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Summary Report

Determination of Pollutant Distribution and Movement by Controlled Laboratory Experiments

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The goal of this project was to directly observe and evaluate the subsurface movement and distribution of selected volatile organic compounds, particularly components of petroleum fuels, through controlled laboratory experiments. Sand tank, column, and batch-type laboratory experiments were employed to measure the effect of specific variables associated with underground contamination events. The sand tank experiments were carried out to characterize leak sources and contaminant movement. Leak rate, petroleum type, soil type, temperature, and backfill configuration were examined to determine which materials and methods produced results that had the best application to field and regulatory situations. The spatial and temporal propagation of leaking fluids was measured and recorded by several methods including gas chromatography and time-lapse photography. The spatial and temporal measurements of vapor concentrations were mathematically modeled using two-dimensional inverse methods. Diffusion parameters of Effective Diffusion Coefficient, D_e, and Sorption-corrected Porosity, A*, were determined, with D_e for gasoline generally ranging from approximately 0.0024 cm^2/sec for clay to 4.4 cm^2/sec for pea gravel. Calculated diffusion parameters were used to predict three-dimensional propagation of vapors, and results were compared with field and laboratory values. Additionally, the sand tanks were used to measure the distribution of light non-aqueous phase liquids around the water table during conditions of vertical water table movement. Some of the results from the research indicate that the distribution of hydrocarbons in these situations is more extreme than previously recognized, and that entrapped diesel fuel in sands ranged from 33 to 67 liters/cubic meter. Dimensional analysis as well as color-density dye studies were also performed on the physical modeling.

In other work, plastic columns equipped with fiber optic sensors were used to measure diffusion parameters from gasoline and diesel sources. One-dimensional mathematical modeling was applied to observed concentration values to calculate diffusion parameters. The data were compared with the findings of other researchers, and the reproducibility of results was evaluated. Generally, experimental reproducibility was quite good, and the fiber optic probes showed a large dynamic range to maximum responses of 22,000 to 35,000 ppmv for gasoline and 43,000 to 62,000 ppmv for diesel fuel. Field operation of fiber optic devices was also evaluated.

Sorption studies of selected organic compounds on various soils were carried out in enclosed steel chambers. The chambers allowed measurement of sorption in soil media configured to simulate actual field conditions. Soil moisture content, temperature, soil type, vapor pressure, and soil organic content were incrementally varied. Moisture content of an unsaturated soil was generally the most important variable affecting sorption in vadose zone materials. Partitioning coefficients were

found to be relatively independent of the degree of saturation when gravimetric water contents exceeded 2-5%. These findings correlate well with sorption-corrected porosity values obtained from inverse mathematical modeling of physical sand tank and column models. While some compounds displayed sorption fitting a Freundlich isotherm, dry soils typically exhibited nonlinear isotherms and finite sorption kinetics. Hydrogen-bonding compounds also displayed nonlinear isotherms and finite sorption and desorption kinetics in the presence of water. A recalcitrant fraction was observed to be resistant to desportion, especially with certain compounds in clays.

Goals and Objectives of the Research

The goal of this project was to directly observe and evaluate the subsurface movement and distribution of selected volatile organic compounds, particularly components of petroleum fuels, through controlled laboratory experiments. Sand tank, column, and batch-type laboratory experiments were used to measure the effect of specific variables associated with underground contamination events. Many of the studies centered on gaseous migration, and the variables examined included moisture content, soil type/grain size, leak rate, temperature, and vapor densities.

Objectives included: 1) establishing a visual record through time-lapse photography of the movement of organic liquids through unsaturated porous media, 2) augmentation of this visual record with quantitative measurements of vapor concentration and migration, 3) observation of effect of the water table on the distribution of non-aqueous phase liquids, and 4) the quantitation of sorptive partitioning of the gaseous phase organics onto and into porous material and water. This work provided a video which has been extensively used for educational purposes, publications in refereed journals, publications in conference proceedings, and several master's theses.

