Antea USA, Inc.
5910 Rice Creek Parkway, Suite 100
St. Paul, MN 55126 USA

1 November 2019

John T. Hunt, Hydrogeologist
Remediation and Redevelopment Program
Wisconsin Department of Natural Resources
223 East Steinfest Road
Antigo, Wisconsin 54409

Subject: Technical Memorandum – Evidence for and Quantification of LNAPL Mass Depletion

Applicable BRRTS Numbers:

BRRTS No. 02-16-000331 (Terminal)
BRRTS No. 02-16-117873 (Manifold/AST Area)
BRRTS No. 02-16-297979 (Northern Barge Dock)

Dear Mr. Hunt:

This Technical Memorandum evaluates and interprets changes in LNAPL mass, otherwise known as depletion, that are predicted to have occurred in light non-aqueous phase liquid (LNAPL) at the former Amoco Terminal (Superior, Wisconsin) and associated properties (the Site). The changes in LNAPL mass will be evaluated based on methods presented in Kaplan and others (1996). Releases of multiple types of petroleum hydrocarbons have occurred at the Site during its estimated 100 years of operation and this analysis will be applied to four operational Areas of Concern (AOCs) as follows:

1. Terminal (AOCs 1 – 5),
2. AST Area (AOCs 6 and 7),
3. Manifold (AOC 8) and,
4. Northern Barge Dock (AOCs 9 – 13)

The analyses being applied require chromatogram data so that diagnostic ratios of specific petroleum hydrocarbons (PHCs) may be calculated. In a few instances, LNAPL samples were collected and analyzed from different years, which allows analysis and comparison of the diagnostic ratios over time. In addition, a graph of dissolved-phase benzene for key monitoring wells will be presented to support and amplify the LNAPL depletion analysis.

This memorandum will consider the following elements of LNAPL conditions and changes over time at the Site:

- To what degree do Evaporation, Waterwashing, and Biodegradation contribute to LNAPL mass reduction,
- Can the reduction in soluble mass be estimated at the Site,
- Is the LNAPL mass reduction attributable to Evaporation affected by variations in hydrogeologic conditions, such as the presence and persistence of an unsaturated zone, and
- How has the mass of benzene changed in the LNAPL at the Terminal (AOCs 1 – 5).

Background:

During the development of the conceptual site model, 13 Areas of Concern (AOCs) have been identified at the Terminal on the south side of Winter Street, between and Maryland and Susquehanna Avenues (AOCs 1 – 5), the former AST Area (AOCs 6 and 7) and Manifold Areas (AOCs 6 – 8), and the northern Barge Dock (AOCs 9 – 13). The volume of LNAPL in each AOC has been refined over the years using data to calculate oil-specific volumes (OSVs) from soil sample profiles and in-well LNAPL thicknesses measured during periods of low water level, as well as downhole laser-induced fluorescence (LIF) data. As presented in the Site Investigation Reports for the Terminal (Antea Group; December 15, 2017), the Manifold/AST Area, and the north Barge Dock (Antea Group; December 14, 2017), the total volume of residual LNAPL was recalculated for the Terminal, Manifold/AST Area, and northern Barge Dock Area as follows:

Terminal =	11,170 gallons
Manifold/AST Area =	33,415 gallons
Northern Barge Dock =	4,047 gallons

The LNAPL volumes cited above were derived based on soil, LIF, and fluid-level data collected between 2004 and 2013 and are representative of the volumes during that time period. The necessary data for volumetric analysis were not collected prior to 2004 so that the actual volumes of LNAPL released at the Terminal and associated properties over the lifetime of the facility are not known.

The ITRC (2009) noted that "if some quantities of chemicals are being *naturally* lost from the source zone at some rate due to volatilization, dissolution, biodegradation, and sorption, then the source zone itself must be depleting to some degree". These processes were undoubtedly at work on the LNAPL that was released at the site, but lacking initial volume estimates the challenge is how to quantify the volume, or mass, of petroleum that has been depleted through natural processes.

Though the volume, or mass, of the LNAPL depletion as a whole cannot be calculated, the use of diagnostic ratios has been used to demonstrate the depletion of certain PHCs as compared to a standard (Kaplan and others, 1996). The use of diagnostic ratios for estimation of petroleum mass depletion is described below.

Petroleum Hydrocarbon Diagnostic Ratios:

Kaplan and others (1996) provide standard diagnostic ratios for an "87 Octane Gasoline" and a "92 Octane Gasoline", as well as typical ratios that would be expected in "Water" and "Soil" shortly after a release. The diagnostic ratios that quantify mass-depletion processes include "Evaporation", "Water Washing", and "Biodegradation". The advantage of using ratios rather than the chromatogram data for individual PHCs is that ratios remain fairly consistent over time and across refiners; whereas the raw chromatogram data may be influenced by differences in sample size, analytical equipment, and analytical method.

