



Project Summary

Assessment of the Potential for Transport of Dioxins and Codisposed Materials to Groundwater

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Parameters relevant to the sorptive transport of polychlorodibenzo-p-dioxins (PCDDs) through soils were evaluated in laboratory experiments involving batch shake testing and saturated-flow soil column techniques. The experiments were conducted using water/methanol mixtures and four uncontaminated sorbents (two surface soils from Times Beach, MO and aquifer materials from Traverse City, MI and Lula, OK). Five ^{14}C -labeled PCDD congeners, including 2,3,7,8-tetra (T_4CDD), 1,2,3,4,7-penta, 1,2,3,4,7,8-hexa, 1,2,3,4,6,7,8-hepta, and octa (O_8CDD), and three codisposed materials pentachlorophenol (PCP), and chlorobenzene (CB) were used. The partition coefficient (K_D) for sorption of T_4CDD from water was found to be in good agreement with the water-phase K_D predicted by log-linear extrapolation according to the cosolvent theory by using K_D data generated for water/methanol mixtures. This observation validates the use of log-linear extrapolation to estimate water-phase K_D values for PCDDs using cosolvent data. K_D values for sorption of PCDDs by surface soils at volume fraction solvent (f_s) of 0.5-0.9 were reduced by a factor of up to 2.5 when PCP or CB were present. Reductions in K_D for PCDDs in the presence of PCP and CB increased with decreasing f_s to enable a better understanding of the influence of codisposed materials such as PCP and CB on the mobility

of PCDDs under environmental conditions typified by low f_s (i.e., $f_s < 0.5$). Sorption K_D values for the aquifer materials were normalized on organic carbon content (f_{oc}) to yield values of K_{oc} which were in general agreement with K_{oc} values determined for the surface soils. This observation suggests that sorption by the organic matter content or the aquifer materials was sufficient to mask sorption to mineral surfaces. Desorption of PCDDs from the surface soils appeared to be reversible but was limited by kinetics, with roughly 50-90% of reversible-desorption equilibrium being attained within a contact period of 30-50 days.

This Project Summary was developed by EPA's Robert S. Kerr Environmental Research Laboratory, Ada, OK, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Polychlorodibenzo-p-dioxins as environmental contaminants have perhaps received most widespread national attention because they were present in waste oils that were used for dust control in Missouri. PCDD-contamination of soils and sediments in various locations throughout the United States and in other countries have been documented.

Concentrations of PCDDs in soil and sediment samples as high as 1600 ppb to 100 ppm have been observed.

Until recently it was believed that PCDDs were relatively immobile in soils because of their low water solubilities, and that there was little potential for PCDDs to be leached from contaminated soils. Field observations have shown that PCDDs move faster through soils than would be expected based on their water solubilities. Numerous theories have been proposed to explain the "facilitated transport" of PCDDs and other highly hydrophobic organic contaminants, including a cosolvent which accounts for enhanced mobility in terms of the reduction in soil sorption in the presence of cosolvents.

The research presented in the full report involved three basic objectives; 1) determine the relative effect of the presence of codisposed materials on the sorptive transport of PCDDs through surface soils, 2) evaluate the equilibrium sorption of PCDDs by aquifer materials, and 3) evaluate the kinetics of desorption of PCDDs from surface soils.

Procedure

Solutes

All PCDDs used in the experiments were radiolabeled with C-14. Individual stock solutions of the radiolabeled PCDDs were prepared by dissolving them in methanol.

Other radiolabeled compounds used in the experiments included pentachlorophenol (PCP), methanol and water. All radiolabeled compounds were used as received from the supplier.

Soils and Aquifer Materials

The soils obtained from Times Beach, MO were the same as those used in previous investigations of the sorption of PCDDs to soils. These soils were air dried, sieved through 0.3 mm standard sieves, and characterized for pH, cation exchange capacity, organic matter content, organic carbon, organic nitrogen and texture. The soils are referred to here as soil 91 (low-organic carbon soil) and soil 96 (high-organic carbon soil).

Lula, OK and Traverse City, MI aquifer materials were provided by the EPA Project Officer and were used as received.

