Final

Addendum

One-Dimensional Thermal Remediation Treatability Study

Montrose Chemical Superfund Site

Los Angeles County, California

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1.0 Objectives of Thermal Remediation Treatability Study Addendum

Thermal remediation (steam injection or electrical resistance heating) are under consideration for recovery of chlorobenzene DNAPL for the Montrose Superfund site in Los Angeles County, California. A treatability study for thermal remediation, consisting of one dimensional steam injection column experiments and measurement of the physical properties of site DNAPL as a function of temperature, has been completed, and the report was finalized on July 12, 2006. Subsequent to the completion of the work plan for the treatability study, it was agreed that changes in the physical properties of the Montrose DNAPL as the chlorobenzene evaporated - leaving behind a DNAPL that was enriched in DDT - would be measured. The physical properties measured at Kerr Lab included density, viscosity, and surface and interfacial tension. Each of these was measured as a function of the percent (by mass) of the DNAPL that had evaporated, and the temperature. The boiling point of the DNAPL was to be measured at a different laboratory facility to be contracted by Montrose.

2.0 Methods Development

Standard methods are not available for measuring the physical properties of DNAPL as part of the liquid evaporates. Thus, initially laboratory trials were undertaken to develop methods to be used to make these measurements. It was desired to keep the methods as close to standard methods as possible, while allowing accurate measurement of the properties as a function of temperature after a known mass of the DNAPL had evaporated. Each of these methods development tests performed is described below. The methods actually used to measure the properties are described in the Methods section.

2.1 Evaporation Technique and Rate. The purpose of this test was to try to determine a method that can be used to evaporate off the more volatile components of the DNAPL to obtain a sample of the residual for density, viscosity, and surface and interfacial tension measurements. A small amount of DNAPL recovered from well UBT-1 was poured into a 50 ml beaker, and suspended in a water bath at 90°C. Approximately 58% of the initial weight of DNAPL evaporated quickly (in about 3 hours). The residual remaining was a liquid at 90°C, but a solid at room temperature. The residue was a brown/purple color, with white crystals visible. Further attempts to evaporate more of the DNAPL resulted in the loss of an additional 1.6% of the initial mass. An attempt was made to determine the melting point of the residual. At 40°C, the residual was syrup-like; at 35°C it was gelatin-like. An actual melting point was not determined.

2.2 Density Measurements. A method to determine if the density of the DNAPL changes as the volatile fraction evaporates was tested. Ten milliliters (ml) of DNAPL from UBT-1 was poured into a 10 ml graduated cylinder, and the weight of the DNAPL was obtained. The graduated cylinder was suspended in a water bath at 90°C to evaporate the volatile fraction. Periodically it was weighed and a volume reading was taken (after the cylinder at equilibrated to room temperature, which was approximately 24°C) to determine the density as a function of the percent of the DNAPL that had evaporated. Figure 1 is a graph showing the results of this test. The density of the remaining DNAPL increased from 1.1975 gm/ml initially to approximately 1.37 gm/ml after approximately 60% had evaporated. Initially the density increase was small as the sample evaporated; however, the density began to increase more rapidly after about 35%

of the mass had been evaporated. After about 55% had evaporated, the residual was a solid at room temperature. At the time that the test was ended, the evaporation rate was very low (i.e., what remained was mostly non-volatile).

Ten ml graduated cylinders with an accuracy of +/- 0.1 ml are not as accurate as the volumetric flasks (+/-0.03 ml). Thus, this method of determining density as the composition of the DNAPL changes is not as accurate as the method used for density measurements as a function of temperature. However, the results will meet the data quality needs for this project.

2.3 Viscosity Measurements. A method for determining changes in viscosity as the volatile fraction of the DNAPL is removed is desired. Approximately 30 ml of DNAPL from UBT-1 was added to a 50 ml flask, and about 23% of the volatile fraction was allowed to evaporate. Eight milliliters of the remaining liquid was used to measure viscosity as a function of temperature by the method outlined in RSKSOP-273, the same method that was used to measure viscosity as a function of temperature of the original DNAPL in the treatability study. The liquid was then poured back into the beaker, an additional 15% was evaporated off, and another set of viscosity measurements were made. Again after the measurements, the sample was poured back into the beaker and another 14% of the mass was allowed to evaporate off, and the viscosity measurements were repeated. The results are shown in Figure 2. It can easily be seen that removal of 23% of the sample by evaporation had only a small affect on the viscosity of the remaining liquid. After 38% had been evaporated, the residual became a semi-solid at about 45°C, so viscosity measurements were only made at higher temperatures. After approximately 52% of the sample had evaporated, the residual was a semi-solid at about 75°C.

Figure 2 shows that the viscosity increased significantly (even at high temperatures) as more of the volatiles were lost from the sample. The viscosity of liquids is known to decrease exponentially as the temperature increases, and that would likely be the case with these residual liquids also.

2.4 Surface and Interfacial Tension. A method for determining if the surface and interfacial tension of the DNAPL changes as the volatile fraction is removed was desired. An approach essentially identical to that used in the treatability study (RSKSOP-274) was used, but before making the measurements, part of the sample was allowed to evaporate away. For each set of measurements (surface tension and interfacial tension) at a different percent evaporated, a new sample of the DNAPL is obtained.