Kaplan and others (1996) state that:

> *"evaporation ratios compare the distribution of different members of the same hydrocarbon type (i.e., paraffins and Isoparaffins) with different Henry's law constants. Water washing ratios compare benzene and toluene with nonaromatic hydrocarbons of about the same molecular size and volatility. Total aromatics content is compared also with total paraffins and naphthenes. The biodegradation parameters compare olefins (hydrocarbons highly susceptible to biodegradation) with paraffins, as well as isoparaffins plus naphthenes with paraffins."*

The diagnostic ratios are calculated from the chromatogram data that quantifies the mass or concentration of dozens of PHCs. The diagnostic ratios were calculated for LNAPL samples collected at the Terminal (AOCs 1 – 5), AST Area (AOCs 6 – 7), the Manifold (AOC 8), and the northern Barge Dock (AOCs 9 – 13). The standard diagnostic ratios for an "87 Octane Gasoline" were used for comparison as being more representative of the petroleum in the subsurface and more common than a "92 Octane Gasoline", as provided in Kaplan and others (1996).

Tables 1, 2, 3, and 4 present the diagnostic ratios and calculated percent mass reduction for each chromatogram dataset for the Terminal, the AST Area, the Manifold, and the northern Barge Dock, respectively. Figures 1, 2, 3, and 4 depict the percent mass reduction for each chromatogram dataset as bar graphs for the Terminal, AST Area, the Manifold, and northern Barge Dock, respectively.

Tables 1 through 4 present the quantitative results of the ratios of particular PHCs as described earlier. Three mechanisms, or pathways, of degradation are included: Evaporation, Waterwashing, and Biodegradation. Each table shows the diagnostic ratios for the "87 Octane Gasoline" and a Standard Gasoline/Diesel/Wax (G/D/W) analyzed by Torkelson Geochemistry (TGI Project No. 04115; April 30, 2004). Samples of LNAPL from the cited wells were analyzed by Torkelson Geochemistry (Tulsa, Oklahoma) or Pace Energy, formerly ZymaX (Pittsburgh, Pennsylvania) to provide quantitative chromatogram data for dozens of individual PHCs. The quantitative chromatogram data were used to calculate the following diagnostic ratios:

Mass Reduction Process	PHCs in Ratio	Acronym	Standard Ratios for "87 Octane Gasoline"[1]
Evaporation	n-Pentane/n-Heptane	n-C5/n-C7	2.1
Waterwashing	Benzene/Cyclohexane[2]	Benzene/CHX	4.3
	Toluene/Methylcyclohexane	Toluene/MCHX	10.8
Biodegradation	3-Methylhexane/n-Heptane[3]	3-MHX/n-C7	1.6
	Methylcyclohexane/n-Heptane	MCHX/n-C7	0.6

[1]Source: Kaplan and others (1996)
[2]Calculation of the Benzene/Cyclohexane ratio was not possible for LNAPL samples collected at the AST Area, the Manifold, and northern Barge Dock because Cyclohexane was not reported in the analyses
[3]Calculation of the Methylcyclohexane/n-Heptane ratio was not possible for LNAPL samples collected at the AST Area, the Manifold, and northern Barge Dock because Methylcyclohexane was not reported in the analyses

The diagnostic ratios compare favorably for the "87 Octane Gasoline" and the Standard G/D/W samples, though the Toluene/MCHX ratios appear to be affected by a deficit in Toluene or enrichment of Methylcyclohexane in the Standard G/D/W sample. The favorable comparison of the MCHX/n-C7 ratios suggests that Toluene is deficient in the Standard G/D/W sample as compared to the "87 Octane Gasoline" sample.

Discussion

Terminal (AOCs 1 – 5);
Source data/Analysis date: Torkelson (April 2004) and Pace Energy (July 2019)

In Table 1, the diagnostic ratios developed for LNAPL samples collected from Terminal wells indicate order of magnitude reductions as a result of Evaporation and Waterwashing. Samples of LNAPL were collected for chromatogram analysis in April 2004 and July 2019 from monitor well MW-32 (AOC 2), and recovery wells RW-4 (AOC 1) and RW-6 (AOC 5). In July 2019, LNAPL samples were also collected from monitor well MW-27 (AOC 2) and recovery well RW-5 (AOC 4).

Evaporation and Waterwashing diagnostic ratios were calculated for LNAPL samples collected in 2004 and 2019 for wells MW-32 and RW-4. The change in the Evaporation diagnostic ratio between 2004 and 2019 at monitor well MW-32 appears to suggest that the diagnostic ratio increased. This would appear to suggest that the LNAPL mass increased slightly, but it is more likely the result of less-evaporated confined LNAPL being drawn or forced into the monitor well from under the silty clay confining layer overlying the saturated sand. The Evaporation diagnostic ratio for the two LNAPL samples collected from recovery well RW-4 show a decrease of 0.26, which indicates Evaporation was active in further reducing mass between 2004 and 2019. The decrease in the Evaporation diagnostic ratio at recovery well RW-4 is consistent with the sustained unsaturated zone at the Terminal, which would be conducive to Evaporation. Evaporation appears particularly active at recovery well RW-5, where the n-C5/n-C7 ratio is just 0.01 as compared to 2.1 for an “87 Octane Gasoline”.