Solvents

Methanol and methylene chloride solvents used in the experiments described were pesticide grade and were used as

received from the supplier. Water was treated by reverse osmosis, activated carbon bed and a pair of mixed bed deionizers. Further, the water was dosed with 0.01% NaN_3 , as a biocide and its ionic strength was adjusted to 0.01M using CaCl_2 . The pH of the water was adjusted to 7.0 using NaOH.

Scintillation Cocktail

An insta-gel liquid scintillation cocktail obtained from United Technologies was used for all radioisotope analyses.

Analyses

Liquid Scintillation Counting

Analytical determinations were made by liquid scintillation counting (LSC) using a Model 1219 Rackbeta counter.

Liquid-phase solute concentrations (C or C_e) were determined by sampling three aliquots of 1-3 ml of liquid phase and adding the sample to 10 ml of Insta-gel cocktail in 20-ml glass counting vials.

Soil-phase solute concentrations (S or S_e) were determined primarily by the difference of the total solute minus liquid-phase solute. However, to confirm mass balances direct determination of soil-phase solute concentrations was made to determine mass balances.

Data Manipulation

Isotherm data were evaluated by linear regression to determine best-fit parameters for sorption constants. Best-fit estimates of K_D , the coefficient of determination (r^2), and the standard error of the estimate (s) were calculated using standard equations.

Values of K_{obs} were determined from the effluent concentration profiles obtained from saturated-flow soil column experiments. K_{obs} is the value of K_D calculated from the proper equation under the assumption of local equilibrium and a value of V_r equal to the ratio of sorbing solute to nonsorbing solute retention time as determined by the center-of-mass of the respective effluent peaks.

Least-squares regression analysis was used to determine the best-fit estimates of the slope (m) and intercept (b) for proposed cosolvent equations. The values of m and b and the regression statistics were determined by using standard techniques.

Desorption data were regressed according to empirical exponential and power-curve models.

Solubility Determinations

Batch techniques already described to evaluate $T_4\text{CDD}$ solubility in water/methanol mixtures were used to evaluate

the solubilities of the other PCDDs. Experiments were conducted in 1-ml glass microvials. PCDD crystals were pre-coated onto the inner wall near the bottom of vial by delivering a working solution containing PCDD and the evaporating the solvent with nitrogen. One ml of liquid phase was then added to the pre-coated microvial, the vials were capped and covered with aluminum foil and then placed on a shaking table. The vials were shaken daily for 15 minutes for contact periods up to 28 days.

Batch Shake Testing

The batch shake testing technique which was used to generate data presented in this report was based on published procedures to evaluate sorption and desorption of PCDDs to/from soils.

Experiments Involving Water/Methanol Mixtures

Batch experiments involving water/methanol mixtures were conducted in 1 ml conical glass centrifuge tubes.

Tubes were dosed by direct addition of soil or aquifer material (0.2-1.0 gm), liquid phase and solute (delivered by direct dosing of stock solutions). A liquid-phase volume of 12-ml was added to the tube except for experiments involving PCP solute, in which case the tubes were filled completely with liquid phase.

Experiments conducted to evaluate the sorption of PCDDs in the presence of PCP and CB were performed at concentrations from 1-10% of solubility.

After dosing, the tubes were placed horizontally on a shaking table and were shaken for 15 minutes every hour. Contact periods ranged from 2 hr to 30 days and varied according to the type of experiment (kinetic/equilibrium) and the soil-solute-liquid phase system under study. Following contact, tubes were removed from the shaking table and centrifuged at $2,000 \times g$ for 10 minutes to achieve adequate separation of liquid and solid phases.

Water-Phase Experiments

Two batch procedures were utilized to generate isotherm data for the sorption of $T_4\text{CDD}$ from water by soil 91. Both sets of experiments were conducted using 50-ml round bottom glass centrifuge tubes fitted with Teflon-lined screw caps. Soil and water doses to the tubes were approximately 50 mg and 40 ml.

PCP Screening Experiments

Preliminary experiments were conducted to validate mass balances and

centrifugation procedure used to evaluate sorption of PCP.

Using general batch shake test procedures mass balance experiments were conducted with and without soil to assess recovery of PCP.

