

Distinguishing the Contributions of Multiple Sources from a Gasoline Release

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Introduction

The T2VOC model (Falta, et al., 1995) with the T2CG1 conjugate gradient package (Moridis and Pruess, 1995) was used to simulate the motion of gasoline released from a petroleum storage terminal. An aboveground storage tank lost 15.5 m³ of gasoline over a 56-hour period. Plant workers recovered 1.25 m³ of gasoline by removing over 6 m³ of the saturated surface soil. Sixteen years later, the local government remediated the site with the petroleum company bearing the cost. At that time, the local government remediated a neighboring downgradient site. The second site also had decades-old gasoline releases. In both cases, the remediation method was the excavation and replacement of the contaminated soil. A dispute arose as to who should pay for the cleanup of the second site. Resolving the dispute using field data alone was not possible, since much of the contaminated soil was removed during the remediation process. There was also a dispute concerning the groundwater flow direction at the time of the releases due to a subsequent engineering project of a major scope.

To protect itself from potential liability, the first petroleum company used T2VOC to determine the potential distance and extent of contamination resulting from their release. This project utilized the unique capabilities of T2VOC because the simulation was to include the full history of the gasoline spill in three dimensions. This history included the release itself, the removal of some surface soil, the movement of gasoline through the unsaturated zone, the depression of the water table and the forward motion of the free-phase plume until it was overcome by capillary forces, and the degradation of the plume. Clearly this problem required a simulator that could handle vadose zone hydrology as well as groundwater flow. It had to be able to handle several phases simultaneously.

Procedure

Soil borings taken before the excavation revealed the stratigraphy. A permeable sand was divided by a thin silt layer. The lower sand was underlain by dense glacial clay. The core from one boring had been preserved. A petrophysical laboratory used samples from this boring to determine the unsaturated flow parameters for use in the Parker functions (Parker, et al., 1987). These parameters are the irreducible water saturation S_m , an exponential parameter n , and the parameter α . Porosity and permeability of the strata were measured as well. These values are presented in Table 1. A 5,415-block grid was devised for a 95 x 75 m² area that was 9.5 m deep. The grid blocks were 5 x 5 m squares of varying thickness. The grid was oriented in the

direction of groundwater flow in the vicinity of the release. A cross section of the grid is presented as Figure 1.

Local meteorological data made it possible to determine the air pressure, the deep percolation rate, and the moisture content of the soil. Groundwater monitoring data allowed the determination of boundary conditions. Groundwater flowed in a southeasterly direction, and curved more eastward in response to the subterranean topography as one moved away from the point of the release. Dynamic steady state was determined in one dimension for the corners of the domain. These columns were used to obtain dynamic steady state in two dimensions for the four sides. Achieving dynamic steady state in three dimensions with T2VOC was challenging because the silt layer was near the water table.

Next, the gasoline release was simulated. Eye witness accounts of the release and records of product loss helped in the construction of the loss scenario. The release was a spray of gasoline that continued undetected for up to 56 hours. Using an evaporation model, it was conservatively estimated that 20% of the gasoline was lost to evaporation (Seginer, 1967; Sutton, 1953; Mackay and Matsugu, 1973). The mass of the remaining gasoline was introduced to the model by placing a "COM3" source in the GENER block for a surface grid block at the location of the release.

Benzene and xylene were used as surrogates for the complex mixture of hydrocarbons that constitute gasoline. Chemical properties were mostly taken from Reid, et al. (1987). The model predictions were not very sensitive to the differences between these two constituents. The biodegradation rates were taken from land treatment data (API, 1984). The lower end member was taken from the error bar on the degradation rate of benzene. This value was divided by 10 to account for the reduced oxygen content at depth.

Runs were conducted with several choices for the length of the release event, and the final results were not sensitive to the length of the time of the release. However, the model ran more smoothly with a longer release time. Therefore, 56 hours was chosen. A model run for a 56-hour release using benzene as the surrogate resulted in a column of grid blocks extending to the water table whose pores were over 50% saturated with "gasoline." The water table was depressed, as expected from the literature (van Dam, 1967).