The diagnostic ratios that measure Waterwashing are 1 to 2 orders of magnitude less than the standard for an “87 Octane Gasoline”. Waterwashing diagnostic ratios were calculable for Benzene/CHX and Toluene/MCHX for all wells. For three wells (MW-32, RW-4, and RW-6) the Waterwashing diagnostic ratios were calculated for LNAPL samples collected in 2004 and 2019. The diagnostic ratios for Waterwashing for the three wells sampled and analyzed 15 years apart suggest that Waterwashing depleted LNAPL mass, especially as indicated by the Benzene/CHX ratio (see the results for MW-32 and RW-4, in particular). The diagnostic ratio of Toluene/MCHX calculated as 3 to 4 orders of magnitude less than the value reported for an “87 Octane Gasoline”, suggesting substantial mass reduction through Waterwashing. The Waterwashing diagnostic ratio also suggested substantial, but slower, Waterwashing at recovery well RW-5.

The results for the Biodegradation diagnostic ratios are mixed. The 3-MHX/n-C7 ratio indicates Biodegradation is actively reducing the petroleum mass, though at a lesser rate than Evaporation or Waterwashing. For seven of eight analyses, the MCHX/n-C7 ratios are higher than the value cited for an “87 Octane Gasoline” which renders interpretation impossible. The remaining Biodegradation ratio of 0.38 (for recovery well RW-5) is nearly two-thirds of the ratio cited for an “87 Octane Gasoline”, suggesting that Biodegradation is a less robust process for degrading the full spectrum of PHCs.

The lower half of Table 1 presents an interpretation of the percent reduction in mass represented by the decline of the various diagnostic ratios as compared to the ratios for “87 Octane Gasoline”. The contribution from Evaporation, based on the most recent laboratory results, ranges from 71.30% to 99.29%. The variation in the percent of mass reduction attributable to Evaporation may be the result of variation in LNAPL composition or lack of an unsaturated zone beneath the surficial silty clay that extends over the entire site at varying thicknesses.

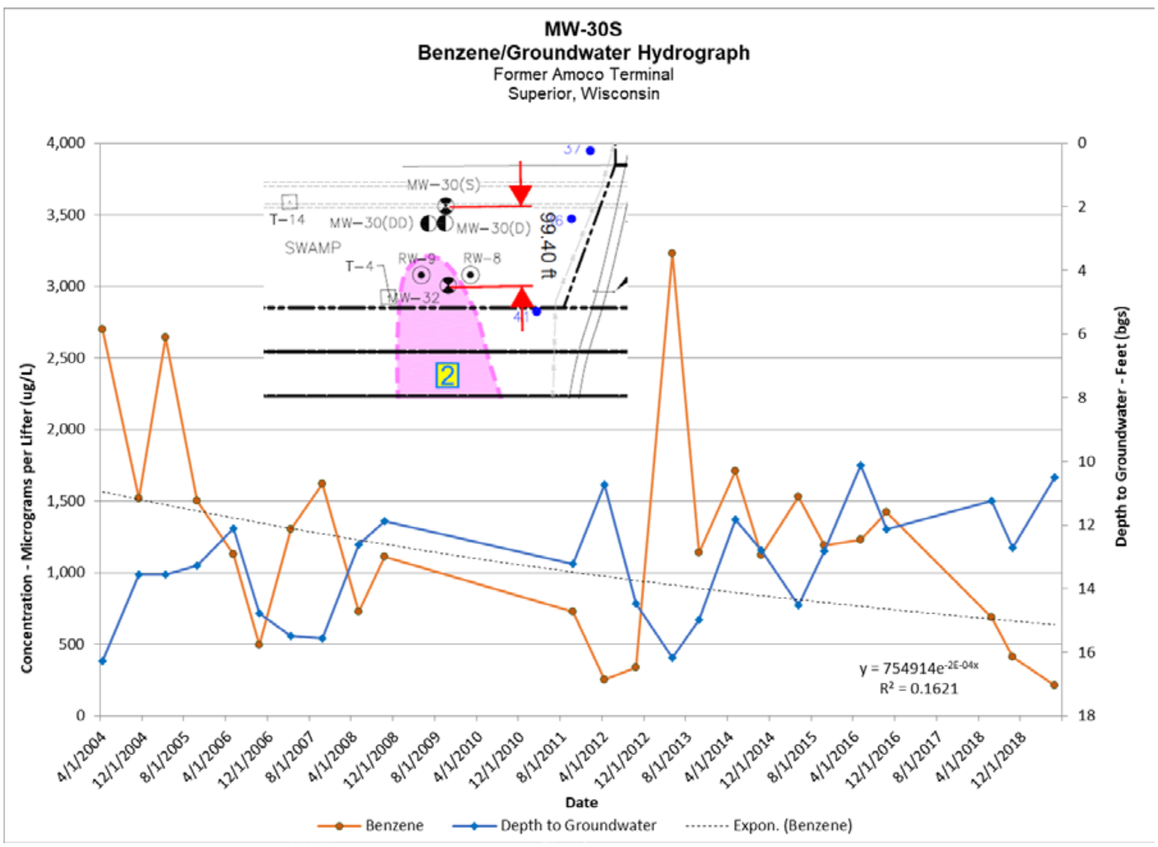
The percent mass reduction attributable to Waterwashing is typically greater than 96 percent based on the more recent chromatogram data and derived diagnostic ratios (see MW-27, MW-32, and RW-4). Based on the diagnostic ratio of Benzene/CHX, Waterwashing between 2004 and 2019 accounted for about 9% of the additional LNAPL mass removal as indicated at wells MW-32 and RW-4, and about 11% at well RW-6. The Benzene/CHX diagnostic ratio also provides an estimate of the total Benzene mass that has been Waterwashed from the LNAPL in the subsurface, which is calculated as greater than 90% at all sampling locations except recovery well RW-5 (AOC 5).