Figure 3 shows the surface and interfacial tension of DNAPL collected from UBT-1 after 19%, 37%, and 57% had evaporated. The figure shows that the surface tension of the DNAPL increased from 27.7 dynes/cm to 36.1 dynes/cm as the chlorobenzene evaporated off. The interfacial tension, however, remained constant at approximately 11.3 – 11.5 dynes/cm.

3.0 Methods for Physical Properties of DNAPL After Partial Evaporation

3.1 Density measurement. In order to make density measurements on Montrose DNAPL after partial evaporation of chlorobenzene from the DNAPL, a small amount of DNAPL (approximately 20 ml) was placed in a 50 ml beaker, and the weight of the DNAPL was obtained. The beaker was then suspended in a water bath at 90°C and DNAPL was allowed to evaporate. When approximately 20 percent of the mass of the

DNAPL had evaporated, approximately 8 ml of the remaining DNAPL was poured into a weighed graduated cylinder with a ground glass stopper. The cylinder and its contents were equilibrated to 90°C without allowing additional evaporation, and the weight and volume were determined. The cylinder was then equilibrated to 20°C, and the volume was read from the cylinder. From this data, the density at both 20° and 90°C can be calculated for DNAPL after a known percentage of the DNAPL has evaporated. Starting with a fresh DNAPL sample each time, density measurements were also made after approximately 35 and 50 percent of the DNAPL was evaporated.

3.2 Viscosity measurement. In order to make viscosity measurements on Montrose DNAPL after partial evaporation of chlorobenzene from the DNAPL, a small amount of DNAPL (approximately 20 ml) was poured into a 50 ml beaker, and the weight of the DNAPL was obtained. The beaker was then suspended in a water bath at 90°C and DNAPL was allowed to evaporate. When approximately 35 percent of the DNAPL had evaporated, 8 ml was added to a disposable sample container for the Brookfield viscometer, and viscosity measurements were made at temperatures of 60° to 120°C, using a 20°C increment. Starting with a fresh DNAPL sample each time, viscosity measurements were also made after the evaporation of approximately 50 percent of the DNAPL. For these high percentage evaporations, higher temperatures had to be used for the viscosity measurements, as the remaining DNAPL was a solid at increasingly higher temperatures as more of the chlorobenzene evaporated. The maximum temperature used for these measurements was 120°C, as this is approximately the maximum temperature expected in the field during thermal remediation.

3.3 Surface and Interfacial Tension. In order to make surface and interfacial tension measurements on Montrose DNAPL after partial evaporation of chlorobenzene from the DNAPL, a small amount of DNAPL (approximately 20 ml) was poured into a beaker that is used for making these measurements, and the weight of the DNAPL was obtained. The beaker was then suspended in a water bath at 90°C and DNAPL was allowed to evaporate. When approximately 20 percent of the DNAPL had evaporated, the surface and interfacial tension of the DNAPL was measured using the Fisher Tensiometer and the procedure outlined in the RSKSOP-274. Starting with a fresh DNAPL sample each time, surface and interfacial tension measurements were also made after the evaporation of approximately 35 percent and 50 percent of the DNAPL. Only one sample was used for the surface and interfacial tension measurements at each evaporation.

4.0 Results

4.1 Density. Density as a function of the percent mass of DNAPL that had evaporated and temperature is presented in Table 1 and shown in Figure 4. The density increases as the percent evaporated increases, going from approximately 1.22 gm/ml at 20°C when none had evaporated (see Final Treatability Study Report, July 12, 2006) to 1.38 gm/ml when approximately 50 percent has evaporated. This is approximately a 12 percent increase in density with a 50 percent decrease in the overall mass of the DNAPL. The slope of the line for density as a function of temperature appears to increase with increasing percent evaporated, going from 0.00063 – 0.00086 gm/ml/^{o}C at around 20 percent evaporated, to 0.0012 – 0.0014 gm/ml/^{o}C at around 50 percent evaporated. The

DNAPLs as received (none evaporated) decreased in density at a rate of about 0.001 gm/ml/^{o}C.

Table 1. Density of Montrose DNAPL after Partial Evaporation as a Function of Temperature (gms/ml)

Sample/Temperature	20°C	90°C
UBT-1-2		
21% evaporated	1.241	1.197
25% evaporated	1.279[1]	1.274
33% evaporated	1.290	1.226
50.7% evaporated	1.382	1.282
UBT-2		
19.5% evaporated	1.244	1.192
38.5% evaporated	1.323	1.256
49% evaporated		1.274
50.1% evaporated	1.396	
UBE-1		
19.8% evaporated	1.240	1.180
38% evaporated	1.282	1.219
49% evaporated	1.375	1.276
UBT-3		
23% evaporated	1.233	1.181
33.6% evaporated	1.285	1.220
49% evaporated	1.384	1.296

[1]Sample was mostly solid with a small amount of liquid at the top

4.2 Viscosity. Viscosity as a function of the mass of DNAPL that had evaporated and temperature is presented in Table 2 and shown in Figure 5. The data shows that as chlorobenzene is evaporated from the DNAPL, its viscosity increases. The effect of temperature on viscosity is consistent in that all the samples show an exponential decrease in viscosity as the temperature increases, as would be expected. The change in viscosity after the evaporation of approximately 20 percent of the sample was found during Methods Development to be small (almost negligible), thus, this measurement was not repeated, and viscosity measurements concentrated on higher percents evaporated. After the evaporation of approximately 35 percent of the sample, there is a significant increase in the viscosity the residual. The residual was found to be a solid or semi-solid at temperatures up to approximately 40°C, thus, viscosity measurements started at 60°C. At high temperatures, the viscosity becomes approximately the same as the viscosity of the DNAPL before evaporation. However, after the evaporation of about 50 percent of the sample, the viscosity remains higher than the viscosity of the unevaporated sample even at temperatures up to 120°C, which is approximately the highest temperature expected in the field during thermal remediation. With additional evaporation of the sample above 50 percent, it appears that the viscosity will increase substantially, while maintaining the same exponential shape with respect to temperature.

