 cm pathlength); dieldrin analysis was done by gas chromatography with an electron capture detector. The hexane flow rate was 90 mL/min, and the surfactant solution flow rate was 10 mL/min.

The results of the countercurrent extraction experiments for surfactant recovery are given in Table 2. Figure 2 plots the dieldrin concentration in

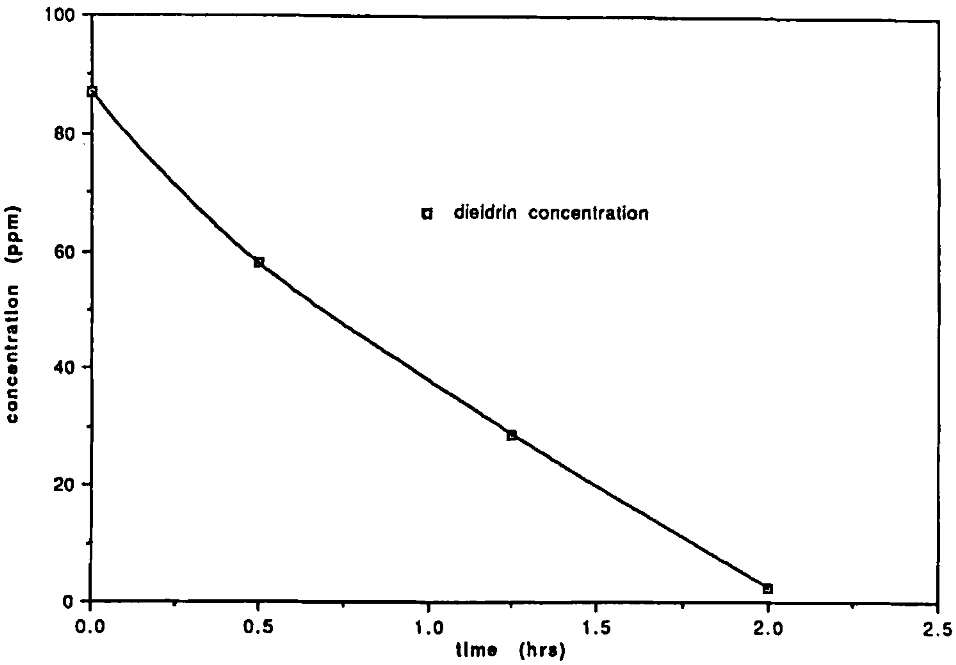


FIG. 2. Dieldrin concentration in effluent SDS solution versus time in the continuous flow countercurrent extraction unit.

the surfactant solution versus the time during the course of the countercurrent extraction. Figure 3 shows a similar plot for the removal of PCBs from the surfactant solution by countercurrent extraction. These results are in agreement with Underwood's conclusion (*14*) that countercurrent solvent extraction is an effective method for the removal of nonvolatile hydrophobics from SDS solutions. Gannon has shown that the resulting surfactant solutions are as effective as fresh surfactant in solubilizing hydrophobic contaminants (*14*).

Volatile Contaminants

Two types of experiments were done to investigate the removal of volatile contaminants (trichloroethylene, toluene, xylene, 1,2-dichlorobenzene) from SDS solutions. In the first, a thin film of contaminant-laden surfactant was allowed to flow over an inclined glass plate in an exhaust hood. A pump recirculated the solution over the glass plate from a collection sump; the apparatus is sketched in Fig. 4. About 3 L of 50 m*M* SDS solution spiked with a volatile organic compound (VOC: toluene, xylene, or trichloroethylene) was placed in the glass trough C (35 × 23 cm) of the

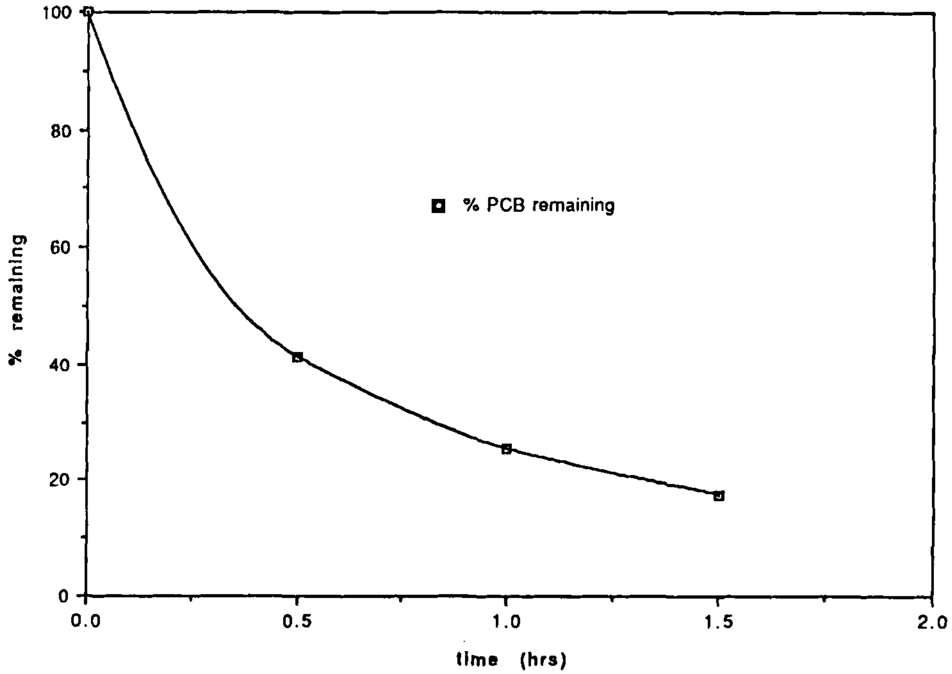
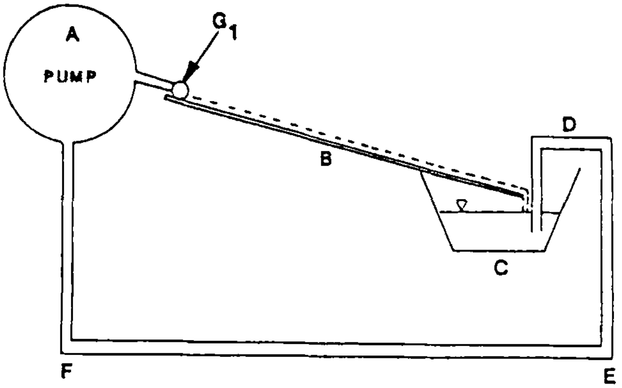
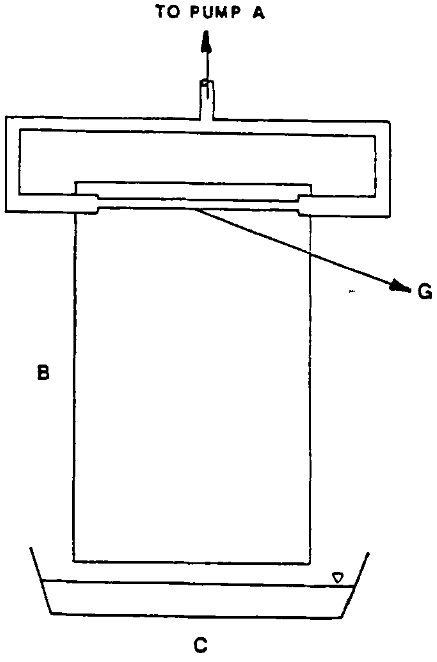


FIG. 3. Percent PCB remaining in effluent SDS solution versus time in the continuous flow countercurrent extraction unit.



ELEVATION



PLAN VIEW

FIG. 4. Flat plate apparatus for removal of volatile organics from surfactant solution by thin film aeration.

apparatus. The pump and Teflon tube DEF carried the surfactant solution to both ends of the copper tube G (7 mm i.d.) mounted at the elevated end of the sloping glass plate B (60 × 30 cm). Small holes were drilled into the copper tube at intervals of 1.5 cm except for the last 5 cm at each end. The pump was operated at a speed such that the surfactant was discharged through the holes in the copper tube and evenly spread in a thin film on the glass plate. The pump continuously recirculated the VOC-laden surfactant solution at a rate of 30 mL/min. Samples were collected from the glass trough at 30 min intervals to follow the progress of the VOC removal. Toluene and xylene were determined by UV spectrophotometry; trichloroethylene, by gas chromatography with a Hall detector.

The inclined plate apparatus did not lend itself well to scale-up, so additional aeration experiments were carried out with a countercurrent flow column packed with 1/2 in. ceramic Raschig rings. This apparatus is diagrammed in Fig. 5. The column is 76 cm long by 7.5 cm in diameter. A stainless steel mesh (B) with 3 to 4 mm diameter holes drilled in it was placed in the bottom of the column to support the Raschig rings. The packed column had a retention time for the downflowing liquid of about 4 min at the flow rates used in the study. Air entered the column at C through a flowmeter, and VOC-laden surfactant solution trickled down from the upper end of the column, delivered at the desired flow rate by a pump through a glass pipette nozzle at D. A wad of glass wool at C below the pipette helped to spread the surfactant more evenly over the column packing. Samples of the surfactant solution effluent were collected from the discharge port at the bottom of the column for determination of VOC. The level of the liquid at the bottom of the column was controlled by raising or lowering the tube E, which was open to the atmosphere. Air exhausted from the column at F was discharged into a fume hood.

A second column, quite similar to that described above, was constructed. It was 90 cm long and was packed with 1/4 in. Raschig rings. Aeration experiments were carried out with this column, and with the two columns used in series, with the effluent liquid from the first directed to the influent port of the second; see Fig. 6.

The results of the thin-film aeration experiments for the removal of VOCs from 50 m*M* SDS solutions are summarized in Table 3. The progress of the removals of toluene, trichloroethylene, and *o*-xylene are shown in Figs. 7, 8, and 9, respectively.