Kinetic Evaluations

Time series experiments involving sorption of PCP from water by soils 91 and 96 and sorption of P₅CDD and O₈CDD by the two aquifer materials were conducted to determine the contact time necessary to attain sorption equilibrium and to qualitatively evaluate sorption kinetics.

Experiments involving PCP were conducted by using 0.3 g of soil and a PCP dose such that initial concentration in the liquid phase was 0.035 µg/ml. Liquid volume in these experiments was 15-17 ml as necessary to completely fill the centrifuge tube in order to minimize volatile losses of PCP into the headspace. Tubes were contacted for various times and prepared in triplicate for each contact periods.

Experiments involving aquifer material utilized contact periods of 2-72 hr. These experiments were performed at a f_s of 0.65 for O₈CDD. P₅CDD and O₈CDD were chosen on the basis of known kinetic data for surface soils which indicated that these PCDDs bound the kinetic behavior of all PCDDs studied.

Saturated-Flow Soil Column Testing

Saturated-flow soil column testing was performed to validate the use of the column techniques for estimating the K_D of the PCDDs. These column techniques were then applied to study the sorption of PCDDs in the presence of PCP and CB.

These soil column experiments used either a glass column (2.5 cm x 25 cm) fitted with an adjustable plunger, to accommodate variable soil masses in the column, or a stainless steel column (0.48 cm x 10 cm).

Column Packing

The glass column was slurry packed by adding a known mass of soil (15-25 g) to roughly 20 ml of liquid phase and slowly pouring portions of the slurry into the top of the column. Solvent was allowed to flow from the column by gravity, and small amounts of slurry or fresh solvent were continuously added to the top of the column to maintain a liquid level above the soil at all times.

The steel column was dry packed with a known mass of soil (2-3g) with the aid of a vacuum pump.

Pore Volume Determination

Carbon 14 labeled methanol and ³H labeled water were used as inert tracers for determination of the hydraulic detention volume (HDV) of the soil column.

Solute Retention Experiments

Pulsed input of the radiolabeled solute similar to that used to evaluate column HDV was used in column retardation experiments. A plot of effluent sample concentration versus cumulative effluent volume was prepared, and the solute retention volume was determined from the center-of-mass of the effluent solute peak.

Results and Discussion

Solubility Determinations

The results of experiments to determine the solubility of P₅CDD, H₆CDD, H₇CDD and O₈CDD in methanol are summarized in Table 1.

Values of σ_s determined from the solubility data for each of the PCDDs and for PCP are also listed in Table 1. These values represent the slope of the log-linear relationship between the log of the mole fraction solubility and the volume fraction cosolvent.

Sorption to Surface Soils

The time series experiments suggest that equilibrium for sorption of PCP to soil 91 was achieved in less than one day of contact, while a 30-day contact period was necessary for equilibrium when soil 96 was used.

Table 1. Summary of Results for Solubility Determinations for PCDDs and PCP in Water/Methanol Mixtures

| | Measured Solubility, mg/L | | σ_s |
|--------------------|---------------------------|---------------------|------------|
| f_3 | 0.50 | 1.0 | |
| T ₄ CDD | | | |
| Mean | | 10.6 | 6.25 |
| St. Dev. | | 0.5 | |
| n | | 33 | |
| P ₅ CDD | | | |
| Mean | 0.10 | 52 | 6.09 |
| St. Dev. | 0.2 | 2 | |
| n | 18 | 6 | |
| H ₆ CDD | | | |
| Mean | | 20 | 7.01 |
| St. Dev. | | 2 | |
| n | | 15 | |
| H ₇ CDD | | | |
| Mean | | 24 | 7.35 |
| St. Dev. | | 2 | |
| n | | 12 | |
| O ₈ CDD | | | |
| Mean | | 4.0 | 7.35 |
| St. Dev. | | 0.6 | |
| n | | 56 | |
| PCP | | | |
| Mean | 3.1x10 ³ | 180x10 ³ | 3.8 |
| St. Dev. | 0.6 | | |
| n | 9 | | |