Note that the method used to make the measurements shown in Figure 5 was different from that used during Methods Development in that a fresh sample was

obtained for each percent evaporation tested. It is believed that trying to re-use the original sample after additional evaporation as was done during Methods Development caused errors in the mass of the residual remaining, and thus in the calculation of the percent evaporated. This accounts for the differences in the viscosity measured at a given percent evaporation in Figure 2 from that in Figure 5. The data in Figure 5 are believed to be more accurate than that in Figure 2, and the reproducibility of the data shows this to be the case.

Table 2. Viscosity of Montrose DNAPL as a Function of Percent Evaporated and Temperature (centipoises)

	10°C	20°C	30°C	40°C	50°C	60°C	80°C	90°C	100°C	120°C
UBT-1-2 0% evaporated	2.92 +/- 0.082	2.73 +/- 0.041	2.28 +/- 0.101	2.01 +/- 0.020	2.00 +/- 0.00	2.00 +/- 0.00				
UBT-1-2 40% evaporated						3.66 +/- 0.058	2.88 +/- 0.042		2.22 +/- 0.147	2.00 +/- 0.00
UBT-1-2 55% evaporated							8.65 +/- 0.100		5.57 +/- 0.102	4.05 +/- 0.055
UBT-1-2 60.2% evaporated								21.13 +/- 0.464	15.75 +/- 0.250	9.2 +/- 0.265
UBE-1 0% evaporated	3.28 +/- 0.117	3.08 +/- 0.108	2.56 +/- 0.074	2.34 +/- 0.049	2.04 +/- 0.049	1.97 +/- 0.041				
UBE-1 38% evaporated						3.32 +/- 0042	2.77 +/- 0.004		2.20 +/- 0.105	2.00 +/- 0.00
UBE-1 51% evaporated							5.508 +/- 0.020		3.70 +/- 0.055	3.06 +/- 0.049
UBT-2 37% evaporated						3.04 +/- 0.066	2.29 +/- 0.080		1.92 +/- 0.042	1.90 +/- 0.00
UBT-2 53% evaporated							8.033 +/- 0.103		5.29 +/- 0.074	3.90 +/- 0.055
UBT-1-1 0% evaporated	3.44 +/- 0.038	2.91 +/- 0.049	2.58 +/- 0.076	2.27 +/- 0.082	1.98 +/- 0.026	1.87 +/- 0.041				
UBT-1-1 36% evaporated						4.042 +/- 0.049	3.26 +/- 0.049		2.27 +/- 0.041	1.97 +/- 0.052
UBT-1-1 51% evaporated							6.26 +/- 0.049		4.29 +/- 0.038	3.26 +/- 0.049

4.3 Surface and Interfacial Tension. Surface and interfacial tension data as a function of the amount evaporated at a temperature of 90°C is presented in Table 3 and shown in Figures 3 and 6. Because the methods for measuring surface and interfacial tension were not changed from the methods development phase to the measurement phase, the data in Figure 3 are considered actual data and not just preliminary data. It can be seen that as the percent evaporated increases, the surface tension of the DNAPL increases at 90°C. After evaporation of approximately 55 percent of the DNAPL by weight, the surface tension increases from approximately 27 to 35 dynes/cm. Interfacial tension, however, does not show an increase as chlorobenzene evaporates from the sample, but remains at about 11 – 12 dynes/cm.

Table 3. Surface and Interfacial Tension of the Montrose DNAPL as a Function of Percent Evaporated at 90°C

	DNAPL Surface Tension	Groundwater Surface Tension	Interfacial Tension
UBT-1-2 19.5% evaporated	28.11 +/- 0.13	55.75 +/- 0.49	11.28
UBT-1-2 36% evaporated	31.37 +/- 0.37	56.30 +/- 0.18	11.28
UBT-1-2 56.5% evaporated	36.15 +/- 0.14	54.43 +/-0.23	11.54
UBE-1 17% evaporated	26.85 +/- 0.18	56.98 +/- 0.86	12.23
UBE-1 43% evaporated	31.23 +/- 0.18	51.55 +/- 0.14	12.05
UBE-1 58% evaporated	35.44 +/- 0.16	53.61 +/- 0.28	11.80

5.0 Discussion

Table 4 lists some of the physical properties of chlorobenzene and DDT found in reference materials. It must be noted that although the properties of chlorobenzene appear to be well established, for DDT, a wide range of values for density, solubility, and boiling point can be found in different sources that are available on the Internet. Without knowing which value for density is correct, it is not possible to predict how evaporation of chlorobenzene from the DNAPL will affect the density of the remaining DNAPL. Viscosity would be expected to increase due to the increased percentage of DDT, which is normally a solid with a melting point of 110°C. Melting point is one of the few physical properties of DDT that is reported fairly consistently in reference materials as approximately 109 - 110°C. The high melting point of DDT would suggest that as chlorobenzene is evaporated from the DNAPL, the melting point of the remaining residual would be expected to increase. It is not possible to predict how evaporation of chlorobenzene would affect the surface and interfacial tension of the DNAPL. However, it is known that dissolved solids increases the surface tension of water, thus, an increase in surface tension might be expected as the percent DDT in the DNAPL increases.