The SAVE file from the release scenario was used to depict the initial conditions of the long simulation covering the 20 years that followed. One modification to this INCON file was that the VOC concentration was zeroed out in all phases in the surface block where the release took place. This was done to simulate the replacement of some of the contaminated sand by the plant workers. There was a string of warm-start runs to cover the ensuing period of 20 years.

Results

In the simulation, soil gas transport ceased to be important after the initial months. Over the next five years, the free-phase plume moved 40 m from the source. Most of the longitudinal motion of the free-phase plume occurred in the first three years (Figure 2). The final two years of free-phase migration was transverse (Figure 3). During this time, the size of the free phase increased in boxes with a y coordinate of L, while the free phase decreased on the upgradient side. The free-phase plume contaminated no new grid blocks after the fifth year. Beginning with the sixth year, the plume began to shrink, beginning from the upgradient side. The free-phase plume disappeared entirely after the twelfth year. The dissolved-phase plume continued to

decrease until the end of the twentieth year, when the maximum concentration of surrogate was less than 5 $\mu\text{g/L}$ everywhere in the domain.

Discussion

The forward motion of the free-phase plume was halted when the size of the gasoline phase in the pores became too small at the leading edge to overcome capillary forces. Thus the prediction by the T2VOC model was governed by the values chosen for the unsaturated flow parameters. Biodegradation played a lesser role in stopping the plume. Biological action limited the increase in concentration in the dissolved phase ahead of the free phase. This action is only important when the plume is moving slowly and marginal increases in hydrocarbons would cause a phase change. Biodegradation became more important in later stages of the simulation, when the free-phase plume was halted.

Note that the geometry of the grid played a role in the evolution of the free-phase plume in the latter stages of its motion (years 3 to 5). The drop in the silt layer at row M created a permeability trap for the gasoline at a point in the plume's history in which the size of the free phase was becoming small (Figure 4). This effect is artificial, because the silt layer at the site slopes gently, without a "stair step." The grid contained such a step to account for the slope within the limits of the discretization. Without such a trap, the plume would not have widened at row L. It may have traveled somewhat farther along its longitudinal axis, until the size of the free phase at the leading edge was too small to continue to overcome the surface tension of the grains. That the free phase traveled as far as it did is a tribute to the low value (0.09) of the irreducible water saturation, S_m . The sand at this site was very well sorted. This was particularly true of the upper sand.

Although the subject of surrogate chemicals is a wide topic worthy of a study in itself, it is important to consider. Benzene was chosen as our surrogate, even though it constitutes only a few percent of most gasoline. The monoaromatic hydrocarbons are an important component of gasoline, but xylene is more abundant than benzene, and the isomers of trimethylbenzene are more abundant than xylene. Branched alkanes are most abundant, led by isopentane. To exactly simulate a release such as this one would require a program that allowed multiple volatile constituents. The more mobile constituents of gasoline are the most prone to biodegradation and evaporation. In a release that began as a spray on a warm week in the summer, the gasoline that actually entered the subsurface environment would have had its composition skewed to the heavier end, and would have moved more slowly. It would lose its more mobile constituents first. The less mobile, less degradable constituents would have governed the latter history of the plume. Thus it is likely that the free-phase plume would not have traveled as far as the pure benzene, but it would have survived longer than 12 years.

There are simple methods of estimating the extent of a free-phase plume by hand calculations. Van Dam (1967) presented one such method. His method produces the diameter of a circular plume with a capillary tongue in which the principles of multiphase flow dictate stabilization of the plume. Using this simple method, the plume was computed to have a diameter of 50 m. The plume simulated by T2VOC had a longitudinal extent of 45 m when the small (5 m) upgradient segment is included (Figure 2). Given the simplicity of the van Dam model, this agreement should be considered good.