Four compounds, the least volatile of which was 1,2-dichlorobenzene (vapor pressure 1.2 torr at 20°C), were air stripped from 50 m*M* SDS in columns packed with Raschig rings. Residence times in the columns were approximately 4 min, which was sufficient to remove 98% of the more

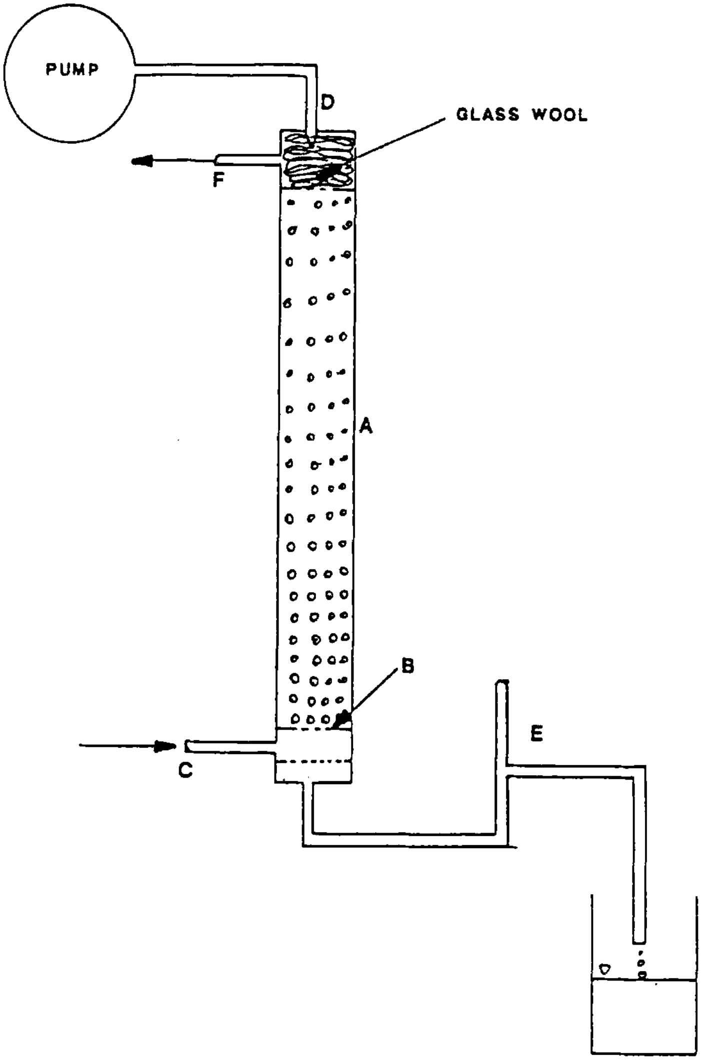


FIG. 5. Packed column for air stripping of volatile organics from surfactant solution.

volatile compounds, while the less volatile dichlorobenzene required a longer stripping time. This was achieved by using the two columns in series, as described above. The results are summarized in Table 4.

These preliminary results indicate the feasibility of reclaiming VOC-laden surfactant solution for reuse by packed column aeration.

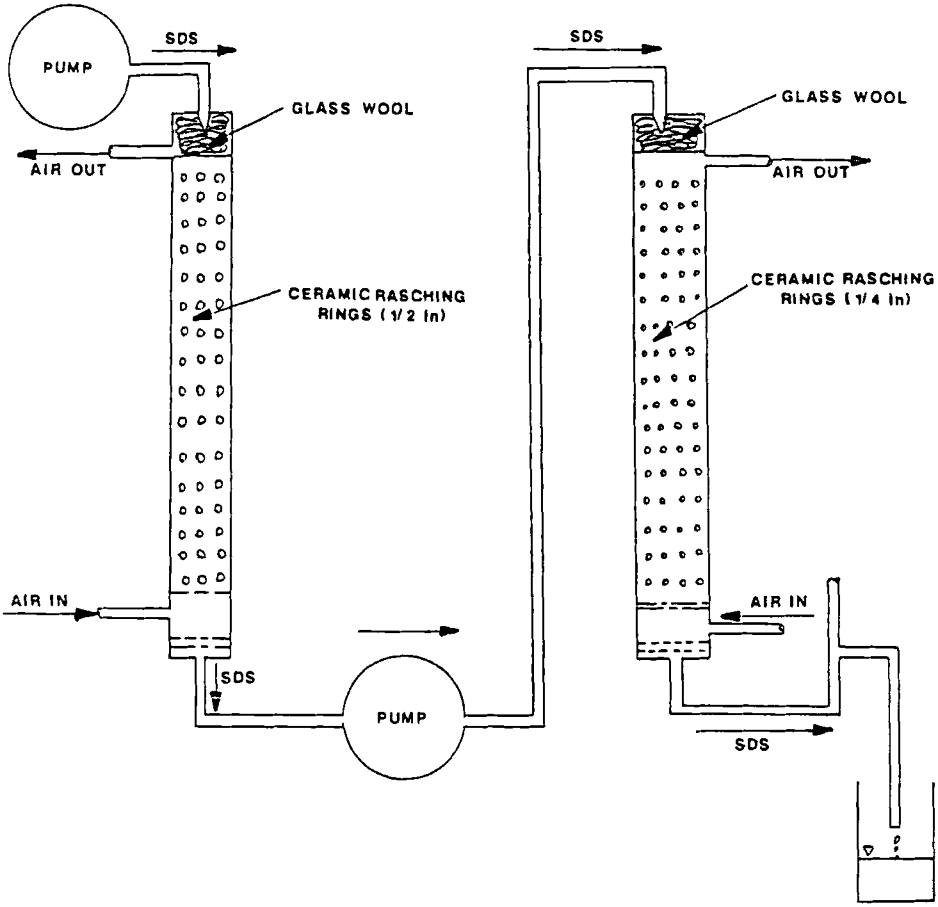


FIG. 6. Series operation of packed columns for air stripping of volatile organics from surfactant solutions.

TABLE 3
VOC Removal by Thin Film Aeration, Flat Plate Configuration

Compound	Initial concentration[a] (mg/L)	Final concentration (mg/L)	Percent removal	Treatment time (h)
o-Xylene	50	0.7	99	3.0
Toluene	500	10.8	98	1.5
Trichloroethylene	500	5.8	99	2.5

[a] In 50 m*M* SDS solution.

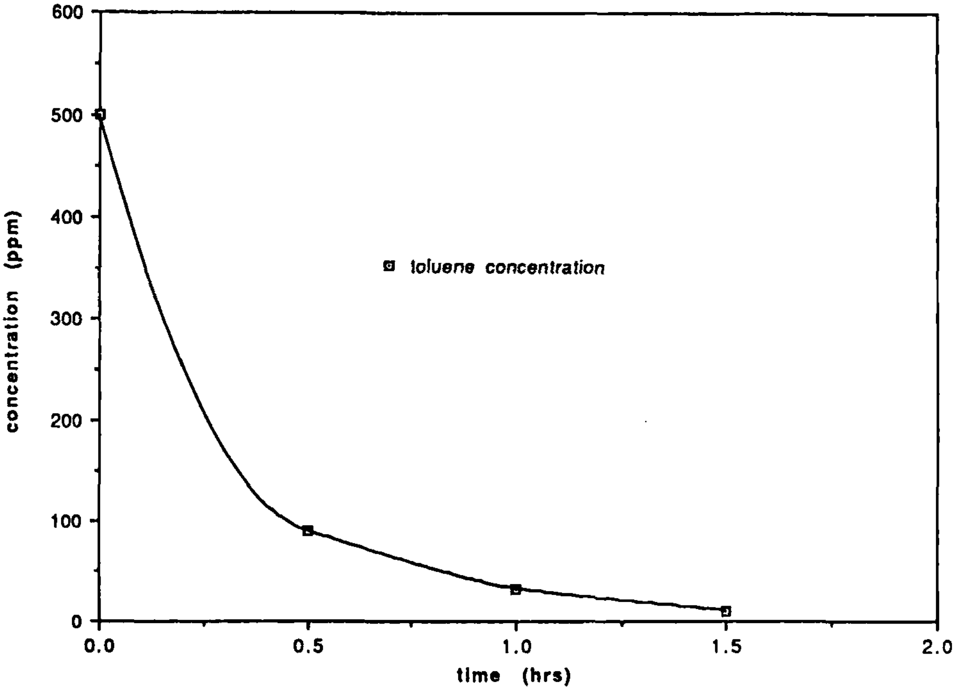


FIG. 7. Toluene concentration in SDS solution versus time in the flat-plate thin-film aeration unit.

Correlation of Partition Coefficients

Earlier work by Valsaraj et al. (*16*) and Gannon et al. (*14*) indicated that there may be a useful correlation between octanol/water partition coefficients, K_{ow}, and the micellar phase/water partition coefficients, K_{sw}, which arise in surfactant flushing and surfactant washing. Since a very large number of octanol/water partition coefficients are available in the literature (*17*, *18*), such a correlation would permit the easy estimation of micellar phase/water partition coefficients, of which relatively few have been determined.

The micellar phase/water partition coefficients for dieldrin and heptachlor were determined as follows. Surfactant solutions (50 m*M* SDS) and deionized water were each saturated with excess amounts of dieldrin or heptachlor. These solutions were stirred for 24 h to allow equilibration, settled for 24 h, filtered through 0.45 μm membrane filters, and analyzed by gas chromatography (electron capture detector). The logs of the par-

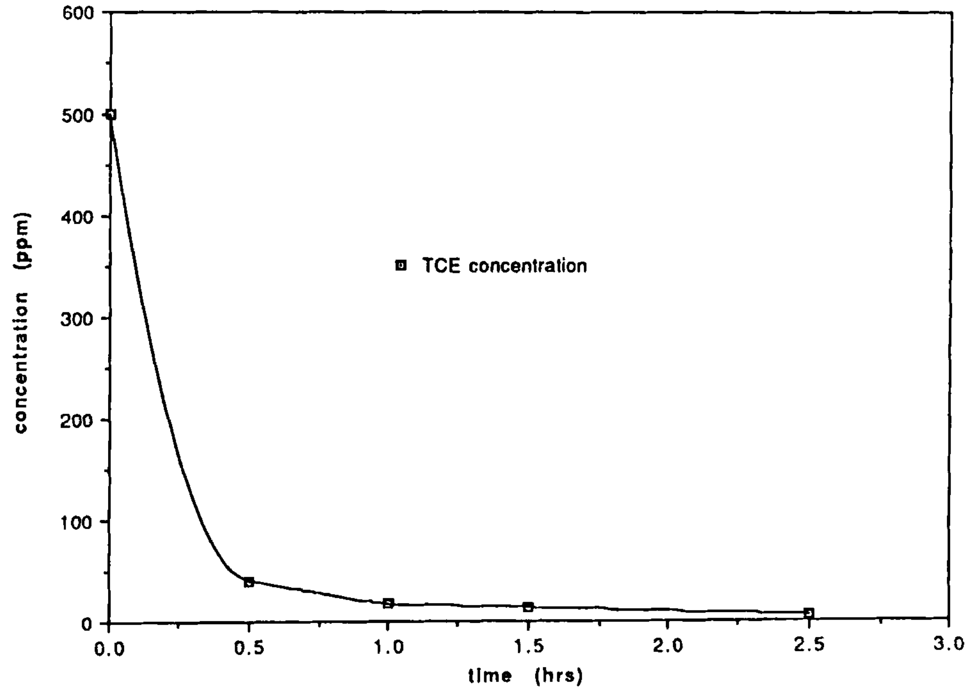


FIG. 8. Trichloroethylene concentration in SDS solution versus time in the flat-plate thin-film aeration unit.

tition coefficients obtained for these two compounds were 4.94 (dieldrin) and 5.30 (heptachlor).