The increase in density as the chlorobenzene evaporated, leaving behind a DNAPL enriched in DDT, indicates that the density of DDT is likely greater than that of

chlorobenzene. There is not a linear relationship between percent evaporated and the density (see Figure 1), indicating that there are interactions between the chlorobenzene and DDT molecules that effects the density of the mixture. The obvious dark color of the DNAPL even after 60 percent has evaporated indicates that chlorobenzene was likely still present in the residual DNAPL, and thus the densities measured are not indicative of pure DDT. Figure 4 shows that the slope of the line for density versus temperature changes only slightly as the chlorobenzene evaporates.

As expected, the viscosity of the residual DNAPL increases as the chlorobenzene evaporates, however, the increase in viscosity also is not a linear function of the amount evaporated. The high viscosities as DDT becomes the dominant component of the DNAPL indicates that as thermal remediation proceeds, DDT remaining in the soil will decrease in mobility compared to the DNAPL itself. Thus, it will not tend to be mobilized to other areas, however, it also would not be readily recoverable as a liquid, even at the temperatures used for thermal remediation, as stable displacement by a steam front requires that the liquid being displaced have a viscosity which is no more than three times that of water (Stewart and Udell, 1988).

Based on the known effects of dissolved solids on the surface tension of water, it could have been expected that the surface tension of the residual DNAPL as the chlorobenzene evaporated would increase due to the increased proportion of dissolved solids (DDT) remaining. Indeed, it was found that the surface tension at 90°C increased as the chlorobenzene evaporated, however, the interfacial tension did not. Hunt et al. (1988) derive equations for order of magnitude estimates of the maximum length of ganglion that can be supported in porous media both above [$L_{v,max} \sim 2\sigma_{oa}/r_t g\rho_o$] and below the water table [$L_{v,max} \sim 2\sigma_{ow}/r_t g(\rho_o-\rho_w)$]. In these equations, $L_{v,max}$ is the maximum vertical length of ganglion that can be supported, σ is the tension between two fluids, r_t is the pore throat dimension, g is gravity, and ρ is the density. Subscripts a, o and w indicated air, oil (NAPL), and water phases, respectively. Thus, increases in the density of the DNAPL would tend to reduce the ganglion length that can be supported, and mobilize residual DNAPL. Increases in tension would tend to increase the length of the ganglion that can be supported, and residual DNAPL would remain stable. As the volume of liquid in the ganglion and thus its length decreases (due to evaporation or dissolution of chlorobenzene), the ganglion will become more stable. These equations would indicate that as the chlorobenzene evaporates, the residual DNAPL above the water table is likely to remain trapped in the soil pores, as increases in density are likely to be offset by increases in the surface tension. Small changes in the density difference between the NAPL and water as chlorobenzene evaporates will decrease the maximum ganglion length that can be supported below the water table, reducing the amount of residual DNAPL that can be trapped in soil pores as the chlorobenzene evaporates. However, the volume of DNAPL in the ganglion will be reduced by the loss of the chlorobenzene. From this discussion it can be inferred that existing stable ganglion in the subsurface both above and below the water table will not be mobilized by evaporation of chlorobenzene from the DNAPL.

Table 4. Physical Properties of Chlorobenzene and DDT

	Chlorobenzene	DDT
Specific Gravity or Density	1.1066 at 4°C[a]	1.016 – 1.55 gm/ml at 20°C
Viscosity	0.753 cP at 25°C[b]	
Interfacial Tension	37.4 dynes/cm at 20°C[c]	
Surface Tension	35.97 dynes/cm[c]	
Boiling Point	131.7°C[b]	185°C - ~350°C
Melting Point	- 45°C[a]	110°C[a]
Solubility	490 mg/l at 25°C[b]	

a - Verschueren, 1983
b - Davis, 1997
c - Mercer and Cohen, 1993

6.0 Conclusions

As chlorobenzene is stripped from the DNAPL preferentially by vaporization, it can be expected that the physical properties of the remaining DNAPL will remain fairly constant until more than 20 percent by weight of the DNAPL has evaporated. When more than 20 percent has evaporated, the melting point, density, viscosity, and surface tension of the remaining DNAPL will increase, while its interfacial tension will remain the same. All of these changes must be taken into consideration when assessing any changes in mobility that might occur when the subsurface is heated and chlorobenzene is preferentially evaporated from the DNAPL. Although the DNAPL is a liquid now in the subsurface, as chlorobenzene is removed, higher temperatures will be required for the residual to remain a liquid. Above the water table, increases in density are likely to be offset by increases in surface tension, and the DNAPL is likely to remain trapped in pore spaces. The interfacial tension remains constant as the chlorobenzene is removed, however, the loss of volume of DNAPL will likely offset the increased density, thus the residual DNAPL below the water table is not likely to be mobilized based on these forces. Increases in viscosity will tend to slow any movement if the residual DNAPL were to be mobilized.