There was also a good match between the location of the free-phase plume predicted by T2VOC and field data. The local government excavated soil for which benzene, toluene, ethylbenzene, or xylene were detectable above stringent state standards. During the excavation, measurements were made on the boundaries to determine if further removal was required. That the boundaries of the excavation and the predicted maximum extent of the free-phase plume matched is a further confirmation of the T2VOC modeling effort.

The T2VOC model allows a user much more than an estimate of the free-phase plume extent. It gives an investigator a window into the history of the evolution of the plume as a whole, with all of its phases and components. It also helps one delineate the contribution of the various transport mechanisms, such as soil vapor transport by diffusion and density-driven flow and account for losses to the atmosphere, as well as the motion of free-phase and dissolved-phase plumes. T2VOC allows a user to bring in as much topographic detail as the study warrants (and the CPU-size allows).

Conclusions

The T2VOC model simulated the motion of a gasoline plume in a specific stratigraphic setting. The maximum extent of the free-phase plume predicted by T2VOC matched the location of the excavation and the size predicted by hand calculations using a formula derived from the generalized three-phase flow equations (van Dam, 1967). This match helped establish the model results and its detailed account showing the motion of hydrocarbons in every phase. The T2VOC model demonstrated the limited extent of the motion of the release. This helped vindicate the petroleum company that employed it of responsibility for contamination beyond its property line.

References

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Table 1. Petrophysical Properties of the Site Soils

Soil Type	Grain Density kg/m ³	Porosity -	Permeability (h) m ²	Permeability (v) m ²	Unsaturated Flow Parameters		
					S _m -	n -	α l/m
Upper Sand	2635	0.399	5.961E-12	6.336E-12	0.013	1.521	101.94
Silt	2660	0.429	1.086E-15	1.678E-13	0.09	1.424	4.1
Lower Sand	2650	0.401	1.697E-12	1.697E-12	0.06	1.84	5.2
Clay	2740	0.395	5.645E-16	5.645E-16	0.36	1.86	3.2