The octanol/water partition coefficients, K_{ow}, and the SDS micellar/water partition coefficient, K_{sw}, were plotted against each other on a logarithmic scale for the two pesticides (dieldrin and heptachlor), and for six compounds studied previously. SDS micellar/water partition coefficients for methylene chloride, chloroform, and carbon tetrachloride were determined by Valsaraj et al. (*16*); those for 1,4-dichlorobenzene, naphthalene, and biphenyl were determined by Gannon et al. (*14*). The plot is shown in Fig. 10. The correlation is satisfactory over a quite wide range; the correlation coefficient is 0.981. A least-squares fit of the eight points gives the equation

$$\log_{10} K_{sw} = 1.12 \log_{10} K_{ow} - 0.686$$

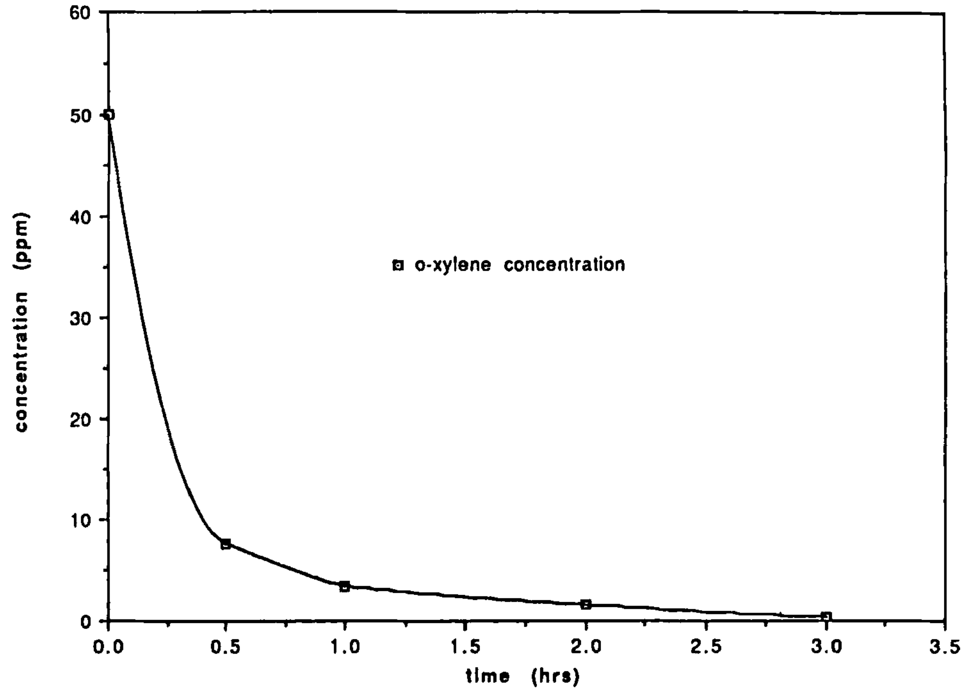


FIG. 9. *o*-Xylene concentration in SDS solution versus time in the flat-plate thin-film aeration unit.

as a means for estimating micellar/water partition coefficients from octanol/water partition coefficients.

III. MATHEMATICAL MODELING

In the following sections, mathematical models for the removal of hydrophobic contaminants from soils by surfactant washing are derived and their behaviors are examined. These include models for batch soil–batch surfactant operation, batch soil–continuous flow surfactant operation, and countercurrent continuous flow soil–continuous flow surfactant operation. Diffusion controlled mass transfer from the interiors of lumps of soil is handled by a lumped parameter method.

Our earlier modeling work has been focused on *in-situ* surfactant flushing of contaminated soil by injection and recovery wells; much of this is directly relevant to above-ground soil washing with surfactant solutions. The site of interest may be such as to make *in-situ* treatment infeasible; the geology of the site may be such that control of the movement of the surfactant

TABLE 4
Results of Thin Film Aeration in Packed Columns

Compound	Initial concentration (mg/L)	Final concentration (mg/L)	Percent removal	Liquid flow rate (mL/min)	Air flow rate (mL/min)	Treatment time (min)
o-Xylene	50	0.6	99	30	500	4
Toluene	500	11	98	28	500	4
Trichloroethylene	30,000	4,100	86	26	500	4
1,2-Dichlorobenzene	500	95	81	11	1,500	8

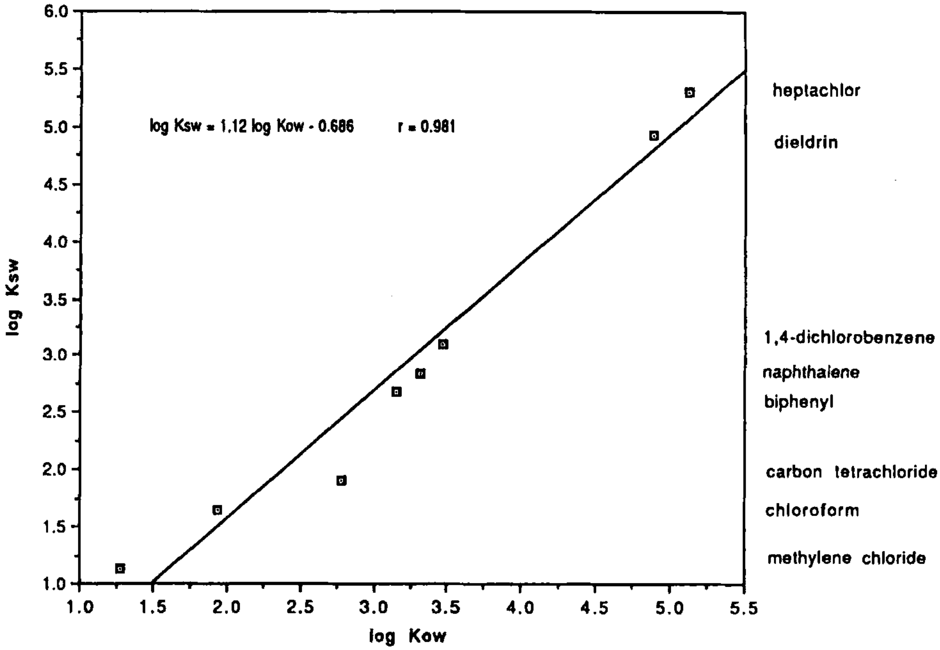


FIG. 10. Correlation of octanol/water partition coefficient (K_{ow}) with SDS surfactant/water partition coefficient (K_{sw}).

solution would be difficult and complete recovery of the contaminant-laden surfactant solution would be impossible to guarantee. Above-ground surfactant washing of excavated soil may then be proposed as a means of on-site treatment of the contaminated soil. Our previously developed mathematical model for soil surfactant flushing in lab columns (*12*) can be applied without change to the continuous-flow surfactant washing of soil in large containers in an upflow or a downflow mode. We here present models for describing soil surfactant washing in the batch mode. The first model makes the assumption that equilibrium with respect to contaminant transport is achieved between the contaminated soil and the surfactant solution contacting it. The second model, derived from the first, assumes that the soil is "lumpy" and that contaminant must diffuse out from the interiors of the lumps to come in contact with surfactant solution; diffusion kinetics are handled by means of a lumped parameter model. The third model describes continuous-flow surfactant washing of batches of soil in which diffusion transport from the lumps of soil may be important. The fourth model describes operation of a countercurrent flow soil washing column with inclusion of diffusion transport.

Batch Process Surfactant Soil Washing, Equilibrium Model

Analysis

See Fig. 11 for a sketch of the apparatus. The container (of volume V, cubic meters) is charged to the top with pulverized contaminated soil (of porosity ν) and is then filled with surfactant solution (of concentration C, kg/m^3). The initial contaminant concentration in the soil is m_0 (kg/m^3), and the contaminant concentration in the soil after the surfactant solution has been allowed to equilibrate with the soil and is then drained away is m (kg/m^3). We assume that the concentration of contaminant in the surfactant solution after equilibration, c (kg/m^3), is given by

$$c(m,C) = [c_0 + K_D(C - \mathrm{cmc})]\frac{m}{m_{1/2} + m} \qquad (1)$$

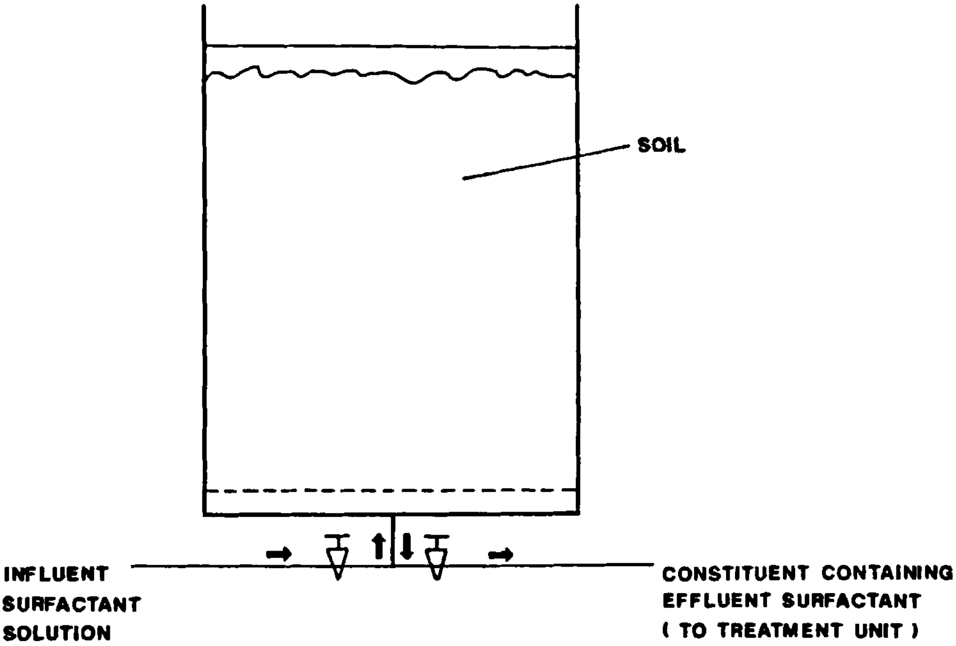


FIG. 11. Schematic of the batch soil washing apparatus.