In a porous medium undergoing heating, there are also other forces that will come into play that will affect the stability and/or movement of DNAPL, and these forces are to be examined in the experiments to be performed by Dr. Kent Udell.

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6. Surface and interfacial tension of Montrose DNAPL UBE-1 after partial evaporation.

Figure 1. Montrose DNAPL UBT-1 density at 24 C after partial evaporation.

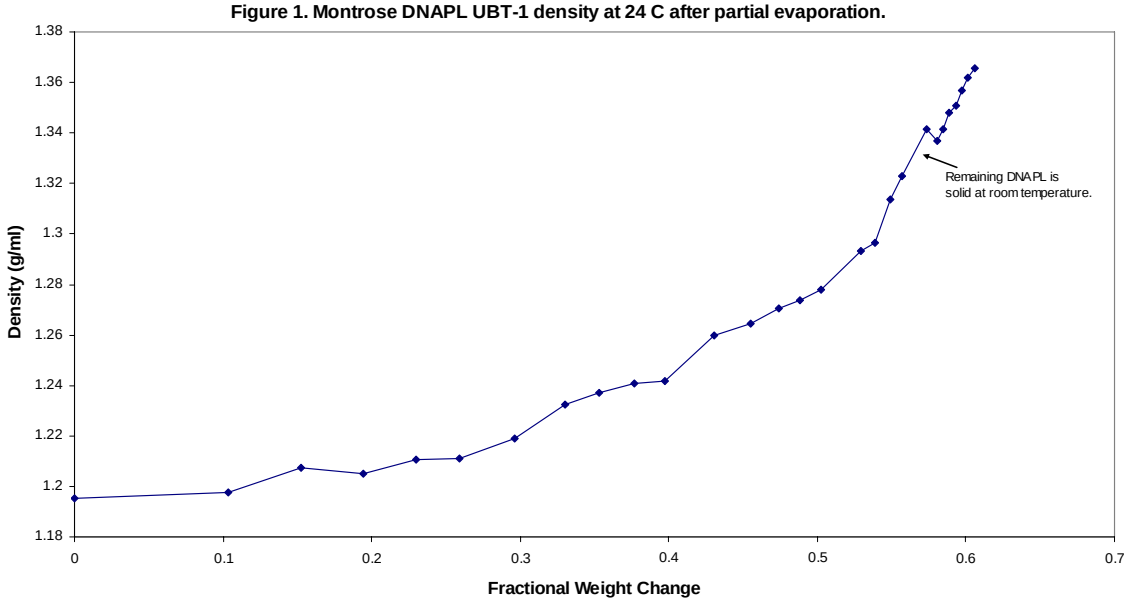

Figure 2. Montrose DNAPL UBT-1 viscosity after partial evaporation as a function of temperature.

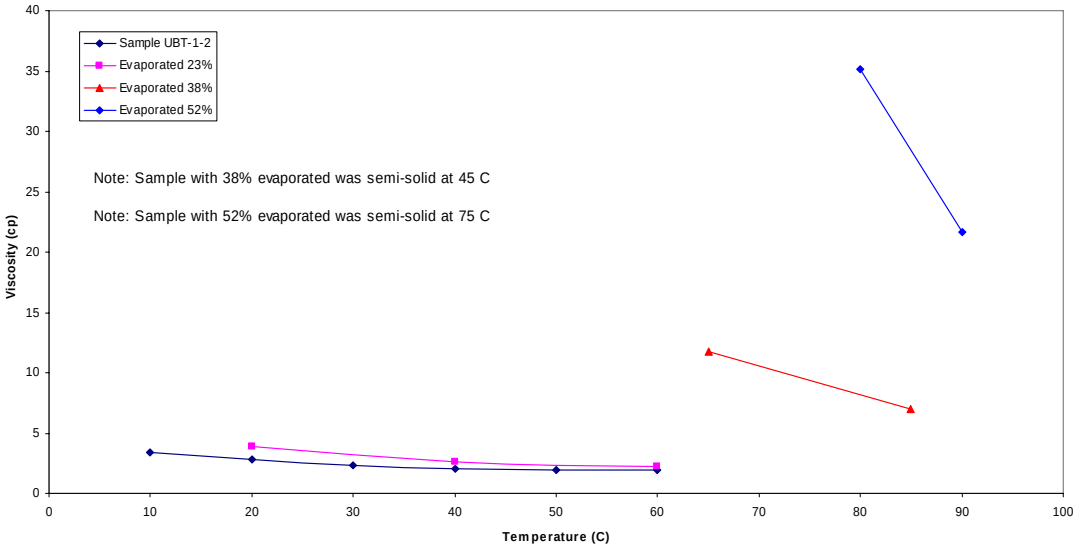

Figure 3. Surface and interfacial tension of Montrose DNAPL UBT-1 after partial evaporation.