On a percentage basis, the mass reductions that may be estimated through the Toluene/MCHX diagnostic ratio are all greater than 92% for samples collected in 2004 and in 2019. The Waterwashing diagnostic ratios indicate that the LNAPL found at all locations at the Terminal has been subjected to Waterwashing, which has produced substantial mass reductions.

On a percentage basis, Biodegradation is indicated as contributing 75.00% to 84.20% to mass reduction based on the 3-MHX/n-C7 ratio. Based on the MCHX/n-C7 ratio, the percentage of LNAPL mass reduction attributable to Biodegradation at recovery well RW-5 is 37.25%, but it is the only sample for which the MCHX/n-C7 ratio could be calculated. At recovery well RW-6, the percentage of mass reduction attributable to Biodegradation (77.77%) is reported to slightly exceed the contribution for Evaporation (71.30%), but both are less than Waterwashing (90.98% or 93.21%).

Figure 1 is a bar graph that depicts the percent of mass reduction attributable to Evaporation, Waterwashing and Biodegradation for each LNAPL sample. The graph demonstrates that Waterwashing is the primary mechanism for mass reduction for seven of eight LNAPL samples evaluated, with the only exception being the LNAPL sample collected from recovery well RW-5 where Evaporation is somewhat more active than Waterwashing.

The relationship between the depletion of LNAPL mass, and specifically Benzene, may be demonstrated by reviewing the trend in dissolved-phase Benzene at a monitor well near the residual LNAPL mass. At the northern end of AOC 2, monitor well MW-32 has typically contained measurable LNAPL since it was installed in 1991. Monitor well MW-30S is located about 100 feet north of monitor well MW-32, as shown as an embedded map in the hydrograph below.



The hydrograph for monitor well MW-30S starts in 2004 and ends in 2019, the same years that LNAPL samples were collected from monitor well MW-32 (see Table 1). In Table 1, note that as of 2004 it appeared that over 91% of the Benzene had solubilized from the LNAPL.

And by 2019 the predicted percentage of solubilized Benzene had increased to over 99%. Over the same time period, the dissolved-phase Benzene reported for samples collected from monitor well MW-30S decreased from 2,700 micrograms/liter (ug/L) to 212 ug/L. This constitutes a 92% reduction in Benzene concentration at monitor well MW-30S between 2004 and 2019.

The case can be made that Benzene has been depleted from the residual LNAPL to the point that there is very little Benzene mass remaining in the groundwater. Consequently, samples collected from monitor well MW-30S have reported decreasing Benzene concentrations, especially since 2016 as Benzene depletion approached and achieved over 99% at the Terminal source area.

In summary, the diagnostic ratios indicate that Waterwashing is the primary mechanism for LNAPL mass depletion at the Terminal with Evaporation also making a significant contribution. Specifically focusing on estimates of Benzene mass reduction, the Benzene/CHX diagnostic ratio indicates that Benzene mass typically has been reduced by 90% to more than 99%, though at one location (RW-5) Benzene mass reduction was estimated as 78.11%.

The diagnostic ratio 3-MCH/n-C7 indicates mass reductions of 75% to 84% that may be attributed to Biodegradation. The other Biodegradation diagnostic ratio (MCHX/n-C7) produced mostly negative percentages, suggesting that LNAPL mass depletion through Biodegradation is inconsistent and makes a lesser contribution as compared to Waterwashing or Evaporation.

And finally, a comparison of Benzene depletion at monitor well MW-32 and the trend in the Benzene concentration at monitor well MW-30S indicates that Benzene has been depleted by more than 99%, while concentrations of dissolved-phase Benzene reported for monitor well MW-30S have declined an order of magnitude between 2004 and 2019.

AST Area (AOCs 6 and 7)

In Table 2, the diagnostic ratios developed for LNAPL samples collected from AST Area wells indicate mass reductions of 2 to 3 orders of magnitude that may be attributable to Waterwashing, based on the diagnostic ratio of Toluene/MCHX. Waterwashing may be enhanced in the AST Area as a result of a high water table and thick overlying clay unit, that frequently produces confined LNAPL conditions.