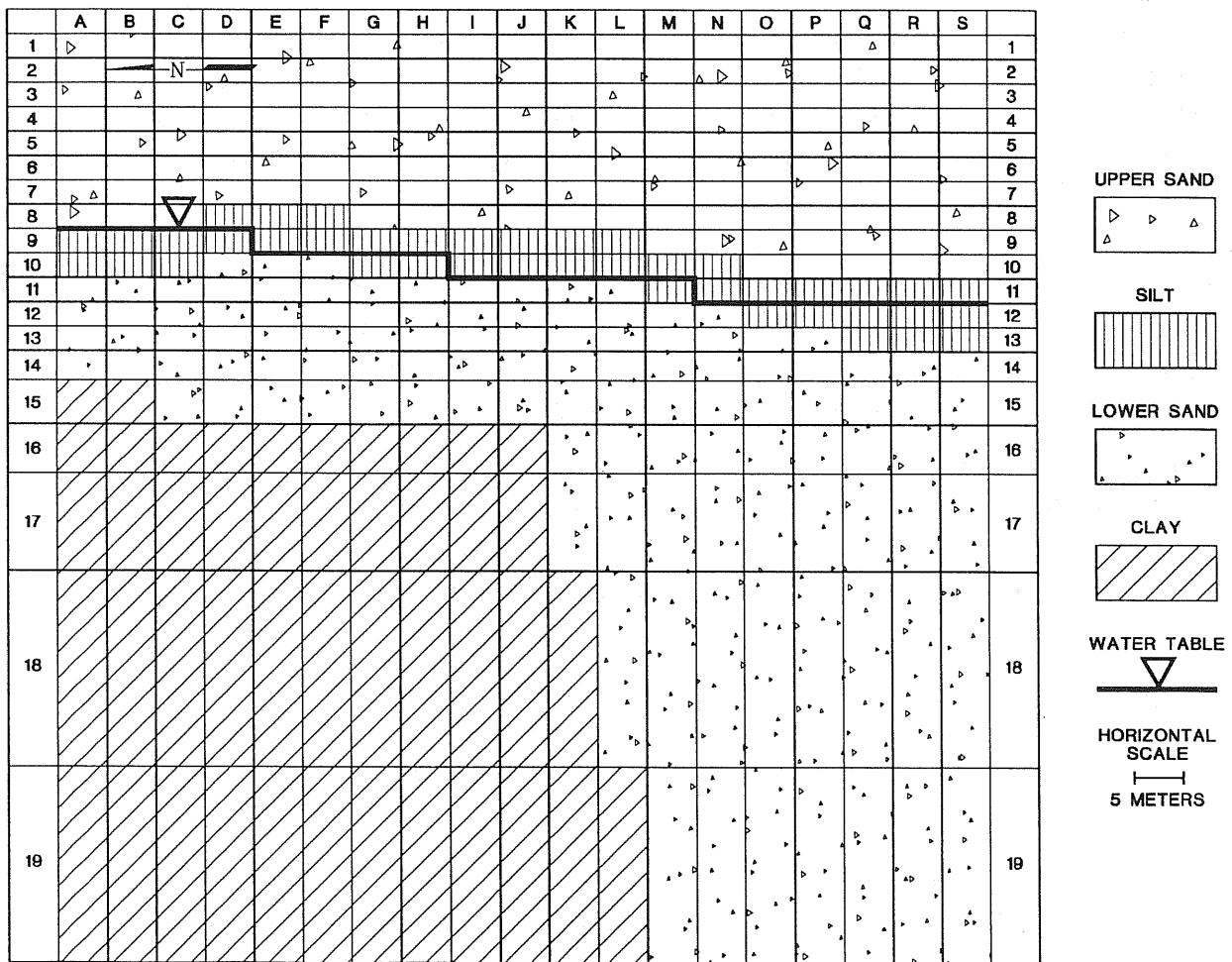


Figure 1. Cross Section of the Three-Dimensional Grid.

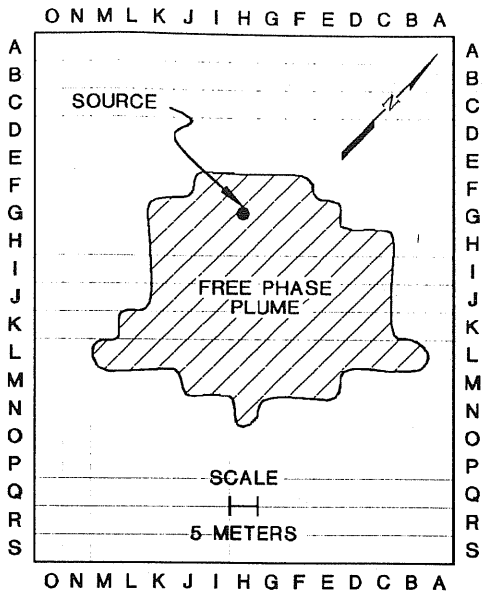


Figure 2. Extent of the Free-Phase Plume at 3 Years.

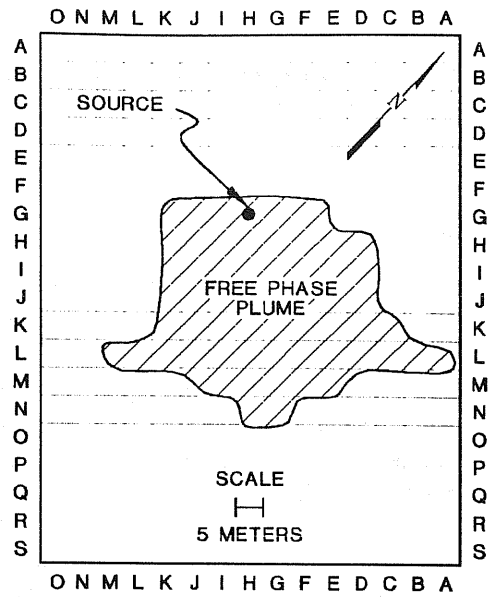


Figure 3. Maximum Extent of the Free-Phase Plume at 5 Years.

