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REACTIONS OF ORGANIC
WASTES AND SOILS

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REACTIONS OF ORGANIC
WASTES AND SOILS

By

K. C. Knoll

Water and Waste Management Department
Environmental and Life Sciences Division

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K. C. Knoll

ABSTRACT

The passage of certain organic wastes from a radionuclide separations plant has little effect on the permeability of the soil for later passage of a high salt aqueous waste, or on the ion exchange properties of the soil. Soil removed ^{239}Pu and ^{241}Am slowly from some of the organics and not at all from others. Radionuclides were leached from soils most noticeably by two of the wastes. One was a mixture of 0.4M di-(2-ethylhexyl) phosphoric acid and 0.2M tributylphosphate in paraffin hydrocarbons (C_{10} to C_{14}); the other was hydroxyacetic acid. Both of these removed ^{85}Sr and ^{241}Am and to a lesser extent ^{239}Pu .

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REACTIONS OF ORGANIC WASTES AND SOILS

K. C. Knoll

INTRODUCTION

Research and development studies on the potential problems associated with disposal of organic wastes to the ground have been continued in support of the Hanford Low Level Waste Management Program. To understand the pertinent organic-soil relationships, the following areas of research were studied:

1. Movement of organics through soil.
2. Effect of organics on:
 - Permeability of soil for high salt aqueous wastes
 - Ion exchange properties of soil.
3. Removal by organics of radionuclides previously adsorbed on the soil.
4. Adsorption by the soil of radionuclides carried by organics.

SUMMARY AND CONCLUSIONS

Potential problems associated with the disposal to the ground of certain organic wastes from the Hanford separations plants were investigated. The organic wastes studied were: DBBP, D2EHPA, Fab Oil, hexone, NPH, TBP and hydroxyacetic acid or combinations of these various organics.

Previous percolation of organics through the soil had little effect on the soil permeability for subsequent infiltration of a high salt aqueous waste. Soil removed little or none of the ^{239}Pu and ^{241}Am from any of the organic wastes studied except Fab Oil, from which essentially all of the ^{239}Pu was removed. The effect of Fab Oil on ^{241}Am removal from soil was not studied.

None of the organics except hydroxyacetic acid and 0.4M D2EHPA 0.2M TBP in NPH removed ^{85}Sr , ^{137}Cs , ^{239}Pu and ^{241}Am from the soil in large quantities. The D2EHPA-TBP mixture rapidly and completely leached from the soil the previously deposited ^{85}Sr , ^{241}Am and about 30% of the ^{239}Pu . Hydroxyacetic acid removed no ^{137}Cs from soil, but it did remove the deposited ^{85}Sr , ^{239}Pu , and ^{241}Am at all concentrations of the acid used; the removal became more rapid and complete as the concentration increased.

Ion exchange properties of the soil were not impaired by the previous infiltration of organics.

EXPERIMENTAL PROCEDURES

GENERAL METHODS

The studies involving ion exchange were performed with the organics under study, using gravity-fed soil columns. The columns were 0.8 cm ID glass tubing. Depending upon the organic type, various lengths were used. The effluent was collected at timed intervals in tubes mounted on an automatic sample changer. Gamma activity was measured with a NaI(Th) well crystal.* Alpha activity was measured with a zinc sulfide scintillation counter.

ORGANICS

The organics used in this study are some of those which after plant use may be discarded as waste because of contamination, degradation, or operating losses. They are referred to in the report by their commonly used abbreviations which are explained in the following list:

DBBP - dibutylbutylphosphonate

D2EHPA - di-(2-ethylhexyl) phosphoric acid

Fab Oil - "Fabrication Oil," a mixture of Lard Oil and CCl_4

(25-75 vol%)

* Auto-Gamma Spectrometer, Packard Instrument Co., Inc., LaGrange, Illinois.

Hexone - methylisobutylketone (4 methyl-2-pentanone)

NPH - "Normal Paraffin Hydrocarbons," a commercial mixture of straight chain hydrocarbons including decane, undecane, dodecane, tridecane and tetradecane

TBP - Tributylphosphate.

SOIL

The soil used in these studies was from the bottom of the excavation for the 241 AX Tank Farm. The soil was sieved to remove all particles greater than 2 mm in size.