Mass reduction attributable to Evaporation is variable based on the diagnostic ratio of n-C5/n-C7, which is probably the result of variations in LNAPL composition or a limited unsaturated zone beneath the surficial silty clay.

The diagnostic ratio of MCHX/n-C7 is consistently higher than the value for “87 Octane Gasoline”, suggesting that this diagnostic ratio Biodegradation is not contributing significantly to reducing the petroleum mass in the AST Area.

The lower half of Table 2 presents an interpretation of the percent reduction in mass represented by the decline of the various diagnostic ratios as compared to the ratios for “87 Octane Gasoline”. The contribution from Evaporation, based on the most recent laboratory results, ranges from 37.65% to 96.72%. The variation in the percent of mass reduction attributable to Evaporation may be the result of variation in LNAPL composition or lack of an unsaturated zone beneath the surficial silty clay that extends over the entire site at varying thicknesses.

The percent mass reduction attributable to Waterwashing is typically greater than 96 percent, indicating that the LNAPL found at all locations at the AST Area has been subjected to Waterwashing.

The sole diagnostic ratio calculable for Biodegradation (MCHX/n-C7) produces negative percentages, which would suggest that LNAPL mass is increasing; a distinct impossibility.

Figure 2 is a bar graph that depicts the percent of mass reduction attributable to Evaporation, Waterwashing and Biodegradation for each LNAPL sample. The graph demonstrates that Waterwashing is the primary mechanism for mass reduction in most instances, except for the LNAPL sample collected from recovery well MWAST-8 where the percent mass reduction attributable to Evaporation is nearly equal to Waterwashing. The contribution to mass reduction attributable to Biodegradation was incalculable.

In summary, the diagnostic ratios indicate that Waterwashing is the primary mechanism for LNAPL mass depletion at the AST Area, with percentage reductions consistently greater than 96%. The contribution to mass reduction from Evaporation also making a significant contribution, though the results predicted are inconsistent across the four monitor well locations in the AST Area. The contribution to mass reduction attributable to Biodegradation could not be calculated, with all registering negative percentages, suggesting that LNAPL mass is increasing through Biodegradation; a distinct impossibility.

Manifold Area (AOC 8)

As shown in Table 3, mass reduction attributable to Evaporation is variable based on the diagnostic ratio of n-C5/n-C7, with the ratio ranging from 0.20 to 1.36. This variation across the 7 wells assigned to the Manifold Area is probably the result of variations in LNAPL composition or a limited and variable unsaturated zone beneath the surficial silty clay.

Further in Table 3, the diagnostic ratios for Toluene/MCHX developed for LNAPL samples collected from the Manifold Area wells for Waterwashing are 2 to 3 orders of magnitude less than the value cited for an "87 Octane Gasoline". This suggests significant mass reductions may be attributable to Waterwashing.

The diagnostic ratio of MCHX/n-C7 is consistently higher than the value for "87 Octane Gasoline", suggesting that PHC mass is being added or, more plausible, that Biodegradation is not a good indicator of LNAPL mass depletion at this site.

The lower half of Table 3 presents an interpretation of the percent reduction in mass represented by the decline of the various diagnostic ratios as compared to the ratios for "87 Octane Gasoline". The contribution from Evaporation, based on the most recent laboratory results, ranges from 35.39% to 90.61%. The variation in the percent of mass reduction attributable to Evaporation may be the result of variation in LNAPL composition or lack of an unsaturated zone beneath the surficial silty clay that extends over the entire site at varying thicknesses.

The percent mass reduction attributable to Waterwashing is typically greater than 96 percent, indicating that the LNAPL found at all locations at the Manifold Area is subject to substantial Waterwashing. The sole diagnostic ratio calculable for Biodegradation (MCHX/n-C7) produces negative percentages, which would suggest that LNAPL mass is increasing; a distinct impossibility.

Figure 3 is a bar graph that depicts the percent of mass reduction attributable to Evaporation, Waterwashing and Biodegradation for each LNAPL sample. The graph demonstrates that Waterwashing is the primary mechanism for mass reduction at all well locations, with the percentage of LNAPL mass reduction attributable to Waterwashing registering above 93% for all seven wells assigned to the Manifold Area. Evaporation is nearly equal to Waterwashing for the sample collected from monitor well LRMW-5, which suggests that conditions are more conducive for Evaporation in that area. However, the percentage of LNAPL mass reduction that may be attributed to Evaporation at the remaining 6 wells are all less than 79%.

Biodegradation is not represented on Figure 3 because the diagnostic ratio was either incalculable (unreported petroleum hydrocarbon) or produced untenable results (negative percentages).