where c_0 = contaminant concentration in water, kg/m^3
K_D = distribution coefficient for contaminant in the surfactant being used, dimensionless
C = surfactant concentration, kg/m^3
cmc = critical micelle concentration of the surfactant, kg/m^3
$m_{1/2}$ = isotherm parameter to take into account the strength of the contaminant-soil binding, kg/m^3

The contaminant conservation equation for a 1-m^3 portion of soil then yields

$$m_0 = v_c + m \tag{2}$$

Define

$$K_s = c_0 + K_D(C - \text{cmc})$$

Then Eq. (2) yields

$$m_0 = vK_s \frac{m}{m_{1/2} + m} + m \tag{3}$$

Solution of Eq. (3) for m then yields

$$m = \frac{(m_0 - vK_s - m_{1/2}) \pm \sqrt{(m_0 - vK_s - m_{1/2})^2 + 4m_0 m_{1/2}}}{2} \tag{4}$$

The sign in Eq. (4) is selected so that m lies in the range $(0, m_0)$.

One anticipates that several washings may be needed to reach the desired level of decontamination. This simply involves the recursive use of Eq. (4); after $n + 1$ washings, the contaminant concentration in the soil is given by

$$m_{n+1} = \frac{(m_n - vK_s - m_{1/2} \pm \sqrt{(m_n - vK_s - m_{1/2})^2 + 4m_n m_{1/2}}}{2} \tag{5}$$

where m_n is the contaminant concentration after n washings.

Results

Table 5 lists the standard parameters used in making runs with the equilibrium model for soil surfactant washing. These parameters were se-

TABLE 5

Standard Parameters for the Equilibrium Model for Soil Washing (Tables 6–10)

Soil voids fraction	0.3
Soil density	1.7 g/cm^3
Initial contaminant concentration	10^4 mg/kg aqueous
Solubility of contaminant	1 mg/L
Surfactant concentration	10 g/L
Surfactant critical micelle concentration	1 g/L
Contaminant surfactant distribution coefficient, K_D	2
Isotherm parameter, $m_{1/2}$	1 kg/m^3

lected as reasonable estimates; better values will be available on completion of the laboratory work on surfactant washing. The principal objective of the present calculations is to map out the behavior of the models—how changes in the various parameters affect the results.

Comparison of Tables 6, 7, and 8 shows how surfactant washing is affected by the strength of the binding of the contaminant to the adsorption sites in the soil. The larger the value of $m_{1/2}$, the stronger the binding. Strong binding, such as occurs in the run described in Table 7, reduces the efficiency of the process greatly. One might expect binding to be strongest in soils which are extremely dry (not likely to be a problem in the eastern United States) and in soil with a high content of humic materials.

Comparison of Tables 6, 9, and 10 demonstrates the effect of the size of the contaminant partition coefficient K_D. Increasing K_D from 2 to 10 (Tables 6 and 9, respectively) roughly doubles the efficiency of the process;

TABLE 6

Residual Contaminant Soil Concentrations after Various Numbers of Washings. Parameters as in Table 5

Number of washings	Contaminant concentration (kg/m^3)
0	17.00
1	12.01
2	7.268
3	3.164
4	0.7866
5	0.1368
6	2.176×10^{-2}
7	3.410×10^{-3}
8	5.331×10^{-4}
9	8.329×10^{-5}
10	1.301×10^{-5}

TABLE 7

Residual Contaminant Soil Concentrations after Various Numbers of Washings. Parameters as in Table 1 except that $m_{1/2}$ = 10 kg/m^3 (stronger binding of contaminant to soil)

Number of washings	Contaminant concentration (kg/m^3)
0	17.00
1	13.86
2	11.03
3	8.542
4	6.429
5	4.702
6	3.348
7	2.328
8	1.588
9	1.067
10	0.7094
35	1.524×10^{-5}

TABLE 8

Residual Contaminant Soil Concentrations after Various Numbers of Washings. Parameters as in Table 1 except that $m_{1/2}$ = 0.10 kg/m^3 (weaker soil binding)

Number of washings	Contaminant concentration (kg/m^3)
0	17.00
1	11.65
2	6.329
3	1.312
4	3.108×10^{-2}
5	5.683×10^{-4}
6	1.033×10^{-5}

TABLE 9

Residual Contaminant Soil Concentration after Various Numbers of Washings. Parameters as in Table 1 except that K_D = 10 (increased partition coefficient)

Number of washings	Contaminant concentration (kg/m^3)
0	17.00
1	1.374
2	5.150×10^{-2}
3	1.843×10^{-3}
4	6.581×10^{-5}
5	2.350×10^{-6}

TABLE 10

Residual Soil Contaminant Concentration after Various Numbers of Washings. Parameters as in Table 1 except that K_D = 0.4 (reduced partition coefficient)

Number of washings	Contaminant concentration (kg/m^3)
0	17.00
1	15.98
2	14.97
3	13.96
4	12.96
5	11.96
6	10.97
7	9.991
8	9.018
9	8.057
10	7.110
34	1.147×10^{-5}

decreasing K_D from 2 to 0.4 decreases the contaminant removal rate to less than a third of its original value.

Dependence of contaminant removal on other model parameters can be explored similarly. For example, increases in soil voids fraction or surfactant concentration result in increased removal rate, while contaminant aqueous solubility generally has little effect.

This model was used to fit the PCB data described earlier in this paper (see Table 1). The parameters which were used in the model are as follows:

Mass of soil sample = 100 g
Porosity = 0.3
Volume of surfactant solution used per washing = 800 mL
Surfactant concentration = 14.4 g/L (50 m*M*)
Surfactant cmc = 2.3 g/L (8 m*M*)
Initial PCB soil concentration = 1150 mg/kg
$m_{1/2}$ (isotherm parameter) = 100 mg/kg
K_D (distribution coefficient) = 7, 8, and 9 (unitless)

Table 11 gives the predicted and observed Aroclor 1260 concentrations in the surfactant washing solutions, and Table 12 gives the predicted and observed residual Aroclor 1260 concentrations in the soil after various numbers of washings.

TABLE 11
Predicted and Observed Concentrations of Aroclor 1260 in the Surfactant Washing Solutions,[a] mg/L

K_D (unitless)	Washing number				
	1	2	3	4	5
9	88.8	45.9	8.08	0.90	0.093
8	80.8	49.7	11.5	1.49	0.17
7	72.2	51.9	16.6	2.65	0.35
Observed (average)	—	—	13.2	1.83	—
Observed (range)	—	—	8.5–16.6	0.43–3.42	—

[a] Based on an average initial concentration of Aroclor 1260 in the soil of 1150 mg/kg.

Batch Process Surfactant Soil Washing, Diffusion Limited Model

Analysis

The model treated above assumes that the length of time for each washing is sufficient to allow the contaminant to come to equilibrium between the mobile surfactant solution and the stationary phase(s) holding contaminant in the soil. This should be a good assumption for soils which are fairly well pulverized, but may be quite poor if the soil is lumpy—i.e., it contains pieces of porous rock, lumps of porous clay of low aqueous permeability, etc. In such media the diffusion of contaminant from the interiors of these blocks may well be a rate-limiting step in the soil washing process. In this section we modify the above model to permit its use on such diffusion-controlled systems. The method used is taken from our earlier work on the flushing of contaminants from blocks of porous rock with water (*19*).

TABLE 12
Predicted and Observed Residual Concentration of Aroclor 1260 in Washed Clay Soil,[a] mg/kg

K_D (unitless)	Washing number				
	1	2	3	4	5
9	440	72.2	8.01	0.83	0.085
8	503	105	13.5	1.49	0.17
7	572	158	27.4	2.65	0.41
Observed (average)	—	—	—	3.43	—
Observed (range)	—	—	—	2.26–4.93	—

[a] Based on an average initial concentration of Aroclor 1260 in the soil of 1150 mg/kg.

We assume that the blocks of porous low-permeability medium can be represented by spheres or radius a (m). (Rectangular solids could also be used, if desired.) Solution of the diffusion equation in spherical coordinates for a spherically symmetric porous solid is done by the method of separation of variables. A boundary condition of zero concentration is assumed at the surface of the sphere. The eigenvalues of the system are given by

$$\lambda_n = D_{\text{eff}}(n\pi/a)^2, \qquad n = 1, 2, 3, \ldots \tag{6}$$

where D_{eff}, the effective diffusion constant of the contaminant in the porous medium (m^2/s), is given by

$$D_{\text{eff}} = D\nu^{4/3} \tag{7}$$

Here D is the diffusion constant of the contaminant in bulk water, ν is the porosity, and Eq. (7) results from assuming complete saturation in Millington and Quirk's formula (*20*).

The smallest member of the spectrum of decay rates given by Eq. (6) is the first, which is

$$\lambda_1 = D_{\text{eff}}(\pi/a)^2 \tag{8}$$

The higher eigenvalues λ_n, $n = 2, 3, 4, \ldots$, correspond to decay rates which are much more rapid than that corresponding to λ_1. Therefore, a conservative estimate of the rate of diffusion transport from the block of porous medium is the assumption that during the duration of one washing we have an exponential decay of the soil contaminant concentration from its initial value at the start of this washing toward the equilibrium value of the soil contaminant concentration as calculated in the previous section. The rate constant for this exponential decay we take to be λ_1. The recursion formula derived in the section above is thus modified as follows.