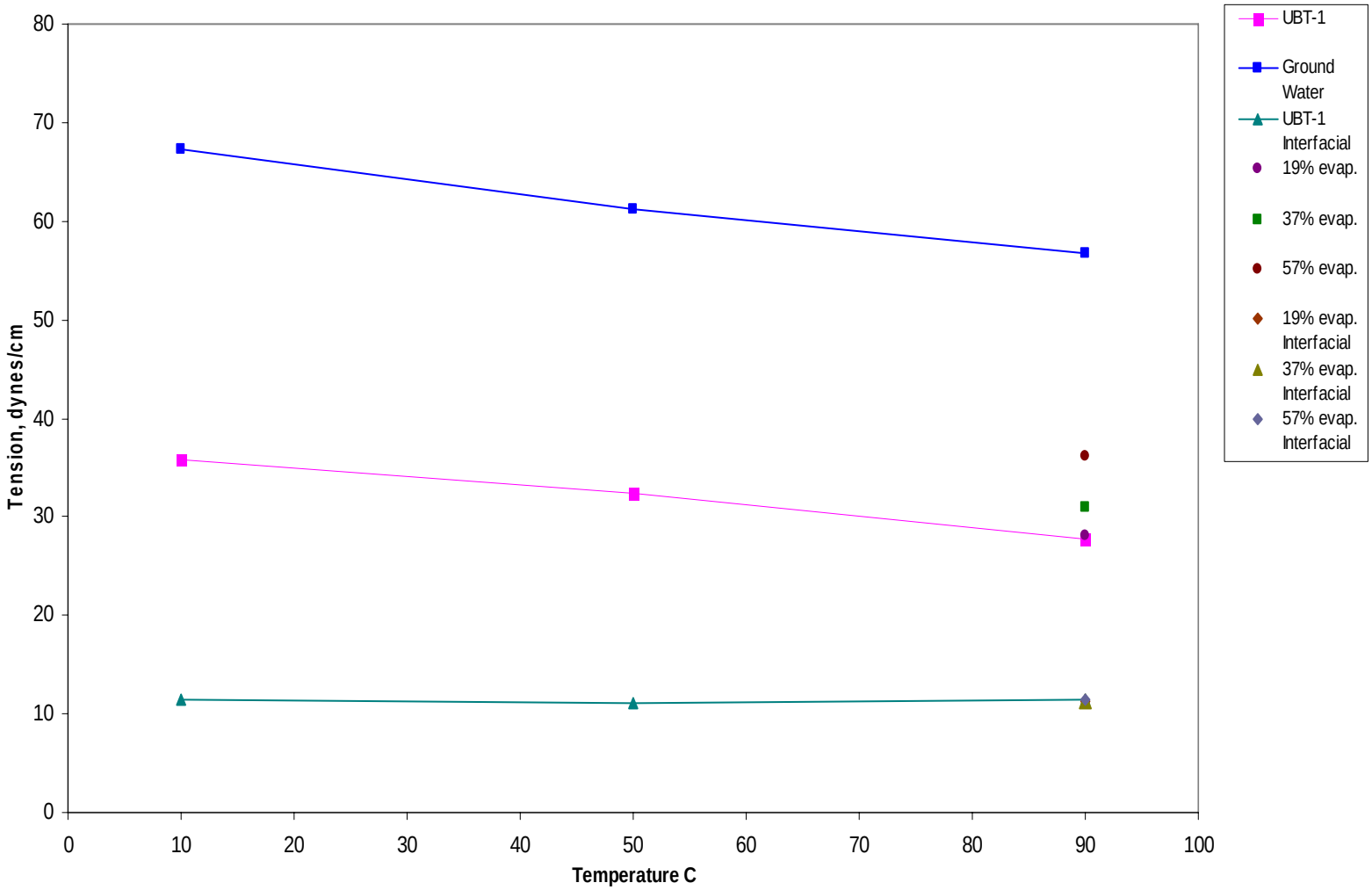

Figure 4. Density of Montrose DNAPL after partial evaporation as a function of temperature.