Table 2. Summary of Isotherm Parameters Determined for Sorption of PCP by Soils 91 and 96

| | Volume Fraction Methanol, f_s | | | | |
|----------------------|---------------------------------|-------------------|-------------------|------|-------|
| | 0.0 | 0.25 ^a | 0.25 ^a | 0.5 | 0.75 |
| Soil 91 | | | | | |
| K_D , mL/g | 18 | 4.5 | 5.0 | 1.1 | |
| r^2 | 0.999 | 0.93 | 0.93 | 0.69 | |
| n | 12 | 13 | 14 | 7 | |
| pH ^b | 7.0 | 6.5 | 6.9 | 6.5 | |
| $K_{m,oc}$, mol/g | 150 | 33 | 37 | 6.9 | |
| $\log(K_{m,oc})$ | 2.18 | 1.52 | 1.57 | 0.84 | |
| Soil 96 | | | | | |
| K_D , mL/g | 180 | 96 | | 12 | 2.0 |
| r^2 | 0.96 | 0.98 | | 0.98 | 0.60 |
| n | 14 | 15 | | 15 | 8 |
| pH ^b | 6.6 | 6.3 | | 6.2 | 6.0 |
| $K_{m,oc}$, mol/g | 130 | 61 | | 6.5 | 0.87 |
| $\log(K_{m,oc})$ | 2.11 | 1.78 | | 0.81 | -0.06 |
| Molar Volume, mL/mol | 18.0 | 20.5 | 20.5 | 24.1 | 29.8 |

^aReplicate isotherms for soil 91 at f_s of 0.25 were determined for contact periods of 2 days and 4 days, respectively.

^bpH is the value of the pH in solution at the end of the contract period.

Table 3. Summary of K_{obs} Values Determined for Sorption of P_5 CDD, H_6 CDD, H_7 CDD and O_8 CDD by Soil 91 from Water/Methanol Mixtures

| | Volume Fraction Methanol, f_s | | |
|----------------------------|---------------------------------|------------------|------------------|
| | 0.75 ^a | 0.9 ^b | 1.0 ^c |
| Molar Volume, mL/mol | 29.8 | 37.9 | 40.4 |
| P_5CDD | | | |
| K_{obs} , mL/g | 1.7 | 0.20 | 0.072, 0.057 |
| $K_{m,oc}$, mol/g | 8.6 | 0.79 | 0.27, 0.21 |
| $\log(K_{m,oc})$ | 0.93 | -0.10 | -0.57, -0.68 |
| H_6CDD | | | |
| K_{obs} , mL/g | 3.6 | 0.23 | 0.10, 0.092 |
| $K_{m,oc}$, mol/g | 18 | 0.91 | 0.38, 0.35 |
| $\log(K_{m,oc})$ | 1.3 | -0.04 | -0.42, -0.46 |
| H_7CDD | | | |
| K_{obs} , mL/g | 4.8 | 0.40 | 0.12, 0.11 |
| $K_{m,oc}$, mol/g | 24 | 1.6 | 0.45, 0.41 |
| $\log(K_{m,oc})$ | 1.38 | 0.20 | -0.35, -0.39 |
| O_8CDD | | | |
| K_{obs} , mL/g | | 0.82 | 0.21, 0.19 |
| $K_{m,oc}$, mol/g | | 3.2 | 0.79, 0.71 |
| $\log(K_{m,oc})$ | | 0.51 | -0.10, -0.15 |

^aExperiments were conducted at a column flow rate of 8 mL/hr (pore velocity of 13.5 m/day), with p_B of 1.4 g/mL and ϵ of 0.79.

^bExperiments were conducted at a column flow rate of 8 mL/hr (pore velocity of 0.77 m/day), with p_B of 1.8 g/mL and ϵ of 0.51.

^cExperiments were conducted at column flow rates of 12 mL/hr and 20 mL/hr (pore velocities of 1.78 and 2.96 m/day), respectively, with p_B of 1.75 g/mL and ϵ of 0.33.

Equilibrium isotherm data for the sorption of PCP by soils were generated by batch techniques at f_s of 0.0, 0.25 and 0.5 and for soil 96 at f_s of 0.75. The results of regression analysis of the isotherm data obtained for all f_s studied are summarized in Table 2.

The K_{obs} values for sorption of PCP by soil 91 were also estimated from column experiments.