First, we calculate m_{n+1}^*, the equilibrium value of m_{n+1}, as above. Then

$$\Delta m^* = m_n - m_{n+1}^* \tag{9}$$

gives the change in soil contaminant concentration which would result if equilibrium were achieved during this washing. Since the process is diffusion limited, the actual change in soil contaminant concentration which takes place during this washing period (of duration Δt) is given by

$$\Delta m = [1 - \exp(-\lambda_1 \Delta t)]\Delta m^* \tag{10}$$

Then the actual soil contaminant concentration after $n + 1$ washes is given by

$$m_{n+1} = m_n - \Delta m \tag{11}$$

Results

Diffusion constants of ethanol, n-butanol, and sucrose in water are 1.24, 0.56, and 0.52×10^{-9} m^2/s (*21*). If we take 1×10^{-9} m^2/s as a representative value of the diffusion constant of the contaminant, a soil porosity of 0.3, and a soil lump radius of 0.5 cm, then the value of λ_1 is 7.928×10^{-9} s^{-1}, and the characteristic time associated with the diffusion process is 1.26×10^8 s, or 1460 days. This would be the washing period required to approach within about 37% of equilibrium in one stage of washing. Such long times are obviously unacceptable, and they indicate that fairly fine pulverization of the contaminated soil is necessary if its permeability is sufficiently low that we can expect the surfactant solution to flow around the soil lumps rather than through them.

The standard parameters used in the model which assumes diffusion-controlled kinetics are given in Table 13. Most of these are identical to the parameters listed in Table 5. A diffusion constant of 1×10^{-9} m^2/s was used in all runs. Tables 14, 15, 16, and 17 show the effects of block size of the porous medium. If one allows the surfactant solution to equilibrate with the contaminated soil for 1 h in each washing, removals are fairly efficient up to a block radius of 2 mm. If, however, the block radius is increased to 5 mm, the rate of removal is decreased enormously. From these results we conclude that granular or lumpy soils should be milled or

TABLE 13

Standard Parameters for the Diffusion-Kinetics-Controlled Model for Soil Washing (Tables 14–17)

Soil voids fraction	0.3
Soil density	1.7 g/cm^3
Initial contaminant concentration	1×10^4 mg/kg
Aqueous solubility of contaminant	1 mg/L
Surfactant concentration	10 g/L
Surfactant critical micelle concentration	1 g/L
Contaminant surfactant distribution coefficient, K_D	2
Isotherm parameter, $m_{1/2}$	1 kg/m^3
Contaminant diffusion constant	1×10^{-9} m^2/s
Block radius of medium	1×10^{-4} m
Duration of each washing	1 h

TABLE 14
Diffusion-Controlled Model. Residual Contaminant Soil Concentrations after Various Numbers of Washings. Parameters as in Table 13

Number of washings	Contaminant concentration (kg/m^3)
0	17.00
1	12.01
2	7.268
3	3.164
4	0.7866
5	0.1368
6	2.176×10^{-2}
7	3.410×10^{-3}
8	5.331×10^{-4}
9	8.329×10^{-5}
10	1.301×10^{-5}

pulverized before surfactant washing so that all lumps greater than about 4 mm diameter are broken up. If the quantity

$$Dv^{4/3}(\pi/a)^2\Delta t$$

is greater than unity, one can expect a washing to remove close to the amount of contaminant predicted by equilibrium calculations. (Here Δt is the duration of a washing.) If this quantity is significantly less than unity, removal will be quite inefficient.

TABLE 15
Diffusion-Controlled Model. Parameters as in Table 13 Except that Block Radius of Medium = 10^{-3} m

Number of washings	Contaminant concentration (kg/m^3)
0	17.00
1	12.02
2	7.275
3	3.173
4	0.7918
5	0.1383
6	2.210×10^{-2}
7	3.478×10^{-3}
8	5.461×10^{-4}
9	8.569×10^{-5}
10	1.345×10^{-5}

TABLE 16
Diffusion-Controlled Model. Parameters as in Table 13 Except that Block Radius of Medium = 2×10^{-3} m

Number of washings	Contaminant concentration (kg/m^3)
0	17.00
1	12.85
2	8.855
3	5.187
4	2.328
5	0.8138
6	0.2549
7	7.710×10^{-2}
8	2.308×10^{-2}
9	6.886×10^{-3}
10	2.053×10^{-3}
14	1.619×10^{-5}

Modeling of a Batch Column with Continuous-Flow Surfactant

Analysis

An alternative design for a soil-washing apparatus is indicated in Fig. 12; here the soil is placed in a column and surfactant solution is passed upward through the column continuously. Such continuous-flow operation should result in savings with regard to pump size, tankage for contaminated and recovered surfactant, and labor.

TABLE 17
Diffusion-Controlled Model. Parameters as in Table 13 Except that Block Radius of Medium = 5×10^{-3} m

Number of washings	Contaminant concentration (kg/m^3)
0	17.00
1	15.76
2	14.53
3	13.32
4	12.12
5	10.94
6	9.783
7	8.656
8	7.570
9	6.534
10	5.563
67	1.107×10^{-5}

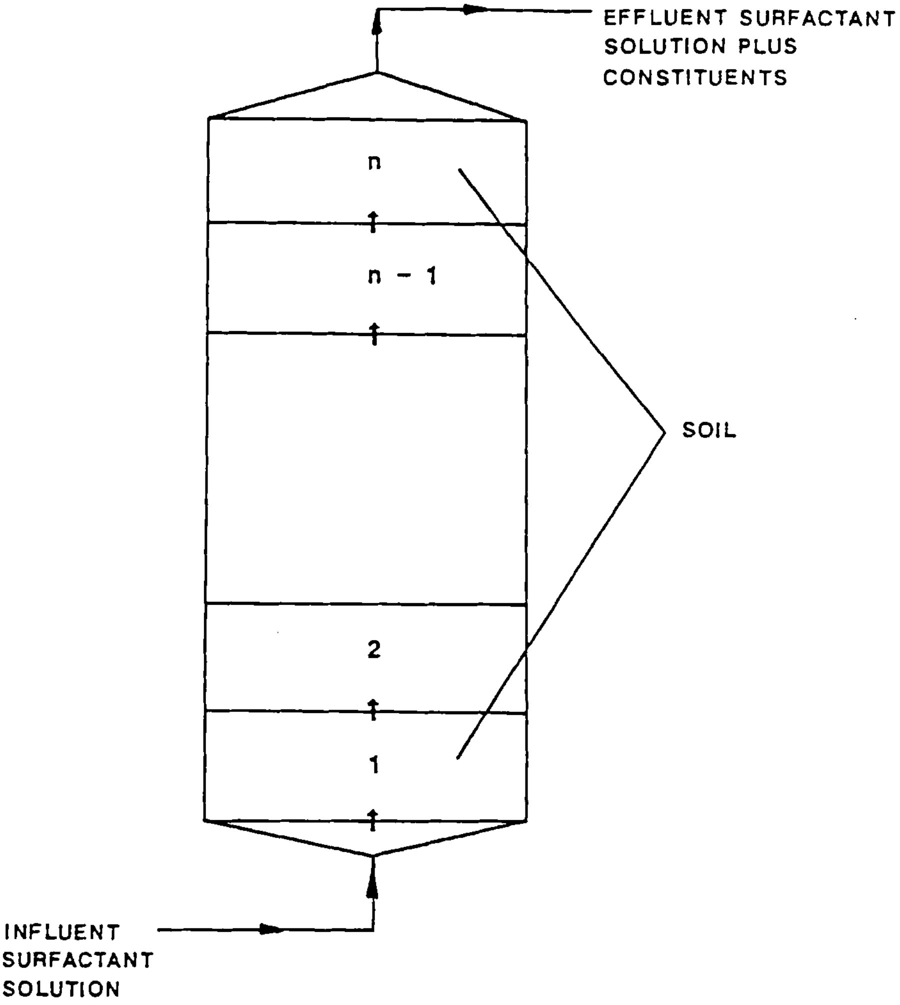


FIG. 12. Schematic of the continuous-flow soil washing apparatus.

We use the notation employed with the previous models, with the following additions. Let

Q = surfactant volumetric flow rate, m^3/s
m_i = soil contaminant concentration in the ith compartment into which the column is partitioned, kg/m^3
c_i = aqueous contaminant concentration in the ith compartment, kg/m^3

c_i^e = equilibrium contaminant concentration in the ith compartment, kg/m^3
m_i^e = equilibrium contaminant soil concentration in the ith compartment, kg/m^3
M_i = mass of contaminant in the ith compartment, kg
R = column radius, m
h = height of column, m
n = number of compartments into which column is partitioned
dz = h/n, thickness of one compartment
K_s = $c_0 + K_D(C - \text{cmc})$, as before

Then

$$M_i = [\nu c_i + (1 - \nu)m_i]\,\Delta V \tag{12}$$

where $\Delta V = \pi R^2 dz$.

Our adsorption isotherm, Eq. (1), yields

$$c_i^e = K_s \frac{m_i^e}{m_{1/2} + m_i^e} \tag{13}$$

The rate of change of contaminant mass in the ith compartment is given by

$$\frac{dM_i}{dt} = Q(c_{i-1} - c_i) \tag{14}$$

We represent diffusion transport of contaminant from the interiors of the porous blocks of the medium by means of a lumped parameter model analogous to that used in the last section. We assume that

$$\left(\frac{dc_i}{dt}\right)_{\text{diff}} = \lambda(c_i^e - c_i) \tag{15}$$

where λ is the same diffusion problem eigenvalue calculated previously—see Eq. (8). We consider a short time interval Δt such that the effect of advection on c_i can be neglected. Then

$$c_i(\Delta t) = c_i^e + [c_i(0) - c_i^e]\exp(-\lambda\Delta t) \tag{16}$$

This yields

$$c_i(\Delta t) - c_i(0) = [c_i^e - c_i(0)][1 - \exp(-\lambda\Delta t)] \tag{17}$$

so that we can represent diffusion transport by

$$\left(\frac{dc_i}{dt}\right)_{\text{diff}} = [c_i^e - c_i(0)]\,\frac{[1 - \exp(-\lambda\Delta t)]}{\Delta t} \tag{18}$$

and

$$\frac{dc_i}{dt} = \frac{Q}{\nu\Delta V}(c_{i-1} - c_i) + (c_i^e - c_1)\,\frac{[1 - \exp(-\lambda\Delta t)]}{\Delta t} \tag{19}$$

We calculate c_i^e from Eq. (13) and the mass balance equation

$$M_i = \Delta V[\nu c_i^e + (1 - \nu)m_i^e]$$

This yields

$$M_i = \Delta V\left\{\nu c_i^e + (1 - \nu)\,\frac{m_{1/2}c_i^e}{K_s = c_i^e}\right\} \tag{20}$$

Rearrangement of Eq. (20) gives a quadratic equation in c_i^e, the desired solution of which is

$$c_i^e = \frac{[b - \sqrt{b^2 - 4\nu M_i K_s/\Delta V}]}{2} \tag{21}$$

where

$$b = (M_i/\Delta V) + \nu K_s + (1 - \nu)m_{1/2} \tag{22}$$

With a formula for c_i^e it is now possible to integrate Eqs. (14) and (19) forward in time to describe the behavior of the column. This is done by a standard predictor-corrector formula.