In summary, the diagnostic ratios indicate that Waterwashing is the primary mechanism for LNAPL mass depletion at the Manifold Area, with percentage reductions consistently greater than 93%. The contribution to mass reduction from Evaporation is also making a contribution, though the predicted percentages are inconsistent across the seven monitor well locations in the Manifold Area. The variability in the predicted percentage of mass reduction attributable to Evaporation may be related to differences in LNAPL composition, but is more likely the result of the variability in or lack of an unsaturated zone. The contribution to mass reduction attributable to Biodegradation could not be calculated, with all registering negative percentages, suggesting that LNAPL mass is increasing through Biodegradation; a distinct impossibility.

Barge Dock (AOCs 9 - 13)

Table 4 is a compilation of the diagnostic ratios developed for LNAPL samples collected from monitor wells located on the northern part of the Barge Dock. The diagnostic ratio for Evaporation (n-C5/n-C7) ranges from 0.10 to 0.49, which when compared to the standard ratio of 2.1 for an "87 Octane Gasoline", suggests Evaporation is actively reducing the LNAPL mass. The diagnostic ratio for Waterwashing (Toluene/MCHX) is 2 to 3 orders of magnitude less than the value cited for an "87 Octane Gasoline", indicating that Waterwashing is highly active in reducing LNAPL mass. The diagnostic ratio of MCHX/n-C7 is consistently higher than the value for "87 Octane Gasoline", suggesting that this diagnostic ratio is not a good measure of Biodegradation at the northern Barge Dock or Biodegradation is not actively reducing the LNAPL mass.

The lower half of Table 4 presents an interpretation of the percent reduction in mass represented by the decline of the various diagnostic ratios as compared to the ratios for "87 Octane Gasoline". The contribution from Evaporation, based on the most recent laboratory results, ranges from 76.58% to 95.36%. The variation in the percent of mass reduction attributable to Evaporation may be the result of variation in LNAPL composition or lack of an unsaturated zone beneath the surficial silty clay that extends over the entire site at varying thicknesses.

The percent mass reduction attributable to Waterwashing is typically much greater than 97 percent, indicating that the LNAPL found at all locations at the northern Barge Dock has been subjected to substantial Waterwashing. The sole diagnostic ratio calculable for

Biodegradation (MCHX/n-C7) produces negative percentages, which would suggest that LNAPL mass is increasing; a distinct impossibility.

Figure 4 is a bar graph that depicts the percent of mass reduction attributable to Evaporation, Waterwashing and Biodegradation for each LNAPL sample. The graph demonstrates that Waterwashing is the primary mechanism for mass reduction at all well locations. Evaporation is indicated as nearly equal to Waterwashing for the samples collected from monitor wells MWRR-8 and MWOW-1, which suggests that conditions are more conducive for Evaporation in those areas. Biodegradation is not represented on Figure 4 because the diagnostic ratio was either incalculable or produced untenable results.

Conclusions

The data and analyses presented above support the conclusion that LNAPL mass is being depleted through several processes; predominantly Waterwashing and Evaporation. The diagnostic ratios provide insights as to the mechanisms at work at the site in reducing the LNAPL mass at the Terminal, the AST Area, the Manifold, and the northern Barge Dock. The key points and findings of the analysis are as follows:

1. Based on diagnostic ratios, Waterwashing is the primary process involved in reducing LNAPL mass and, on a percentage basis, more than 95% of the soluble hydrocarbons typically have been removed from the LNAPL mass at all four areas.
2. The results of the Benzene/CHX diagnostic ratio at the Terminal suggests that more than 90% of the Benzene has been Waterwashed from LNAPL at all but one LNAPL sampling location at or associated with the Terminal.
3. For the wells where LNAPL samples have been collected in 2004 and 2019 at the Terminal, the Benzene/CHX diagnostic ratio indicates that 9% to 11% of the Benzene mass has been Waterwashed in that 15-year period.
4. A comparison of Benzene depletion at monitor well MW-32 and the trend in dissolved-phase Benzene at monitor well MW-30S, indicates that between 2004 and 2019 the Benzene depletion increased from near 90% to over 99%. Over the same time period, the concentrations of dissolved-phase Benzene reported for monitor well MW-30S have declined an order of magnitude.
5. The diagnostic ratios suggest that Evaporation has been active at reducing the LNAPL mass in all four areas with typical percentages of mass removal ranging from 37% to 99%, with the wide range in results suggestive of variations in LNAPL composition or conditions conducive to Evaporation (such as the thickness and persistence of an unsaturated zone), which are typically found north of AOCs 1 - 5.

6. The extent to which Biodegradation is contributing to LNAPL mass reduction is inconclusive, though at the Terminal one diagnostic ratio (3-MCHX/n-C7) indicates that biodegradable hydrocarbons have been reduced by 75% to 84%.

We appreciate your offer and willingness to review the hydrogeological and hydrochemical data and analysis presented in this Technical Memorandum to describe and quantify LNAPL mass depletion through Evaporation, Waterwashing, and Biodegradation.

Thank you for your attention to and consideration of the findings and conclusions in this Technical Memorandum. If you have any questions or requests, please call or send e-mail message.