The $\log(K_{m,oc})$ values for sorption of PCP by soils 91 and 96 plotted against f_s agree with the results obtained from batch and column techniques over the entire range in f_s studied.

Sorption of T_4 CDD from Water

The value of $\log(K_{oc})$ determined from the experiment involving unwashed soil

and a contact period of 48 hours was 6.44, while the value of $\log(K_o)$ determined from the experiment involving prewashed soils and a contact period of ten days was 6.66.

The value of $\log(K_{oc})$ of 6.67 determined by the second procedure corresponds to a value of $\log(K_{m,oc})$ of 5.4. The experimental value of the water phase partition coefficient is in good

agreement with the value predicted by log-linear extrapolation of the water/methanol data, namely 5.30. Based on this observation, it appears that for T₄CDD the cosolvent theory applies over the entire range of f_s , 0.0-1.0 for water/methanol mixtures. This provides strong support for the validity of this theory to PCDDs and other highly hydrophobic organic contaminants, and also provides support for the use of log-linear extrapolation to estimate water-phase K_{oc} values for PCDDs by using data generated from water/methanol mixtures.

Sorption of PCDDs from Mixtures of Water and Methanol

Linear sorption isotherms were observed for all PCDDs studied. The K_D values for the four PCDDs are generally comparable (ranging from 1.8-3.8 ml/g) and do not show the expected trend of increasing with increasing hydrophobicity of the PCDD.

The results of column studies used in sorption experiments are presented in Table 3.

The values of K_D and K_{obs} determined for the PCDDs by batch and column techniques, respectively were normalized on f_{oc} converted to molar units by dividing by liquid-phase molar volume. The results of the batch experiments determined in the present study are in general agreement with the log-linear relationship based on the data of other investigators. The results obtained by column techniques were consistently lower than expected from the log-linear relationship of the batch data only.

The relatively low values of K_{obs} in comparison to K_D were believed to be attributed to non-attainment of local equilibrium within the soil column for the flow rates utilized.

Sorption of PCDDs in the Presence of PCP and CB

The effect of the presence of PCP on the sorption of PCDDs was evaluated by batch and column techniques.

Batch experiments were conducted to generate sorption isotherm data for O₈CDD with both soils at PCP concentrations of 25 and 200 ppm. Contact periods of 2 and 36 days were utilized for soils 91 and 96, respectively. For both soils and both PCP concentrations, the sorption of O₈CDD in the presence of PCP was roughly 30% of the sorption of O₈CDD in the absence of PCP.

Column experiments were conducted for P₅CDD, H₆CDD and H₇CDD using soil 91, with three liquid phases; 1) f_s of 0.75, 2) f_s of 0.75 and a PCP concentration of

1000 ppm, and 3) f_s of 0.75 and a CB concentration of 10 ml/L. For each PCDD studied, the lowest K_{obs} values were observed for the solvent/CB system. The K_{obs} for both solvent/CB and solvent/PCP systems were consistently below K_{obs} for the solvent only. These normalized values show that PCDD sorption generally decreased by 25% in the presence of PCP and 50% in the presence of CB.

Column experiments were also conducted for all PCDDs at f_s of 0.9 with and without PCP present. The results for all PCDDs indicate that there was generally no significant change in K_{obs} in the presence of PCP relative to values in the absence of PCP at a f_s value of 0.9.

The reduced sorption of PCDDs in the presence of cosolutes may be explained by a number of factors, including the effect of the cosolute on the solubility of PCDDs and/or the effect of the cosolute on PCDD-soil organic matter interactions. However, it is suspected that the reduced sorption of PCDDs in the presence of the cosolutes may be explained in terms of either the effect of soil-phase cosolute on the soil-phase activity coefficients of the PCDDs or the results due to the competition between the sorbed cosolutes and PCDDs. This speculation would support the observation that the effects become more pronounced at lower f_s because greater soil-phase concentrations of the cosolutes would be expected via sorption as f_s decreases.

Sorption by Aquifer Materials

Linear isotherms were observed for all PCDDs for f_s values of 0.25 and 0.65 with the exception of T₄CDD and O₈CDD.