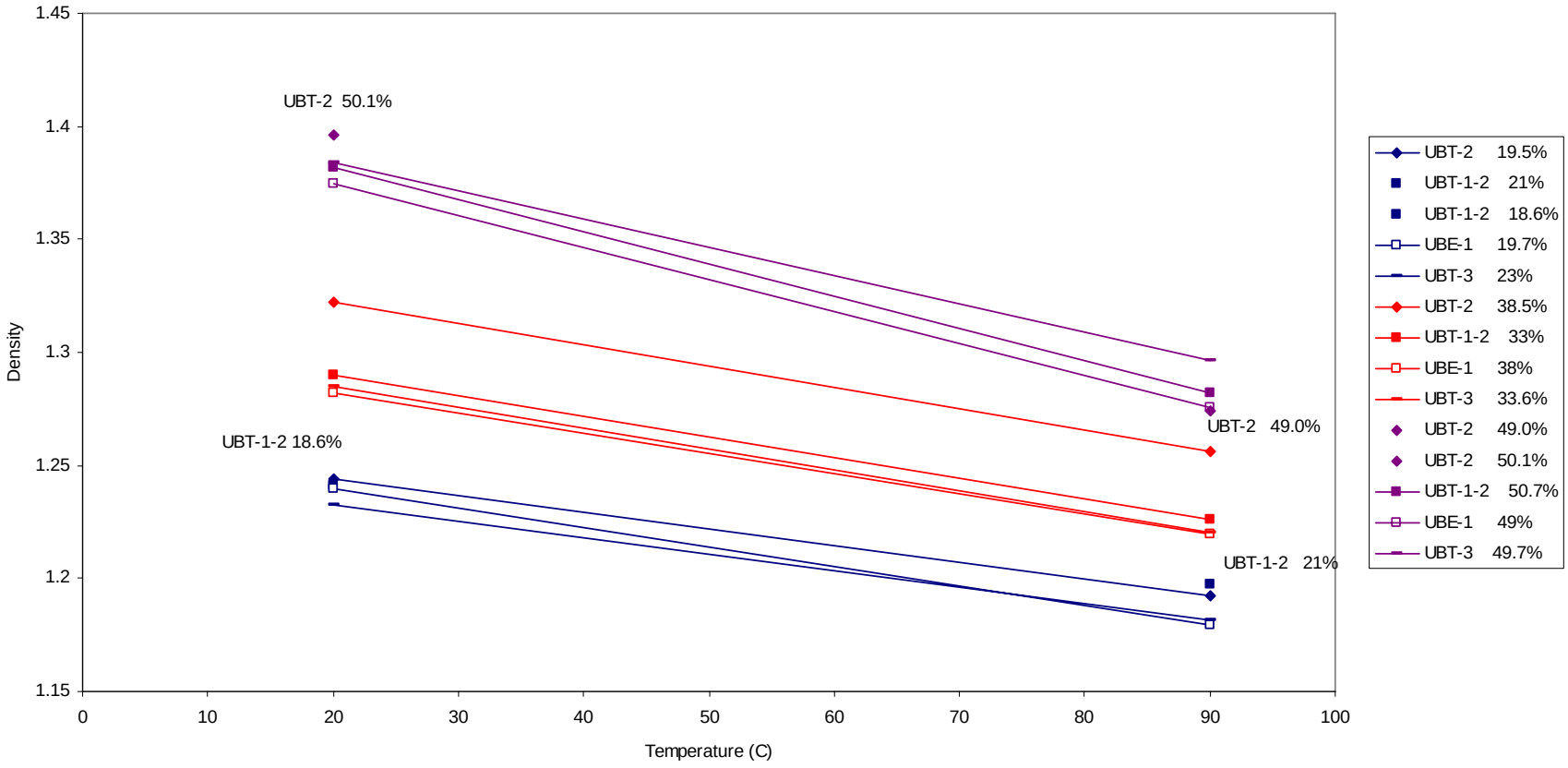

Figure 5. Montrose DNAPL viscosity after partial evaporation as a function of temperature.