Results

A program was written in TurboBASIC for an MMG 286 microcomputer (an IBM PC-AT clone) implementing the model, and several runs were

TABLE 18

Standard Parameter Set for Continuous-Flow Surfactant Soil Washing Column

Column height	2 m
Column diameter	1 m
Column flowrate	1 L/s
Number of compartments into which the column is partitioned	10
Soil porosity	0.3
Soil density	1.7 g/cm^3
Initial contaminant concentration	10^4 mg/kg
Contaminant solubility in water	1 mg/L
Distribution coefficient of contaminant in surfactant, K_D	2
Surfactant concentration	10 g/L
Surfactant critical micelle concentration	1 g/L
Isotherm parameter, $m_{1/2}$	1 kg/m^3
Time increment in numerical integration	10 s
Diffusion constant of contaminant in water	1×10^{-9} m^2/s
Effective diameter of soil lumps	0.1 cm

made to explore its behavior. The standard parameter set is given in Table 18; departures from these values are indicated in the figures.

In Fig. 13 we see the effect on removal rate of variations in the surfactant flow rate through the column. A significant increase in removal rate is seen as the flow rate is increased from 0.5 to 1.0 L/s, but relatively little further increase in removal rate is observed as the flow rate is increased from 1 to 2 L/s. At this point the diffusion of contaminant from the interiors of the soil lumps is becoming the rate controlling factor, and further increases in surfactant flow rate will produce relatively little increases in contaminant removal rate.

Figure 14 shows the effects of increasing the surfactant concentration from 5 to 10 to 20 g/L. The increase from 5 to 10 g/L results in a near-doubling of the rate of removal, but the increase from 10 to 20 g/L results in an increase in contaminant removal rate which is significantly less than a doubling of the removal rate. Again, at a surfactant concentration of 20 g/L, the contaminant removal is apparently limited by diffusion of contaminant from the interiors of the soil lumps, so that little is to be gained by using still higher surfactant concentrations.

Diffusion rates are proportional to the square of the effective diameter of the soil lumps, so one can expect enormous decreases in contaminant removal rates as the lump diameter is increased. This is borne out by the plots in Fig. 15. In these, the lump diameters are 0.2, 0.5, 1, 2, and 4 mm. Diffusion limitation is unimportant for the first two runs, becomes significant at a lump diameter of 1 mm, and is overwhelmingly the controlling factor for lump diameters of 2 and 4 mm. These results demonstrate the

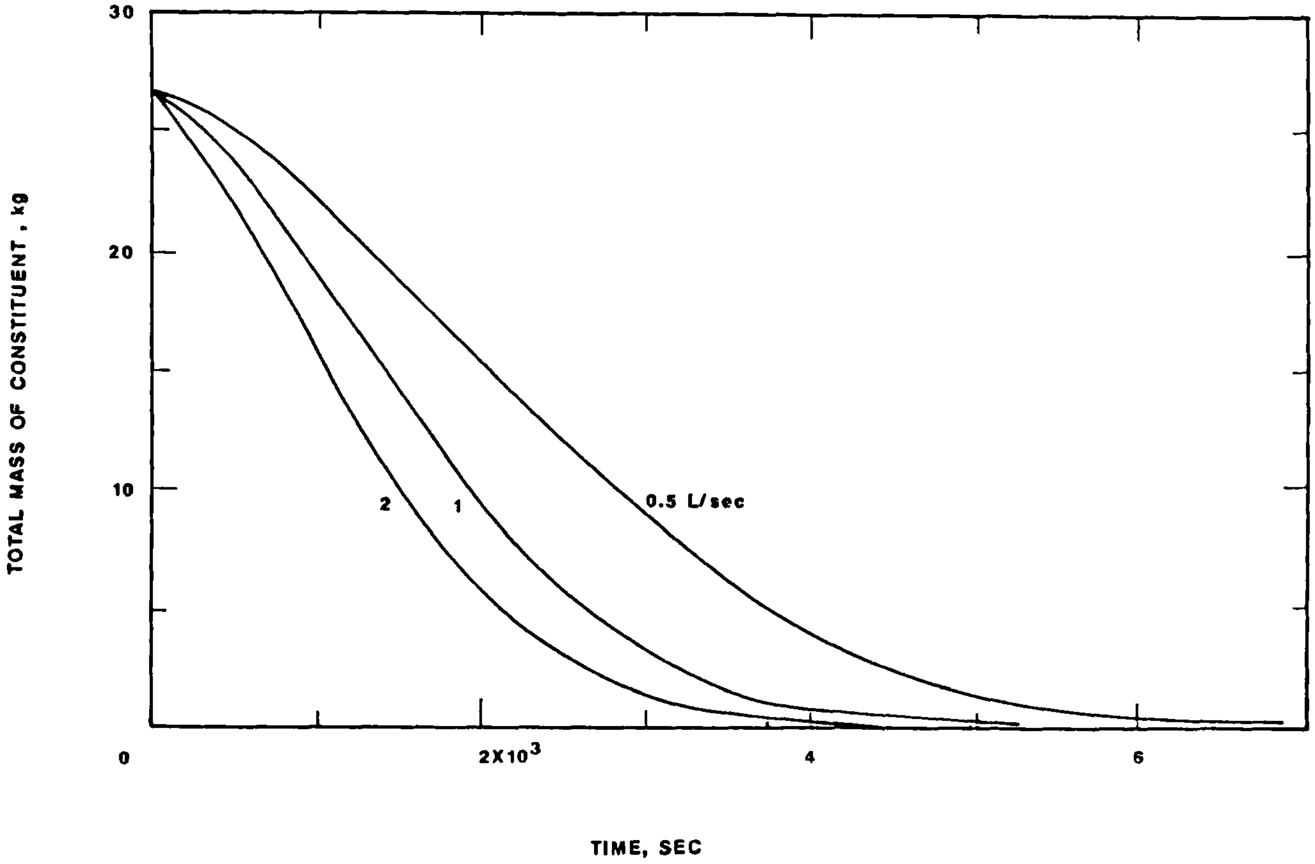


FIG. 13. Plots of total contaminant mass versus time; dependence on surfactant solution flow rate. Other parameters are given in Table 12.

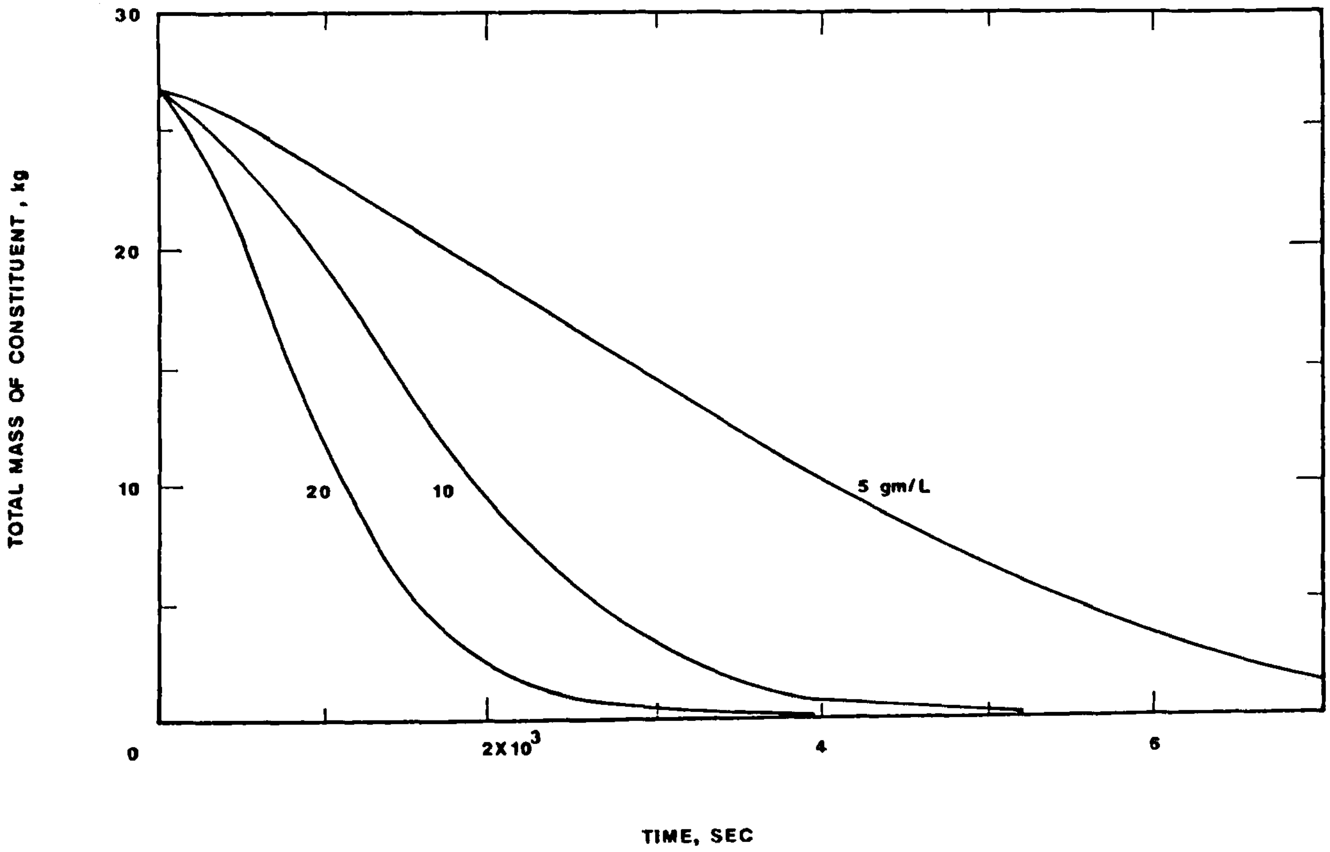


FIG. 14. Plots of total contaminant mass versus time; dependence on surfactant concentration. Other parameters as in Table 12.