Research Approach

There were three components of the research approach: sand tank experiments, column experiments, and batch-type sorption experiments. As the work progressed, the research approach underwent review, at times partial revision, and augmentation to optimize results.

Sand tank experiments were carried out to characterize leak sources and contaminant movement. Experiments were first performed to vary the tank filling procedure to allow the best reproducibility possible in the experimentation. Leak rate, petroleum type, soil type, temperature, and backfill configuration were examined to determine which materials and methods produced results that had the best application to field and regulatory situations. In another aspect of experimentation, it was quickly discovered that the sand tank environment was inadequate to simulate vapor extraction remediation; gaseous advection on the small sand tank scale suffered boundary interferences which were too severe to proceed using the smaller volume tanks proposed in this work.

In vadose zone leak simulations performed in the sand tanks, liquid and vapor measurements were made. The spatial and temporal propagation of leaking fluids was measured and recorded by several methods including gas chromatography and time lapse photography. Contour maps of the distribution of leaked fluids were constructed. The spatial and temporal measurements of vapor concentrations were mathematically modeled using two-dimensional inverse methods. Diffusion parameters of Effective Diffusion Coefficient, D_e, and Sorption-corrected Porosity, A*, were determined. Calculated diffusion parameters were used to predict three-dimensional propagation of vapors, and results were compared with field and laboratory values. Additionally, the sand tanks were used to measure the distribution of light non-aqueous phase liquids around the water table during conditions of vertical water table movement.

Column experiments took on several forms. Experiments were performed to measure the flux of organic compounds across the water table. A glass column equipped with side ports was used to determine the feasibility of this approach. Additionally, plastic columns equipped with fiber optic sensors were used to measure diffusion parameters from gasoline and diesel sources. One-dimensional mathematical modeling was applied to observed concentration values to calculate diffusion parameters. The data were compared with the findings of other researchers. The reproducibility of results was evaluated.

Sorption studies of selected organic compounds on various soils were carried out. Experiments in enclosed steel chambers were conducted. The chambers allowed measurement of sorption in soil media configured to simulate actual field conditions. Soil moisture content, temperature, soil type, vapor pressure, and soil organic content could be controlled and incrementally varied.

Summation of Individual Areas of Research

Sand Tank Experiments

Through controlled laboratory experiments, the effect of specific variables associated with underground contamination events was examined with time-lapse photography and quantitative measurements of vapor concentration and migration. The research approach had several subcomponent activities. Initial sand tank experiments examined the tank filling procedure with the objective to allow the best reproducibility possible in the experimentation. Although several procedures were used, the most reproducible filling technique involved the gravity release of soil into a tank through a overhead funnel equipped with sieves. This methodology is visually shown in a short video (available from authors), and is described in James et al. (1996a).

Another subcomponent of the sand tank activities involved the measurement of liquid and gaseous propagation from a petroleum hydrocarbon leak. The goal of this endeavor was to characterize leak propagation, hopefully in a way amenable to mathematical modeling. This undertaking was successful. The spatial and temporal propagation of leaking fluids was measured and recorded by the methods discussed previously. Contour maps (in regards to the distribution of leaked fluids) were constructed. Time-lapse movement of liquid migration is shown in the video tape. The spatial and temporal measurements of vapor concentrations were mathematically modeled to determine values of coefficients and porosity. For example, D_e for gasoline was generally found to range from approximately 0.0024 cm^2/sec for clay to 4.4 cm^2/sec for pea gravel. Calculated diffusion parameters were used to predict three-dimensional propagation of vapors, and results were compared with field and laboratory values. Mathematical modeling of gaseous movement is detailed in Chaganti (1990), Johnson and Kreamer (1994), Kreamer et al. (1996), and Squire (1996). Calculated gaseous diffusion parameters showed conformance to the few values available in the literature. Optimal leak rates, petroleum types, soil types, temperatures, and backfill configuration were examined to determine those procedures allowing efficient and safe experimental techniques, while retaining applicability to real field and regulatory situations.