EXPERIMENTAL METHODS

Movement of Organics Through Soil

These studies were performed using a falling head permeameter.⁽¹⁾ A glass tube 80 cm long and 1 cm ID was fitted with a small outlet at the bottom. Soil was packed into the lower 40 to 50 cm of the tube to a density of 1.8 g/cm³. The rest of the tube was filled with the liquid to be studied. Measurements were begun when the liquid started to drip from the outlet. The length of the soil column was measured; at timed intervals, the head of the liquid above the soil was measured with a cathetometer. Measurements were made as frequently as necessary to determine the flow of the liquid through the soil.

The permeability was determined using the formula as developed by Wenzel.⁽¹⁾

$$\text{Permeability} = 2.30259 \frac{1}{t} \log_{10} \frac{h_0}{h}$$

where l = length of soil column (cm)
 t = time (seconds)
 h_0 = head of liquid at starting time (cm)
 h = head of liquid at time t (cm)

The permeability is expressed in cubic centimeters per second through a cross sectional area of one square centimeter at 100% hydraulic gradient (decrease of one unit hydraulic head through one unit travel distance).

Effect of Organics in Soil on Permeability

The columns which had been used to measure the permeability of the soil for organic wastes were also used to measure the effect of organics on permeability. After the organic had drained from the column, a solution of nominal aqueous waste,* which is generated in the 234-5 Building, was placed into the permeameters and the permeability of the organic-treated soil for this solution was measured.

Effect of Organics in Soil on Ion-Exchange Properties

Soil columns 10 cm in length were prepared by the procedure outlined previously. Each column was saturated with one of the organics and allowed to drain for 65 hr. Tap water spiked with ^{137}Cs was then percolated through each column and also through a similar column which had not been contacted with organic. Columns were saturated with TBP- CCl_4 ; DBBP- CCl_4 ; D2EHPA-TBP-NPH and Fab Oil.

Removal by Organics of Radionuclides Adsorbed on Soil

Columns were prepared as described in the "General Methods" section. Tap water spiked with a radionuclide was percolated

** Composition of nominal aqueous waste⁽²⁾*

HNO_3	0.15 <u>M</u>	$\text{Ca}(\text{NO}_3)_2$	0.16 <u>M</u>
$\text{AlF}(\text{NO}_3)_2$	0.24 <u>M</u>	$\text{Fe}(\text{NO}_3)_2$	0.65 <u>M</u>
$\text{Al}(\text{NO}_3)_3$	0.40 <u>M</u>	NaNO_3	2.4 <u>M</u>
$\text{Mg}(\text{NO}_3)_2$	0.16 <u>M</u>		

through the column which was then washed with several column volumes of tap water. The difference between the total activity in the effluent and washes and that in the influent gave the radionuclide loading on the soil. The various organics were then percolated through the columns and the effluent was sampled at intervals. The radioactivity in the effluent samples was measured and the amount of activity removed by the organics from the soil was determined.

Adsorption by Soil of Radionuclides Carried by Organics

Columns were prepared as previously described. The organics were spiked with ^{241}Am and ^{239}Pu and percolated through the columns. Effluent samples were collected and the amount of ^{241}Am present was measured by gamma counting, while the ^{239}Pu was measured by alpha counting.

RESULTS

MOVEMENT OF ORGANICS THROUGH SOILS

The permeability of the soil for three organics studied is given in Table 1.

TABLE 1. *Permeability of Soils for Organic Wastes*

<u>Organic</u>	<u>Permeability, $\text{cm}^3/\text{cm}^2/\text{sec}$</u>
TBP- CCl_4 , 20-80%	8.5×10^{-7}
DBBP- CCl_4 , 30-70%	8.5×10^{-6}
0.4M D2EHPA-0.2M TBP in NPH	5.6×10^{-5}

EFFECT OF ORGANICS IN SOIL ON PERMEABILITY

After the organic wastes had contacted the soils, the permeability of the soils for the nominal aqueous waste was determined (Table 2).

TABLE 2. *Permeability of Organic-Contacted
Soils for Nominal Aqueous Waste*

<u>Soil previously contacted with:</u>	<u>Permeability cm³/cm²/sec</u>
TBP-CCl ₄ (20-80%)	2.6×10^{-7}
DBBP-CCl ₄ (30-70%)	2.9×10^{-7}
0.4M D2EHPA-0.2M TBP in NPH	2.9×10^{-7}
No Organic	9.3×10^{-7}

The previous percolation of the organic through the soil had little effect upon the later passage of the nominal aqueous waste.