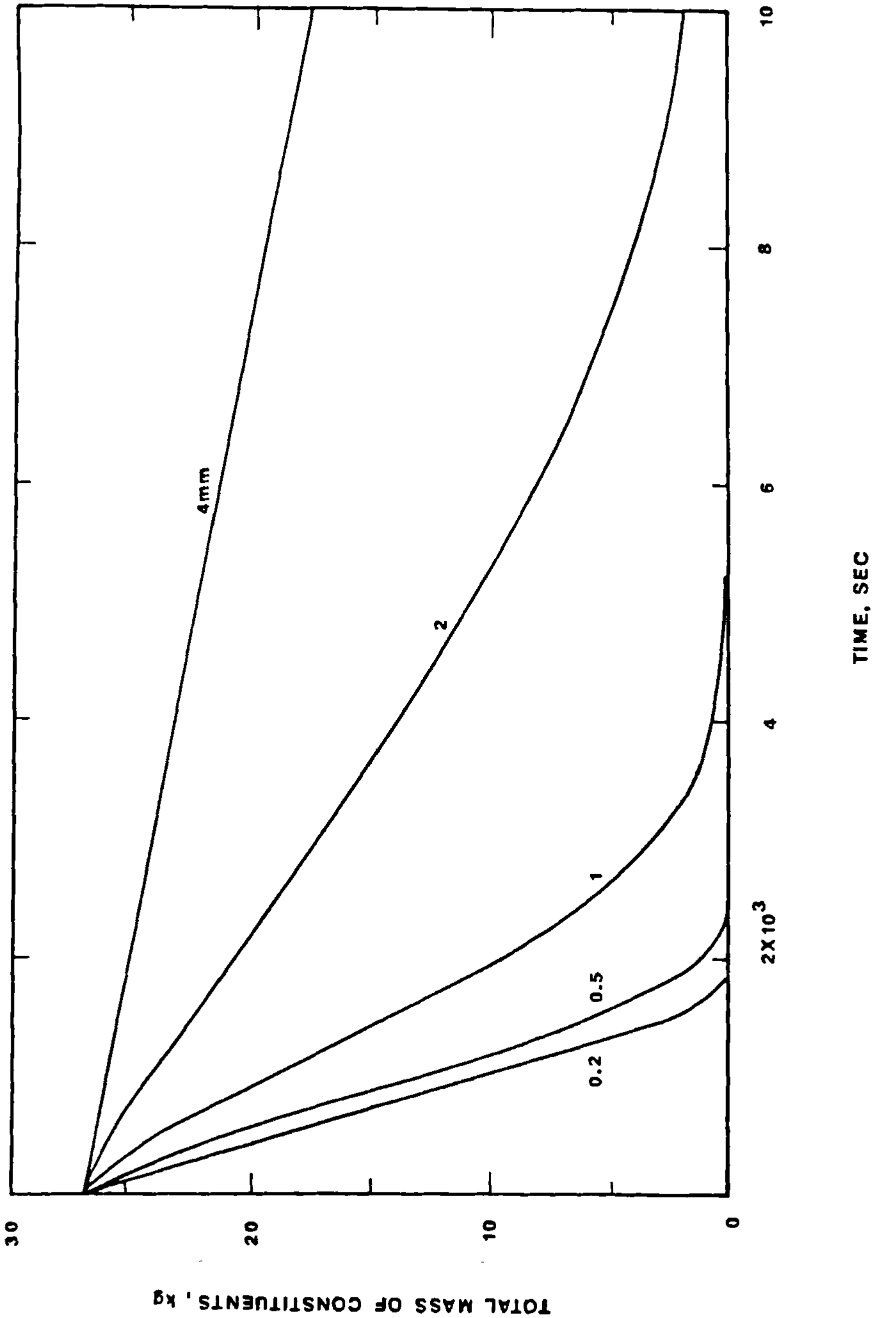


FIG. 15. Plots of total contaminant mass versus time; dependence on soil lump effective diameter. Other parameters as in Table 12.

importance of adequately comminuting the soil to be treated if it contains porous lumps of low permeability and diameter greater than 1–2 mm.

The effect of the number of compartments into which the column is partitioned for mathematical representation is shown in Fig. 16. Increasing the number of compartments from 5 to 40 results in very minor change in the appearance of the removal curve. This parameter, and also the axial dispersion constant, have relatively little effect on the performance of the column. Therefore, little effort need be made to increase the number of equivalent theoretical plates in the column, and minor variations in soil characteristics such as permeability are not expected to seriously interfere with the efficiency of soil decontamination by surfactant washing.

Countercurrent Surfactant Soil Washing

Analysis

The inconvenience and high labor costs of any batch-type operation are avoided if the process is run in a completely continuous-flow mode. We therefore explored a model for the countercurrent washing of contaminated soil, including the effects of diffusion kinetics. The model is sketched in Fig. 17. The countercurrent flow model is partitioned into *n* slabs, as before. Each slab contains a mobile aqueous phase (moving upward) and a mobile soil phase (moving downward). We carry out a mass balance on each phase, including advection of both soil and aqueous phase and diffusion transport between the two. The notation is as follows.

h = height of column, m
R = column radius, m
Q_s = rate of soil loading, m^3/s
Q_w = flow rate of surfactant solution, m^3/s
v_s = downward velocity of soil relative to the lab, m/s
ν = soil porosity
C = surfactant concentration, kg/m^3
c_i^w = contaminant concentration in the aqueous phase, *i*th slab, kg/m^3
c_i^s = concentration of contaminant held in the soil, *i*th slab, kg/m^3
K_D = contaminant surfactant distribution coefficient
c_0 = contaminant solubility in pure water, kg/m^3
$m_{1/2}$ = isotherm parameter, kg/m^3
n = number of slabs used to represent the column
$\Delta V = R^2h/n$ = volume of one slab, m^3
$\Delta V_w = (\pi R^2h/n) - (1 - \nu)Q_sh/(v_sn)$, = volume of mobile water in one slab, m^3

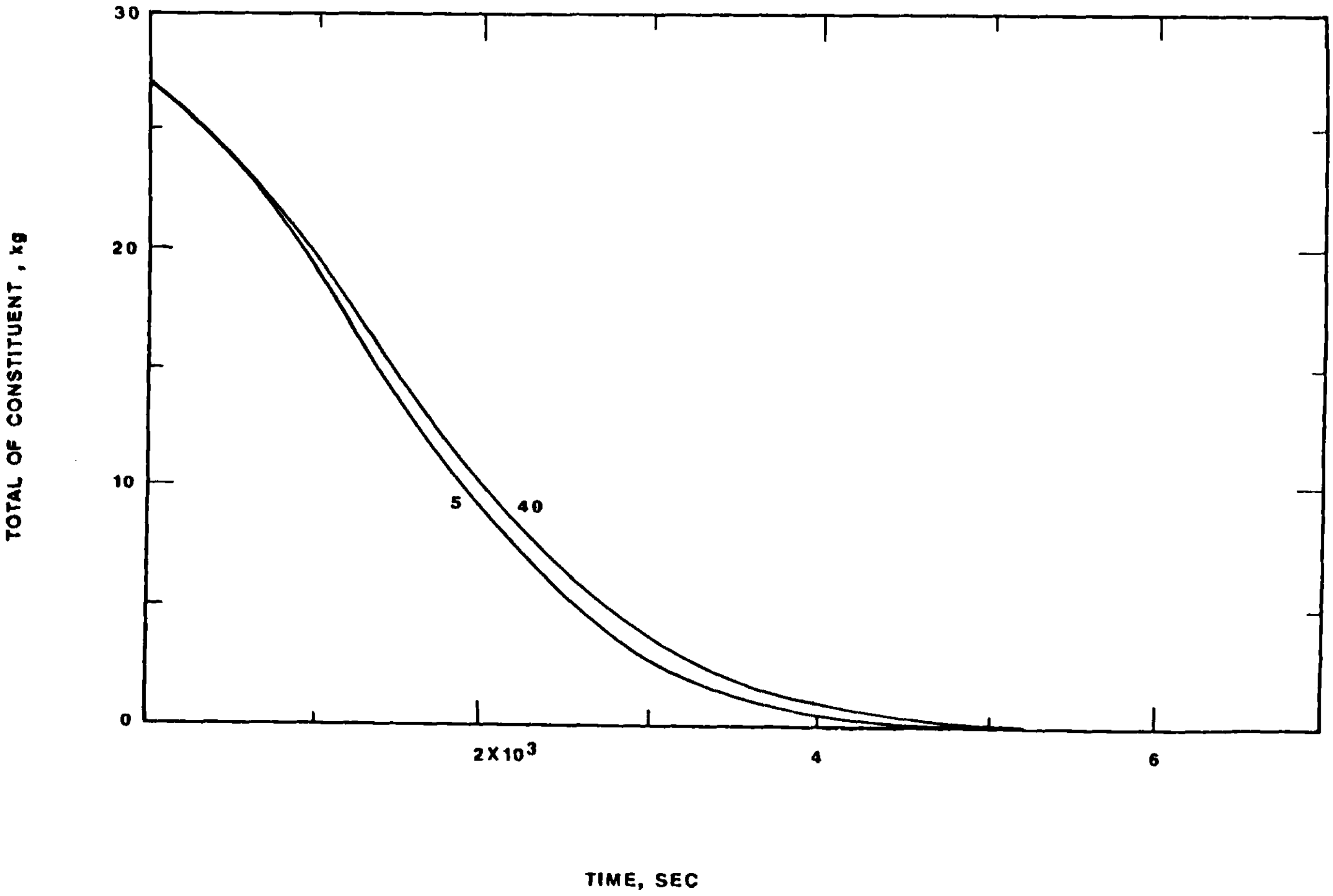


FIG. 16. Plots of total contaminant mass versus time; dependence on the number of compartments into which the column is partitioned for analysis. Other parameters as in Table 12.

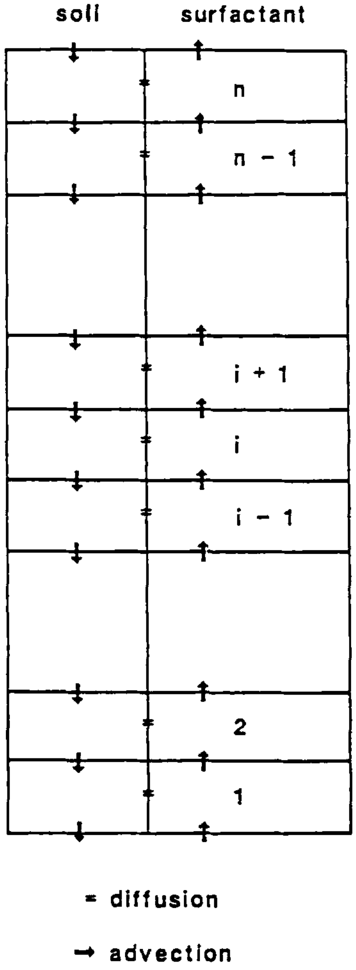


FIG. 17. Schematic of the countercurrent flow soil washing column.