In another aspect of experimentation, the sand tanks were used to measure the distribution of light non-aqueous phase liquids (LNAPLs) around the water table during conditions of vertical water table movement. This aspect of research is shown in the video, and is reported in James et al. (1996a, 1996b), Rajagopalan (1995), and Sabapathi (1993). Results indicated that the distribution of hydrocarbons in these situations is more excessive than previously recognized, and that entrapped diesel fuel in sands ranged from 33 to 67 liters/cubic meter. Dimensional analysis and color-density dye studies were also performed on the physical modeling.

Column Studies

Column studies were undertaken to measure the flux of organic compounds across the water table and capillary fringe, and to determine diffusion parameters from gasoline and diesel sources. A glass column equipped with side ports was used to determine the feasibility of vertical flux measurements. This line of experimentation was basically unsuccessful. Slow diffusion in the aqueous phase (approximately 5 orders of magnitude slower than gaseous diffusion), coupled with advection created by withdrawal of water and vapor during sampling, created results with little reproducibility. Spacing of the side ports was also too wide, and the perturbation of the soil column created by syringe sample withdrawal appeared to be largely responsible for the lack of reproducible results. To gain some understanding of hydrocarbon movement and distribution near the water table, studies of vertical LNAPL distribution around moving water tables were initiated in sand tanks as described earlier (James et al., 1996a, 1996b; Rajagopalan, 1995; Sabapathi, 1993).

Additionally, plastic columns equipped with fiber optic sensors were used to measure diffusion parameters from gasoline and diesel sources (Kreamer et al., 1996). One-dimensional mathematical modeling was applied to observed concentration values to calculate diffusion parameters. The data were compared with the findings of other researchers and the reproducibility of results was evaluated. Generally, experimental reproducibility was quite good, and the fiber optic probes showed a large dynamic range to maximum responses of 22,000 to 35,000 ppmv for gasoline and 43,000 to 62,000 ppmv for diesel fuel. Field operation of fiber optic devices was also evaluated (Kreamer et al., 1996).

Sorption Batch Testing

Sorption studies of selected organic compounds on various soils were carried out in enclosed steel chambers (Fairley, 1993; Houston and Kreamer, 1989; Oja and Kreamer, 1992; Kreamer et al., 1994; Schmeltzer, 1993; Steinberg et al., 1994; Steinberg and Kreamer, 1992, 1993). The chambers allowed measurement of sorption in soil media configured to simulate actual field conditions. Soil moisture content, temperature, soil type, vapor pressure, and soil organic content could be controlled and incrementally varied.

Moisture content of an unsaturated soil was generally the most important variable affecting sorption in vadose zone materials. Partitioning coefficients were found to be relatively independent of the degree of saturation when gravimetric water content exceeded 2 to 5%. These findings correlate well with sorption-corrected porosity values obtained from inverse mathematical modeling of physical sand tank and column models. While some compounds displayed sorption fitting a Freundlich isotherm, dry soils typically exhibited nonlinear isotherms and finite sorption kinetics. Hydrogen-bonding compounds also displayed nonlinear isotherms and finite sorption and desorption kinetics in the presence of water. A recalcitrant fraction was observed to be resistant to desorption, especially with certain compounds in clays.

Research Accomplishments

This research has contributed to many publications, reports, master's theses, a widely distributed video, and provided supporting information for many workshops and conferences.

Publications

Houston, S.L., Kreamer, D.K. and R. Marwig, 1989. A Batch-Type Testing Method for Determination of Adsorption of Gaseous Compounds on Partially Saturated Soils. *Geotechnical Testing Journal, ASTM,* March 1989, p.3-10.

Houston, S.L. and D.K. Kreamer, 1989. Effect of Temperature on the Potential for Gaseous Adsorption by Partially Saturated Soils, *Engineering Geology and Geotechnical Engineering*, Watters (ed.) p.357-361. A.A. Balkema/ Rotterdam/Brook, **Hardbound,** ISBN 90 6191 878 2.