Sincerely,

ANTEA GROUP

Wayne R. Hutchinson, PG, PH
Senior Hydrogeologist

Wayne.Hutchinson@anteagroup.us
Direct Line: 651-697-5119

Jonathan Zimdars
Consultant

Jonathan.Zimdars@anteagroup.us
Direct Line: 651-697-5219

References

ITRC (2009) *Evaluating Natural Source Zone Depletion at Sites with LNAPL* (LNAPL-1): Interstate Technology & Regulatory Council, Washington, DC, 76 pp.

Kaplan, I. R.; Y. Galperin; H. Alimi; R-P. Lee, and S-T. Lu (1996) *Patterns of chemical changes during environmental alteration of hydrocarbon fuels*: Ground Water Monitoring Review, Vol. 16, No. 4, p. 113 - 124

Table 1: Hydrocarbon Ratios Related to Degradation and Mass Reduction
LNAPL Samples Collected From Terminal Wells (AOCs 1 - 5)
Former Amoco Terminal 00406 (Superior, WI)

			AOC 2	AOC 2	AOC 2	AOC 1	AOC 1	AOC 4	AOC 5	AOC 5
	87 Octane	Std (G/D/W)	MW-27	MW-32	MW-32	RW-4	RW-4	RW-5	RW-6	RW-6
Lab		Torkelson	Pace Energy	Torkelson	Pace Energy	Torkelson	Pace Energy	Pace Energy	Torkelson	Pace Energy
Date of analysis		TGI # 04115	7/26/2019	4/30/2004	7/26/2019	4/30/2004	7/26/2019	7/26/2019	4/30/2004	7/26/2019
Evaporation										
n-Pentane/n-Heptane	2.1	2.28	0.18	0.3	0.39	0.36	0.10	0.01	0.65	0.60
Waterwashing										
Benzene/Cyclohexane	4.3	4.16	0.15	0.41	0.03	0.37	0.03	0.94	0.87	0.39
Toluene/Methylcyclohexane	10.8	6.09	0.28	0.15	0.09	0.23	0.04	0.20	0.82	0.73
Biodegradation										
3-Methylhexane/n-Heptane	1.6	1.15	0.28	0.30	0.25	0.32	0.26	0.39	0.40	0.36
Methylcyclohexane/n-Heptane	0.6	0.71	0.64	0.80	0.67	0.79	0.67	0.38	0.89	0.79

% Reduction in Mass Compared 87 Octane Ratios	87 Octane	Std (G/D/W)	MW-27	MW-32	MW-32	RW-4	RW-4	RW-5	RW-6	RW-6
		Torkelson	Pace Energy	Torkelson	Pace Energy	Torkelson	Pace Energy	Pace Energy	Torkelson	Pace Energy
		TGI # 04115	7/26/2019	4/30/2004	7/26/2019	4/30/2004	7/26/2019	7/26/2019	4/30/2004	7/26/2019
Evaporation										
n-Pentane/n-Heptane	2.1		91.25	85.71	81.47	82.86	95.17	99.29	69.05	71.30
Waterwashing										
Benzene/Cyclohexane	4.3		96.60	90.47	99.27	91.40	99.23	78.11	79.77	90.98
Toluene/Methylcyclohexane	10.8		97.40	98.61	99.16	97.87	99.60	98.19	92.41	93.21
Biodegradation										
3-Methylhexane/n-Heptane	1.6		82.81	81.25	84.20	80.00	83.77	75.90	75.00	77.77
Methylcyclohexane/n-Heptane	0.6		-7.39	-33.33	-12.13	-31.67	-11.51	37.25	-48.33	-31.77

Table 2: Hydrocarbon Ratios Related to Degradation and Mass Reduction
LNAPL Samples Collected From AST Wells (AOCs 6 and 7)
Former Amoco Terminal 00406 (Superior, WI)

			AOC 7	AOC 6	AOC 7	
	87 Octane	Std (G/D/W)	AST-2	AST-4	MWAST-6	MWAST-8
Lab		Torkelson	Torkelson	Torkelson	Torkelson	Torkelson
Date of analysis		TGI # 04115	10/21/2002	10/21/2002	4/27/2015	4/27/2015
Evaporation						
n-Pentane/n-Heptane	2.1	2.28	0.85	1.31	0.68	0.07
Waterwashing						
Benzene/Cyclohexane	4.3	4.16	NC	NC	NC	NC
Toluene/Methylcyclohexane	10.8	6.09	0.29	0.40	0.12	0.06
Biodegradation						
3-Methylhexane/n-Heptane	1.6	1.15	NC	NC	NC	NC
Methylcyclohexane/n-Heptane	0.6	0.71	0.83	0.73	0.88	0.91

