Project Number: 05

Start: 06/01/94
End: 05/31/95

Title: Evaluation of Thermodynamic Limitations to Pump-and-Treat Remediation of Petroleum-Contaminated Sites

Investigator: Dr. William R. Wise

Focus Category: Groundwater, Solute Transport, Treatment

Congressional District: Third

Descriptors: Groundwater Quality, Leaching, Oil-Water Interfaces, Organic Compounds, Pollutants, Solute Transport, Thermodynamics, Underground Storage Tanks

Problem and research objectives:

Contamination of groundwater supplies by petroleum is common. The principle cause of the contamination is leakage of underground storage tanks. The leakage of these tanks is occurring because of rust, poor connections in the plumbing, or spills. Currently many polluted groundwater supplies are treated by pump-and-treat technology (water is flushed through the aquifer to sweep or carry the petroleum out of the area). This technology is a slow process and relies on the solubility of the petroleum compounds in water. Because petroleum is hydrophobic there is minimal solubilization into water. To date, most research has focused on the kinetic effects of removing petroleum with water using pump-and-treat technology. The research on the kinetic effects of petroleum partitioning has shown that water must be in contact with the contamination for a minimal amount of time before it becomes saturated with the petroleum. The objective of this project was to investigate the possible thermodynamic limits of removing petroleum from groundwater supplies. Determining the thermodynamic limits of petroleum saturation in water is critical to assessing whether pump-and-treat technology is an effective or practical means of removing the contamination.

The objective of this research was to measure the partitioning of petroleum compounds in water and develop the thermodynamic theory to explain it. With this knowledge it will be possible to determine if pump-and-treat or some other technology would be the most effective in removing contamination. These objectives are to be reached by experimentally measuring the solubility of carefully prepared petroleum solutions in water, developing the thermodynamic model and then testing the model using an actual petroleum sample.
Methodology:

As stated previously, the objective of the experimental work is to measure the partitioning of petroleum components in water as a function of the oil phase composition. This was to be done with two, three, four, six, and eight components. The final test was to measure the partitioning of petroleum components in an actual gasoline sample and determining if the developed thermodynamic theory was able to predict the partitioning of the various components. However, there was a problem with measurement of petroleum components in water. The GC did not have good resolution of octane and there was a limit on the sensitivity. This section will describe the experimental procedures followed for testing the partitioning of two component mixtures in water as a function of oil phase composition.

Petroleum components tested were ethylbenzene, o-Xylene, and octane. Chemicals were bought from Fisher Scientific and Aldrich Chemical companies, the purity was high (98+% grades). Oil mixtures were prepared in 25 and 100 ml volumetric flasks. The flasks were cleaned by rinsing three times each with methanol and water respectively followed by a heat treatment at 180 to 250 degrees centigrade for 30 to 60 minutes. The heat treatment removed any possible residual oil contamination and dried the flasks. Two component oil mixtures were prepared by pipetting known volumes into the flasks of one compound and filling with the second compound of interest. Dilutions of 10% or lower were prepared by pipetting volumes from a more concentrated solution and diluting with solvent (in this case the solvent is octane).

40 ml EPA vials were used to mix the water-oil solutions. The EPA vials were glass with Teflon coated silicone septa. The vials were filled with 30 ml of high purity water and 10 ml oil or petroleum sample. This was done to remove the head space and prevent volatilization of the components. The jar was then placed on a jar tumbler for not less than 24 hours. Tumbler speed was set at 50 or approximately 35 rpm.

After mixing, the vials were removed and placed in a centrifuge with the cap down. The vials were rotated at 2200 rpm for not less than 2 hours at 20°C ± 1 degree. Following centrifugation, the samples they were placed in a constant temperature room at 21°C until tested. Using a centrifuge allowed more rapid separation of phases and testing of samples than letting the samples stand over several hours or days.

Gas chromatography (GC) was used to measure concentrations of petroleum components in the water. The GC used was a Varian model 3400 with a DB 624 Megabore capillary column, equipped with a flame ionization detector (FID). The temperature program consisted of the following parameters, a 2 min hold at 40°C followed by a temperature ramp to 160°C at 10 degree/min, and a 50°C/minute ramp to 220°C. Between each sample a purge cycle was run to remove any carryover in the column. The purge cycle consisted of a temperature ramp to 220°C at 50°C/minute with a 2 to 5 minute hold time.

To ensure that there was not outside contamination of oil products interfering with the test the water used was high purity obtained with a Barnstead E-Pure system. The system consisted of four cartridge filters and a 0.2 micron filter at the outlet. No water was used unless it had a resistivity of 17.3 megohms or greater. This water was
used in all phases of the testing from rinsing to dilution.

Once the solutions were place in 40 ml vials they were not opened. Samples were tested by inserting a Hamilton 1 ul 7000 series syringe needle into the septa and withdrawing a full 1 ul. Before testing, the syringe needle was rinsed with the test solution two times followed by inserting the needle into the vial and drawing the solution in and out of the needle 3 to 5 times to remove trapped air. The sample was then taken and immediately injected into the GC. After each injection the syringe needle was rinsed in methanol and water at least three time in each, respectively. Tests showed very little carry over in the needle. When testing a given batch, concentrations were tested starting with the least concentrated solute and progressing steadily to the most concentrated.

Standard curves were made to calibrate the area counts on the GC to the fraction of saturation. The standard or calibration solutions were prepared by saturating pure water with the compound of interest. This was done by mixing the two phases for 24 to 48 hours. The mixtures were then centrifuged for two to three hours and slowly poured into a separatory funnel. The saturated water was then taken and diluted to obtain a series of concentrations from 0.0001 to 100 percent of saturation for each of the petroleum compounds of interest. Each sample was tested a minimum of three times on the gas chromatograph.

Principal findings and significance:

Using the GC with FID detector and DB 624 Megabore column, octane was detectable at concentrations of 50 to 100 percent saturation in water; EB and o-Xylene were detectable from 0.01 to 100 percent of saturation in water. At saturation the three compounds were detected with poor reproducibility. Octane was the least reproducible, up to 300 percent variation, while EB, and o-Xylene were reproducible to within 8 to 20 percent. The saturated readings were greater than the values predicted using calibration curves. It is believed that variation was caused by micro emulsions (microscopic droplets of pure compound suspended within another phase) of the oil in the water phase. As sample was withdrawn a significant number of these droplets would enter the needle, thus increasing test values. For octane the problem of reproducibility could also be caused by poor separation of the octane and water molecules in the column and thus poor FID detection.

Measurements of partitioning of EB/Octane and o-Xylene/Octane into water as a function of concentration showed that both EB and o-Xylene obeyed Henry’s Law only at very low concentrations, and showed a positive deviation as the concentration is was increased. This same deviation from Henry’s Law was observed for a three component mixture of EB and o-Xylene in Octane (EB and o-Xylene were mixed in octane on an equal volume basis). These experiments show the non-linear nature of partitioning of aromatic compounds between the organic and aqueous phases. This further suggests that there is a thermodynamic limit to practical removal of groundwater contamination using pump-and-treat technology.

M.S. Thesis: Karl E. Lambert, Civil Engineering, M. C. E., August 1995