James, D. E, Kreamer, D.K., Sabapathi, J. and V. Rajagopalan, 1996a. Effects of Vertical Water Table Fluctuations on LNAPL Distribution in Porous Media, 1. Effects of Varying Water Table Rise Rates in Initially Dry Sand. *J. of Contaminant Hydrology.* Accepted 1995 for Publication in 1996.

James, D. E, Kreamer, D.K., Rajagopalan, V. and S.K. Steinberg, 1996b. Effects of Vertical Water Table Fluctuations on LNAPL Distribution in Porous Media, 2. Effects of Varying Grain Size in Initially Moist Sands. *J. of Contaminant Hydrology.* Accepted 1995 for Publication in 1996.

Johnson, T.E. and D.K. Kreamer, 1994. Physical and Mathematical Modeling of Diesel Fuel Liquid and Vapor Movement in Porous Media. *Ground Water*, Vol. 32, No. 4., p. 551-560.

Kreamer, D.K., Brown, C. and D. Sloop, 1996. Report on the Suitability of PetroSense® Probes for Leak Detection at Contaminated Sites. Las Vegas, NV, March 1996.

Kreamer, D.K., Oja K.J., Steinberg, S.M., and H. Phillips, 1994. Vapor Adsorption of a Solvent on Quartz Sands of Varying Grain Size. *Journal of Environmental Engineering, ASCE,* Vol. 120, No. 2, p. 348-358.

Kreamer, D.K., Starr, K., Cogent, S., Johnson, T. and H.A. Phillips, 1990. Gasoline Vapor Compound Ratios as a Tool to Locate Subsurface Fuel Leaks; from *Minimizing Risk to the Hydrologic Environment*, *Selected Papers from the American Institute of Hydrology Conference*, Las Vegas, Nevada, March 13-15, 1990, p.243-249. **Softbound.**

Kreamer, D.K. and K.J. Stetzenbach, 1990. Development of a Standard, Pure-Compound Base Gasoline Mixture for Use as a Reference in Field and Laboratory Experiments. *Ground Water Monitoring Review,* Spring 1990, p.135-145.

Oja, K.J. and D.K. Kreamer, 1992. (Invited Paper). The Effect of Moisture on Adsorption of Trichloroethylene Vapor on Natural Soils. *Proceedings of the U.S. Environmental Protection Agency and National Center for Ground Water Research Symposium on Soil Venting,* April 29 - May 1, 1991, Houston, TX, p 13-28. **Softbound.**

Steinberg, S.M., Fairley, J. and D.K. Kreamer, 1994. Slow Desorption of Toluene from Several Ion-Exchanged Montmorillonites. *J.Soil Contamination* 3(3):249-264.

Steinberg, S.M. and D.K. Kreamer, 1992. Determination of Sorption Isotherms for Volatile Organic Compounds on Soil using Gas Chromatography. *Structure, Bonding, and Kinetics at Mineral Surfaces Symposium*, American Chemical Society, April 5-10, 1992, San Francisco.

Steinberg, S.M. and D.K. Kreamer, 1993. Persistence of Several Volatile Organic Compounds in a Low Organic Carbon, Calcareous Soil from Southern Nevada. *Proceedings of the National Symposium on Measuring and Interpreting VOCs in Soils: State of the Art and Research Needs*. U.S. Environmental Protection Agency, Jan.12-14, Las Vegas, NV.

Steinberg, S.M. and D.K. Kreamer, 1994. Determination of Sorption Isotherms for Volatile Organic Compounds on Unsaturated Calcareous Soil from Southern Nevada Using Inverse Chromatography. *Environmental Science and Technology*. Vol. 27, No. 5, 883-888.

Videos

Two short videos were produced: Physical Modeling of Subsurface Fuel Migration by Controlled Laboratory Tests (10 mins) and Effects of Vertical Water Table Fluctuations on LNAPL Distribution (14 mins). These videos have been shown at approximately 65 conferences and workshops. On request, they have been distributed to approximately 700 people.