Comparison of the experimental data points for the aquifer materials with the data for the surface soils, and their corresponding regression equations, indicates that values of $\log(K_{m,oc})$ for both sorbents are well described by a single curve for T₄CDD, H₆CDD and H₇CDD. For P₅CDD, the experimental values of $\log(K_{m,oc})$ for the aquifer materials at each f_s are significantly greater than those determined from surface soil. For O₈CDD, the experimental values of $\log(K_{m,oc})$ for the aquifer materials are slightly below those predicted for the surface soils.

The general agreement between values of $\log(K_{m,oc})$ for the aquifer materials and the surface soils for PCDDs suggests that f_{oc} alone is the dominant factor determining the extent of sorption for highly hydrophobic organic contaminants such as PCDDs, presumably because the

organic sorption is sufficiently strong to dominate the weaker sorption to minerals.

Desorption From Surface Soils

From limited data, it appears that the sorption of PCDDs from the surface soils into water/methanol mixtures may be reversible, but that desorption is characterized by very low rates.

Preliminary experiments conducted to assess batch and column techniques for the study of sorptive transport of PCDDs through soils in the presence of diesel fuel, were found to be infeasible, owing to the formation of multiple phases. These experiments suggested that relatively stable water/methanol/diesel fuel emulsions were readily transported through the soil column. Further, although the soil column had been apparently flushed of diesel fuel at a high relative velocity, it was observed that the column had a residual capacity to retain significant amounts of diesel fuel which was released from the column as a stable emulsion at low liquid-phase flow rates.

Conclusions

The sorption and desorption of PCDDs by surface soils and the sorption of PCDDs by aquifer materials has been investigated by using batch shake testing and saturated-flow soil column techniques. Experiments were conducted using water and water/methanol mixtures and two model codisposed materials (pentachlorophenol (PCP) and chlorobenzene (CB)).

Sorption isotherm data were generated by batch techniques to evaluate the sorption of T₄CDD from water by soil 91. A contact period of 10 days, and a water prewash procedure which was used to remove nonseparable suspended particles (NSP) from the water phase, appeared to be adequate for evaluating an equilibrium K_D value which was not biased by the inadvertent sampling of NSP during liquid phase analysis. A linear sorption isotherm was obtained which indicated that K_D was 30,600 ($\log(K_D) = 4.49$). A value of $K_{m,oc}$ of 2.58×10^5 ($\log(K_{m,oc}) = 5.41$) was determined by dividing this K_D value by f_{oc} and by the molar volume of water. This corresponds to a value of $\log(K_{m,oc})$ of 5.30 predicted by log-linear extrapolation of K_D data generated by other investigators for T₄CDD and soils 91 and 96 and water/methanol mixtures. This observation provides support for the applicability of the cosolvent theory to the sorption of PCDDs to soils from water/methanol mixtures over the entire

range in f_s from 0.0-1.0, and provides justification for log-linear extrapolation using data generated for water/methanol mixtures to predict equilibrium water-phase K_D values for PCDDs and other highly hydrophobic organic contaminants.

The effect of the presence of PCP on the sorptive transport of PCDDs through soils was studied by using batch and column techniques, in which the liquid phase consisted of water/methanol mixtures ranging in f_s from 0.5-0.9 and containing PCP at concentrations ranging from 1-10% of solubility. These experiments indicated that the sorptive retention of PCDDs by soils was reduced by about a factor of 3 when PCP was present in the liquid phase to that observed in the absence of PCP.

The effect of the presence of CB on the sorptive transport of PCDDs through soils was studied by using column techniques, in which the liquid phase consisted of water/methanol mixtures ranging in f_s from 0.75-0.9 and a CB concentration of 10 mL/L. These experiments indicated that the sorptive retention of PCDDs by soils was reduced by a factor of 2 in the presence of CB at an f_s of 0.75 relative to that observed in the absence of CB. Experiments to evaluate the sorption of PCDDs by aquifer materials included an assessment of sorption kinetics and equilibrium K_D s. The results of these experiments suggested that a two-day contact period was sufficient to achieve sorption equilibrium for all PCDDs studied for these low carbon soil materials. Sorption isotherm data were generally linear, and equilibrium K_D s, when converted to K_m (partition coefficient), were log-linearly related to f_s in accordance with the cosolvent theory. When K_m values were normalized on f_{oc} of the aquifer material, the resulting $K_{m,oc}$ values were in general agreement with $K_{m,oc}$ values determined for surface soils from the Times Beach, MO area. It is suspected that the agreement between aquifer material and surface soil sorption for PCDDs indicates that sorption to organic carbon is sufficient to mask sorption to mineral surfaces.