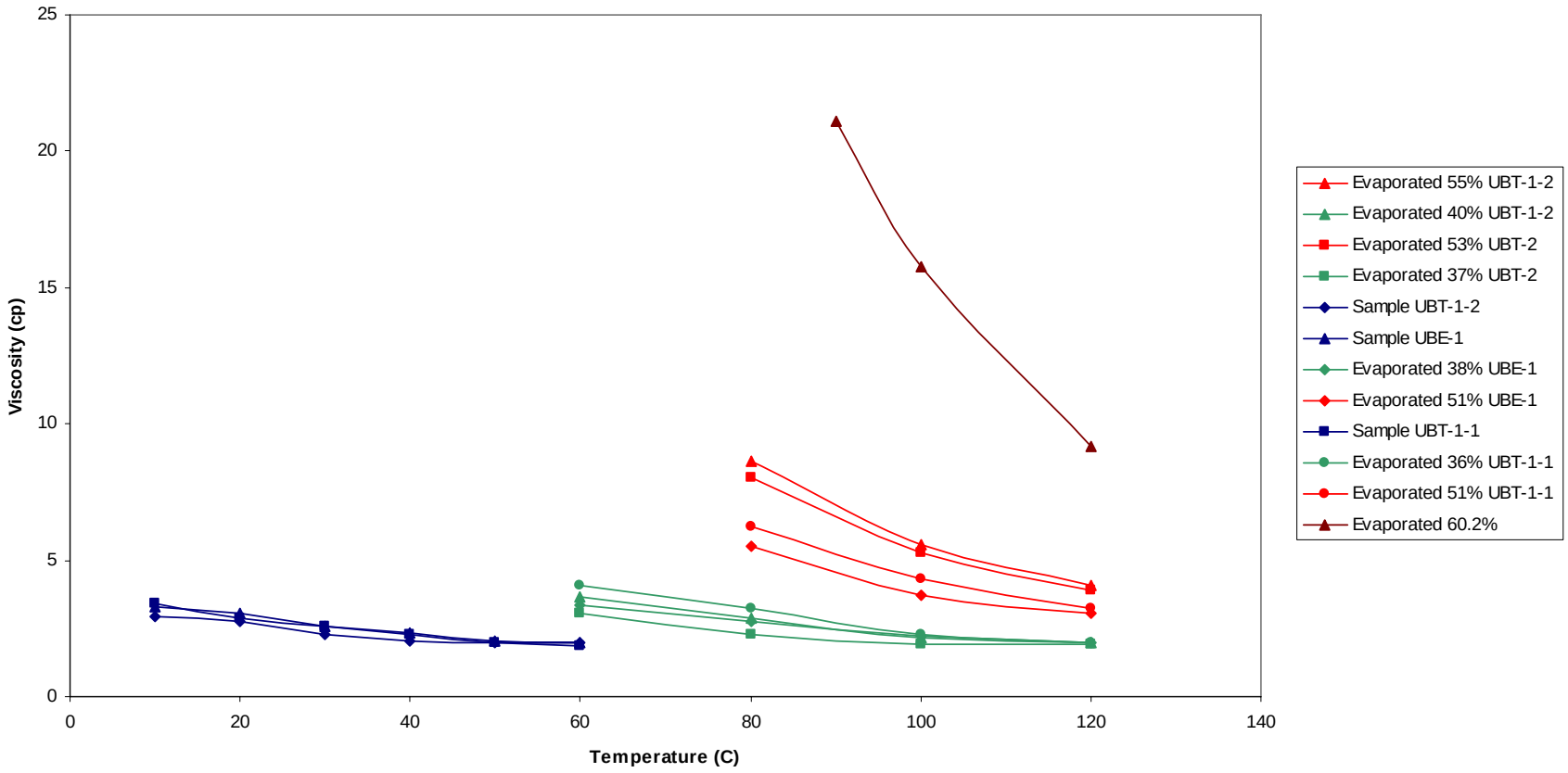
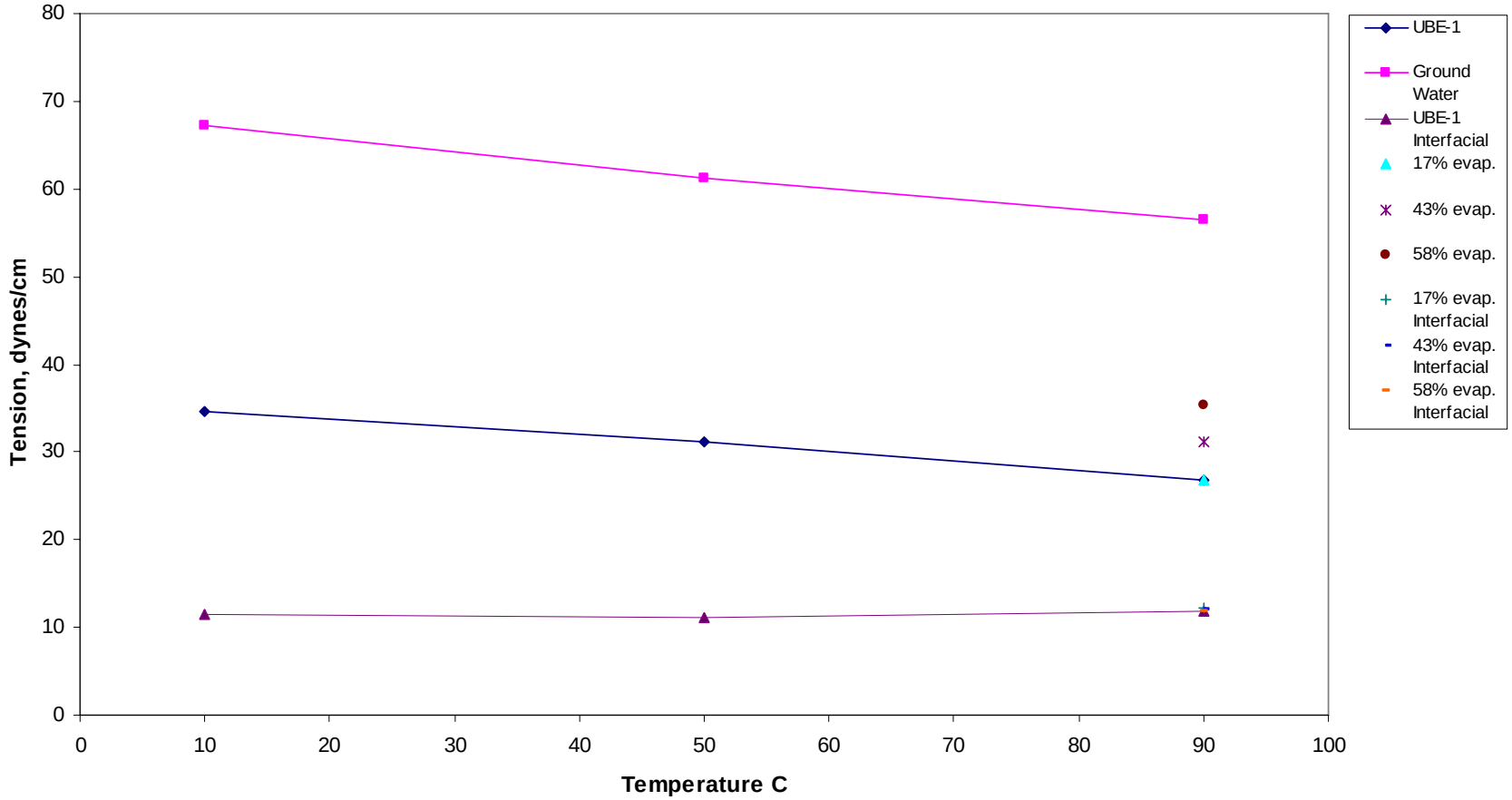
Figure 6. Surface and interfacial tension of Montrose DNAPL UBE-1 after partial evaporation.