EFFECT OF ORGANIC IN SOIL ON ION-EXCHANGE PROPERTIES

Eighty-five column volumes of ¹³⁷Cs traced water were percolated through a column previously contacted with Fab Oil; for all other columns, at least 150 column volumes were percolated. During this time, none showed a breakthrough of ¹³⁷Cs, indicating that no impairment of the ion-exchange properties of the soil was induced by the previous passage of the organic.

REMOVAL BY ORGANICS OF RADIONUCLIDES ADSORBED ON SOIL

TBP-CCl₄ (20-80%)

One hundred and fifty column volumes of this organic were percolated through the column containing ⁸⁵Sr-loaded soil, and 90 column volumes were percolated through the ¹³⁷Cs-loaded column. No activity was removed in either case. When the organic was percolated through soil with adsorbed ²³⁹Pu and ²⁴¹Am, no real breakthrough occurred but rather a very slight leakage of activity. After 130 column volumes had passed through, the amount of activity removed was 5% of the ²³⁹Pu and 10% of the ²⁴¹Am which had originally been adsorbed by the soil.

DBBP-CCl₄ (30-70%)

No ^{85}Sr or ^{137}Cs were removed from soil during the percolation of 160 column volumes of this organic. Eighty column volumes removed about 15% of the ^{241}Am and 40% of the ^{239}Pu (Figure 1).

Fab Oil

Thirty column volumes of Fab Oil removed less than 4% of the ^{239}Pu and less than 1% of the ^{241}Am previously adsorbed on the soil.

0.4M D2EHPA-0.2M TBP in NPH

Strontium-85 removal was rapid and complete, but very little ^{137}Cs was removed from the soil (Figure 2). Americium-241 was also removed rapidly, but less than 30% of the ^{239}Pu (Figure 3).

Hexone

Hexone was percolated through a column of soil previously loaded with ^{85}Sr and ^{137}Cs . Less than 10% of both radionuclides were removed, although 150 column volumes percolated through the ^{85}Sr -loaded column and 75 column volumes through the ^{137}Cs -loaded column. This loss of activity did not occur as a breakthrough but as a leakage of activity.

Hydroxyacetic Acid

The removal of radionuclides from soil by hydroxyacetic acid was determined for 0.25M acid concentration at a pH of about 3.7. To measure the effect of dilution of the acid on uptake from soil, two other concentrations of the acid, 0.125M and 0.025M were percolated through radionuclide loaded soil. Essentially, no ^{137}Cs was removed at any concentration by 100 column volumes of the organic. As the dilution increased, less ^{85}Sr , ^{239}Pu and ^{241}Am were removed as shown in Figures 4 and 5.

FIGURE 1. Removal of ^{239}Pu and ^{241}Am from Soil by DBBP- CCl_4

FIGURE 2. Removal of ^{85}Sr and ^{137}Cs from Soil by 0.4M D2EHPA-0.2M TBP in NPH

FIGURE 3. Removal of ²³⁹Pu and ²⁴¹Am from Soil by 0.4M D2EHPA-0.2M TBP in NPH

FIGURE 4. Effect of Hydroxyacetic Acid Concentration on ^{239}Pu and ^{241}Am Removal from Soil

FIGURE 5. Effect of Hydroxyacetic Acid Concentration on ⁸⁵Sr Removal from Soil

ADSORPTION BY SOIL OF RADIONUCLIDES CARRIED BY ORGANICSTBP-CCl₄ (20-80%)

The soil adsorbed both the americium and plutonium from this organic, but not in large amounts. The 50% breakthrough point for ²³⁹Pu was reached at 30 column volumes; that for ²⁴¹Am at 9 column volumes.

DBBP-CCl₄

²³⁹Pu was not removed from this waste by soil. Americium-241 results were erratic; however, a 50% breakthrough occurred at about 3.5 column volumes.

Fab Oil

Only ²³⁹Pu was run with this organic. The alpha count was erratic; a surge of activity came through initially, but at 10 column volumes there was no more activity in the effluent.

0.4M D2EHPA-0.2M TBP in NPH

The soil removed neither ²³⁹Pu nor ²⁴¹Am from this organic.

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