Theses

Master's theses supported are:

a) from the University of Nevada, Las Vegas:

- Fairley, J., 1993. Desportion Hystoresis in Five Ion Exchanged Montmorillonites. Master of Science Thesis. Water Resources, Department of Geoscience, UNLV.
- Rajagopalan, V., 1995. Influence of Grain Size of a Porous Medium on the Movement of Diesel Fuel Due to Water Table Fluctuations. Master of Science thesis. Water Resources, Department of Geoscience, UNLV.
- Sabapathi, J., 1993. Effect of Water Table Fluctuations on Petroleum Contamination Distribution. Master of Science Thesis. Water Resources, Department of Geoscience, UNLV.
- Schmeltzer, J., 1993. Effects of Soil Moisture, Soil Carbonate and Organic Matter Content on Vapor Phase Sorption of Volatile Organic Compounds Using Inverse Gas Chromatography. Master of Science Thesis. Water Resources, Department of Geoscience, UNLV.
- Squire, J., 1996. Effect of Unsaturated Zone Soil Moisture Content on Vapor Phase Pollutant Propagation in Controlled Laboratory Experiments. Master of Science Thesis. Water Resources, Department of Geoscience, UNLV.
- Starr, K., 1993. Sand Tank Modeling of Hydrocarbon Migration Design, Construction, and Testing. Master of Science Thesis. Water Resources, Department of Geoscience, UNLV.

b) from Arizona State University

- Chaganti, S., 1990. Vapor Transport Modeling in Simulated Leaking Underground Storage Tank Environments. Master of Science Thesis. Department of Civil Engineering, ASU.
- Johnson, T., 1991. Modeling Diesel Vapor Transport In a Simulated Underground Environment. Master of Science Thesis. Department of Civil Engineering, ASU.

Instruction/Technology Transfer

Conferences, lecture series, training, and workshops where information from this research has been presented include:

- Superfund University Training Institute (SUTI) - approximately 6 courses, U.S. EPA
- DNAPL National Workshop Series - 10 courses, U.S. EPA
- Monitoring Well Design National Series - 10 courses, U.S. EPA
- Landfills RCRA Subtitle D National and International Series - 15 courses, U.S. EPA
- U.S. Bureau of Land Management Hazardous Waste Training - 5 courses. U.S. BLM
- Pesticide Managers Training, UC Davis Extension - 5 courses, U.S. EPA
- National Educational courses - 25 courses, National Ground Water Association and Environmental Education Enterprises
- Many National and International Conferences

Project Conclusions and Recommendations

This work supports the contention that vapor monitoring around underground storage tanks is beneficial to leak detection efforts. Problems with the even, radially outward propagation of gases can exist. For example, this research has shown that dry materials tend to sorb vapors, and a recalcitrant fraction, resistant to desorption, can be formed. Organic materials in soils tested did not demonstrate sorptive capacities that would make them effective barriers to vapor migration. Fiber optic probes showed some promise as monitoring devices in varying degrees of vapor saturation.

In sand tank models, colorimetric analysis of dyes, added to leaked fuels, showed correlation to measured hydrocarbon concentrations, but the disparity is generally too great between dye color and hydrocarbon concentration to rely on for quantitative work in scientific studies. In experiments run with air-dried porous material overlying a LNAPL pool floating on a water table, unexpected isolation of product occurred in situations where the water table was raised. The distribution of entrapped hydrocarbon was observed to be much more irregular than similar situations where the vadose zone was originally moist. This suggests the potential for unusual hydrocarbon entrapment when the water table rises in conditions where vapor extraction (enhanced volatilization) techniques have been conducted in an overlying vadose zone. This situation may occur with remediation techniques that involve the combination of dewatering and vapor extraction. Little is known about the physics of interfacial interactions in soils of varying moisture content, and a recommendation from this work is that this be investigated further.

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