Experiments to evaluate the desorption of PCDDs from surface soil were conducted by batch techniques, in which PCDDs were previously sorbed by soil for thirty days prior to the initiation of the desorption experiments. The results of these experiments suggested that desorption appeared to be generally reversible but was limited by kinetics, with roughly 50-90% of reversible-desorption equilibrium being attained within a 30-day contact period.

Recommendations

Additional research in six areas of the transport of PCDDs and related contaminants through soils is recommended:

1. *Sorption of PCDFs.* No data have been reported on the sorptive partitioning of polychlorodibenzofurans (PCDFs). High-purity standards of these contaminants are now available in radiolabeled form, and it is suggested that issues relevant to sorptive partitioning be investigated using several PCDF congeners.

2. *Sorption from Water/Methanol Mixtures.* The sorption of PCDDs as a function of volume fraction cosolvent (f_s) for water-miscible cosolvents is generally well understood. However, further research is necessary to better understand solubility and sorption behavior at low f_s (e.g., f_s below 0.05-0.1). This work should be conducted using PCDDs and PCDFs as well as slightly less hydrophobic contaminants, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Research should also be initiated to evaluate the cosolvent effects attributed to ethylene glycol, a water-miscible solvent which is relevant to the manufacturing process of PCP and thus relevant to waste sites contaminated by PCDDs.

3. *Sorption in the Presence of Codisposed Materials.* Additional research is needed to better understand the sorption of PCDDs and related contaminants in the presence of codisposed materials. Three groups of codisposed materials are important. The first group consists of slightly soluble solvents. Much is known regarding the sorption of hydrophobic contaminants in the presence of miscible cosolvents such as methanol and acetone, but little is known regarding the effect of immiscible solvent such as methylene chloride, benzene, and aniline. The second group consists of slightly soluble solids. For example, the effect of the presence of 2,4,5-trichlorophenol and terpenes, as well as PCP, at low f_s should be evaluated. The third group consists of oil/carrier liquids. There is a significant requirement to further understand the movement of oil through soils, and the manner in which oil movement affects the sorptive transport of PCDDs and codisposed materials. Thus, research should be conducted to evaluate the sorptive transport of oils, oils and PCP, and oils, PCP and terpenes, as well as the sorptive transport of PCDDs in the presence of these materials. This research should focus on evaluating the relative contributions to transport attributed to dissolved oil constituents versus oil

droplets and oil/water emulsions, including water-phase sorption-desorption dislodging of entrapped droplets, and potential for emulsion formation.

4. *Sorption of PCDDs in the presence of colloids.* Much is known regarding the sorptive transport of moderately hydrophobic organic contaminants in the presence of colloidal organic matter, and this work suggests that colloids can substantially increase the mobility of organic contaminants through soils. Additional work is necessary to extend this research to include highly hydrophobic organic such as PCDDs.

5. *Sorption of PCDDs by aquifer materials.* Additional research is needed to evaluate the relative mineral contribution to sorptive transport of PCDDs and similar organics through low f_{oc} aquifer materials. This research should focus on organic contaminants that are very hydrophobic, such as PAHs and PCBs, as well as PCDDs. The research should include a variety of sorbents to enable a better fundamental understanding of the relative effects of K_{ow} , mineral surface area, and f_{oc} on sorption to low- f_{oc} sorbents.

6. *Desorption of PCDDs.* Desorption of PCDDs from soils at low f_s in the presence of codisposed materials, such as oil, should be investigated. This research should include development of a model which incorporates desorption kinetics to enable better prediction of the movement of PCDDs through soils under real-world conditions.

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The complete report, entitled "Assessment of the Potential for Transport of Dioxins and Codisposed Materials to Groundwater," (Order No. PB 89-166 607/AS; Cost: \$21.95, subject to change) will be available only from:

National Technical Information Service

5285 Port Royal Road

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Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

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