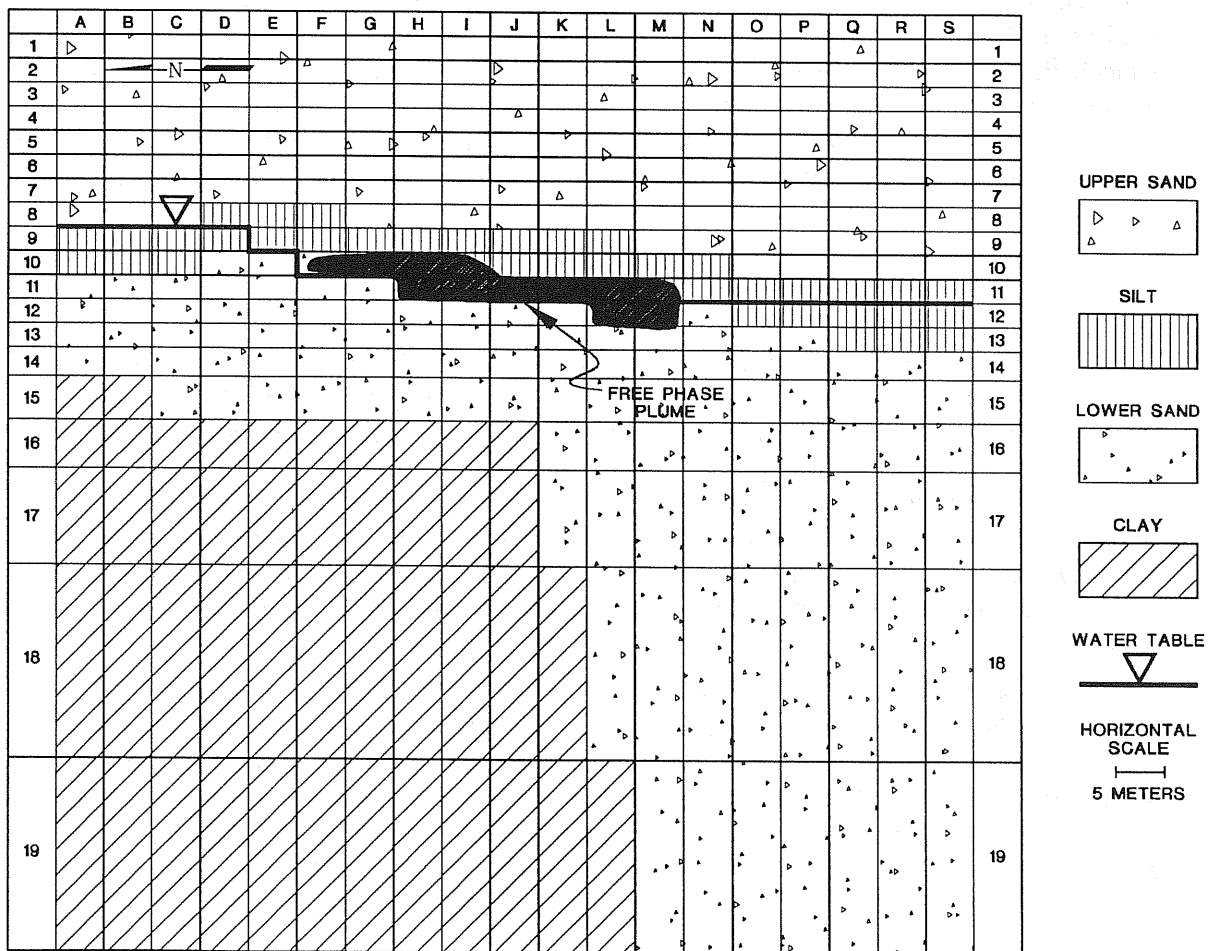


Figure 4. Extent of the Free-Phase Plume at 5 Years, Vertical Cross Section at H.