$\Delta V_s = (1 - \nu)Q_s h/v_s n$ = actual volume of soil (excluding pores) in one slab, m^3

Advective transport alone in the aqueous phase gives

$$\left(\Delta V_w \frac{dc_i^w}{dt}\right)_{\text{adv}} = Q_w(c_{i-1}^w - c_i^w) \tag{23}$$

Similarly, advective transport alone in the soil phase gives

$$\left(\Delta V_e \frac{dc_i^s}{dt}\right)_{\text{adv}} = Q_s(c_{i+1}^s - c_i^s) \tag{24}$$

We next examine diffusion transport between the soil phase and the aqueous phase by means of the lumped parameter approach. The total mass of contaminant in the ith compartment is assumed to remain constant during the very short time interval during which we focus on diffusion transport. Thus

$$M_i = \Delta V_w c_i^w + \Delta V_s c_i^s = \text{constant} \tag{25}$$

We use the same adsorption isotherm as before, so we define

$$K_s = c_0 + K_{\text{D}}(C - \text{cmc})$$

so that at local equilibrium we have

$$c^{we} = K_s \frac{c^{se}}{m_{1/2} + c^{se}} \tag{26}$$

Equation (25) is also valid at local equilibrium, so we have

$$M_i = \Delta V_w c_i^{we} + \Delta V_e c_i^{se} \tag{27}$$

Substituting Eq. (26) into Eq. (27) yields a quadratic equation in c^{se}, the solution to which is

$$c^{se} = \frac{\{-\text{b} \pm \sqrt{[b^2 + 4\Delta V_s M_i m_{1/2}]^{1/2}}\}}{2\Delta V_s} \tag{28}$$

where

$$b = \Delta V_w k_s + \Delta V_s m_{1/2} - M_i$$

We choose the sign in Eq. (25) such that $0 < c^{se} < M_i/\Delta V_s$.

Next we make the lumped parameter assumption that the diffusive mass transport of contaminant between the soil phase and the aqueous phase is governed by

$$\left(\frac{dc^s}{dt}\right)_{\text{diff}} = \lambda(c^{se} - c^s) \tag{29}$$

This equation is then integrated between 0 and Δt, and the result is rearranged to yield

$$c^s(\Delta t) - c^s(0) = -(c^s(0) - c^{se})[1 - \exp(-\lambda\Delta t)] \tag{30}$$

Then we use for the diffusion transport term

$$\left(\frac{dc_i^s}{dt}\right)_{\text{diff}} = (c_i^{se} - c_i^s)\frac{[1 - \exp(-\lambda\Delta t)]}{\Delta t} \tag{31}$$

The expression for $(dc_i^w/dt)_{\text{diff}}$ is obtained as follows. Note that, for diffusion only, M_i in Eq. (27) is constant, so its rate of change with respect to time vanishes. This yields, after rearrangement,

$$\left(\frac{dc_i^w}{dt}\right)_{\text{diff}} = -\frac{\Delta V_s}{\Delta V_w}\left(\frac{dc_i^s}{dt}\right)_{\text{diff}} \tag{32}$$

so that

$$\left(\frac{dc_i^w}{dt}\right)_{\text{diff}} = \frac{\Delta V_s}{\Delta V_w}(c_i^s - c_i^{se})\frac{[1 - \exp(-\lambda\Delta t)]}{\Delta t} \tag{33}$$

Lastly, one combines the diffusive and advective terms to obtain the differential equations modeling the countercurrent flow soil washing column. These equations are

$$\frac{dc_i^w}{dt} = \frac{Q_w}{\Delta V_w}(c_{i-1}^w - c_i^w) + \frac{\Delta V_s}{\Delta V_w}\frac{[1 - \exp(-\lambda\Delta t)]}{\Delta t}(c_i^s - c_i^{se}) \tag{34}$$

and

$$\frac{dc_i^s}{dt} = \frac{Q_s}{\Delta V_s}(c_{i+1}^s - c_i^s) - \frac{[1 - \exp(-\lambda\Delta t)]}{\Delta t}(c_i^s - c_i^{se}) \tag{35}$$

where c_i^{se} is calculated from Eq. (28).

TABLE 19
Standard Parameter Set for the Countercurrent Flow Model

Column height	2 m
Column diameter	1 m
Rate of soil loading	0.001 m^3/s
Flow rate of surfactant solution	0.002 m^3/s
Downward linear velocity of soil in column	0.01 m/s
Soil porosity	0.3
Soil density	1700 kg/m^3 (1.7 g/cm^3)
Surfactant concentration	10 g/L
Surfactant critical micelle concentration	1 g/L
Initial contaminant soil concentration	10,000 mg/kg
Contaminant solubility in water	1 mg/L
Isotherm parameter, $m_{1/2}$	1 kg/m^3
Contaminant distribution coefficient, K_D	2
Effective soil lump diameter	0.1 cm
Contaminant diffusion constant in water	1×10^{-9} m^2/s
Number of slabs into which column is partitioned	10
dt	10 s

Results

The model just described was implemented in TurboBASIC, and runs were made to ascertain the dependence of countercurrent flow column operation on the parameters of the model. The standard parameter set is given in Table 19; variations from this are noted in Tables 20–23. Runs were made starting with a column initially loaded with contaminated soil and also with it initially loaded with clean soil; the same steady-state concentrations were achieved with these two different initial conditions, as expected.

Table 20 shows the effect of soil particle size on column performance. As we might expect from the results from the other models, the effect is extremely large. With the other model parameters having the values given in Table 19, soil clean-up is essentially complete for particles of 1 mm

TABLE 20
Effect of Soil Particle Diameter on Effluent Soil Contaminant Concentration

a (cm)	Effluent soil contaminant concentration (mg/kg)
0.10	3.83×10^{-3}
0.15	6.61
0.20	654
0.25	2980

TABLE 21
Effect of Linear Velocity of Soil through the Column on Effluent Soil Contaminant Concentration

v_s (cm/s)	Effluent soil contaminant concentration (mg/kg)
1	3.83×10^{-3}
2	4.19×10^{-2}
4	0.796
8	14.7
16	169
24	519

diameter or less, but only about 70% of the contaminant is removed if the particles have a diameter of 2.5 mm. Again we find that adequate comminution of the material being washed is essential to success. Scholz and Milanowski (*6*) found this to be the case experimentally in an earlier field study.

The effect of the linear velocity with which the soil is carried through the apparatus is shown in Table 21. Again a rather abrupt deterioration of separation efficiency is observed. A linear velocity of 4 cm/s yields an effluent soil contaminant concentration of less than 1 mg/kg, while a velocity of 8 cm/s yields an effluent soil contaminant concentration of almost 15 mg/kg. In designing a system, one needs to insure that the linear soil velocity is sufficiently small to avoid this loss of efficiency.

The surfactant solution flow rate turns out to be another rather critical variable, as shown in Table 22. A 25% decrease in the flow rate below 10 L/s results in an increase in effluent soil contaminant concentration by five orders of magnitude. A decrease in flow rate to 5 L/s results in only roughly 50% removal of the contaminant. One should select operating parameters such that the surfactant flow rate is comfortably in excess of the critical value below which effluent soil contaminants increase so drastically.

In the models described in this paper, the strength of the binding of contaminant to the soil by adsorption is described by a Langmuir adsorp-

TABLE 22
Effect of Surfactant Solution Flow Rate on Effluent Soil Contaminant Concentration

Q_w (L/s)	Effluent soil contaminant concentration (mg/kg)
5	5370
7.5	97.4
10	3.83×10^{-3}

TABLE 23
Effect of the Binding Parameter $m_{1/2}$ on the Effluent Soil Contaminant Concentration

$m_{1/2}$ (kg/m^3)	Effluent soil contaminant concentration (mg/kg)
1	3.83×10^{-3}
2	9.42×10^{-2}
3	0.879
4	4.87
6	60.9
8	322
10	832

tion-type parameter $m_{1/2}$, which is the soil concentration of contaminant at which the aqueous concentration in equilibrium with the soil has dropped to half of its saturation value. The larger the value of $m_{1/2}$, the stronger the binding of the contaminant to the soil. The results in Table 23 demonstrate that, as expected, the stronger the binding of contaminant to soil, the less efficient is the separation. One might expect this to present a problem in soils containing high concentrations of humic and fulvic acids, which would provide hydrophobic sites to which contaminants such as PCBs may bind relatively strongly. The results indicate the importance of carrying out preliminary lab-scale studies on representative soils from the actual site, at least until adsorption is sufficiently well characterized that one can safely estimate $m_{1/2}$ from soil analyses such as total organic carbon, etc.

IV. CONCLUSIONS

Laboratory-scale surfactant washing has been shown to remove about 99.7% of weathered PCBs from a clayey soil. Treatment of the contaminant-laden surfactant solutions by countercurrent extraction with hexane removes nonvolatile organic contaminants effectively. Thin film aeration in packed columns of surfactant solutions contaminated with volatile organics removes these contaminants. The correlation of micelle/water partition coefficients with octanol/water partition coefficients reported by Valsaraj et al. has been shown to hold for several additional compounds.

Mathematical models have been developed for the washing of batches of contaminated soils with batches of surfactant and in a continuous-flow column apparatus. The dependence of the behavior of these models on their parameters was explored. The effect of diffusion-limited kinetics becomes important for soil lump sizes of 1–2 mm diameter, and is disastrous for lumps much larger than this.

The performance of countercurrent flow soil washing columns depends very sharply on the values of the parameters used in the model. Lab and pilot-scale studies should be used to ascertain the region of parameter sets which lead to effective removals, and care should be taken to insure that the design of the apparatus and the operating parameters used with it are such that they lie well within the domain of efficient operation. In particular, the model indicates that overloading the column, failing to adequately comminute the feed soil, and using insufficient surfactant result in very poor column performance even if one is outside the region of acceptable parameter sets by only a small amount.

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