% Reduction in Mass Compared 87 Octane Ratios	87 Octane	Std (G/D/W)	AST-2	AST-4	MWAST-6	MWAST-8
		Torkelson	Torkelson	Torkelson	Torkelson	Torkelson
		TGI # 04115	10/21/2002	10/21/2002	4/27/2015	4/27/2015
Evaporation						
n-Pentane/n-Heptane	2.1		59.29	37.65	67.77	96.72
Waterwashing						
Benzene/Cyclohexane	4.3		NC	NC	NC	NC
Toluene/Methylcyclohexane	10.8		97.29	96.28	98.89	99.49
Biodegradation						
3-Methylhexane/n-Heptane	1.6		NC	NC	NC	NC
Methylcyclohexane/n-Heptane	0.6		-38.93	-22.27	-46.35	-51.51

Table 3: Hydrocarbon Ratios Related to Degradation and Mass Reduction
LNAPL Samples Collected From Manifold Wells (AOC 8)
Former Amoco Terminal 00406 (Superior, WI)

	87 Octane	Std (G/D/W)	AOC 8 LRMW-1	AOC 8 LRMW-4	AOC 8 LRMW-4	AOC 8 LRMW-5	AOC 8 TWM-3	AOC 8 TWM-6	AOC 8 MRW-3	AOC 8 MRW-5
Lab		Torkelson	Torkelson	Torkelson	Torkelson	Torkelson	Torkelson	Torkelson	Torkelson	Torkelson
Date of analysis		TGI # 04115	3/1/2001	3/1/2001	5/7/2015	3/1/2001	10/21/2002	10/21/2002	2/12/2014	2/12/2014
Evaporation										
n-Pentane/n-Heptane	2.1	2.28	0.82	0.92	1.36	0.20	0.51	0.49	0.45	0.87
Waterwashing										
Benzene/Cyclohexane	4.3	4.16	NC	NC	NC	NC	NC	NC	NC	NC
Toluene/Methylcyclohexane	10.8	6.09	0.40	0.75	0.29	0.05	0.12	0.04	0.22	0.55
Biodegradation										
3-Methylhexane/n-Heptane	1.6	1.15	NC	NC	NC	NC	NC	NC	NC	NC
Methylcyclohexane/n-Heptane	0.6	0.71	1.02	0.88	1.49	1.09	1.16	1.20	1.13	0.97

% Reduction in Mass Compared 87 Octane Ratios	87 Octane	Std (G/D/W)	LRMW-1	LRMW-4	LRMW-4	LRMW-5	TWM-3	TWM-6	MRW-3	MRW-5
		Torkelson	Torkelson	Torkelson	Torkelson	Torkelson	Torkelson	Torkelson	Torkelson	Torkelson
		TGI # 04115	3/1/2001	3/1/2001	5/7/2015	3/1/2001	10/21/2002	10/21/2002	2/12/2014	2/12/2014
Evaporation										
n-Pentane/n-Heptane	2.1		61.11	55.99	35.39	90.61	75.70	76.85	78.74	58.46
Waterwashing										
Benzene/Cyclohexane	4.3		NC	NC	NC	NC	NC	NC	NC	NC
Toluene/Methylcyclohexane	10.8		96.28	93.09	97.30	99.50	98.91	99.65	97.93	94.94
Biodegradation										
3-Methylhexane/n-Heptane	1.6		NC	NC	NC	NC	NC	NC	NC	NC
Methylcyclohexane/n-Heptane	0.6		-70.54	-46.19	-148.31	-81.61	-93.83	-99.66	-88.52	-60.85

Table 4: Hydrocarbon Ratios Related to Degradation and Mass Reduction
LNAPL Samples Collected From Northern Barge Dock Wells (AOCs 9 - 13)
Former Amoco Terminal 00406 (Superior, WI)

	87 Octane	Std (G/D/W)	TWRR-4	MWRR-8 (AOC 11)	MWRR-8 (AOC 11)	MWOW-1 (AOC 13)	MWOW-5 (AOC 12)
Lab		Torkelson	Torkelson	Torkelson	Torkelson	Torkelson	Torkelson
Date of analysis		TGI # 04115	3/14/2003	6/23/2014	5/7/2015	6/23/2014	6/23/2014
Evaporation							
n-Pentane/n-Heptane	2.1	2.28	0.47	0.18	0.10	0.12	0.49
Waterwashing							
Benzene/Cyclohexane	4.3	4.16	NC	NC	NC	NC	NC
Toluene/Methylcyclohexane	10.8	6.09	0.19	0.07	0.07	0.24	0.10
Biodegradation							
3-Methylhexane/n-Heptane	1.6	1.15	NC	NC	NC	NC	NC
Methylcyclohexane/n-Heptane	0.6	0.71	0.78	0.86	0.88	16.97	2.48

% Reduction in Mass Compared 87 Octane Ratios	87 Octane	Std (G/D/W)	TWRR-4	MWRR-8	MWRR-8	MWOW-1	MWOW-5
		Torkelson	Torkelson	Torkelson	Torkelson	Torkelson	Torkelson
		TGI # 04115	3/14/2003	6/23/2014	5/7/2015	6/23/2014	6/23/2014
Evaporation							
n-Pentane/n-Heptane	2.1		77.56	91.58	95.36	94.48	76.58
Waterwashing							
Benzene/Cyclohexane	4.3		NC	NC	NC	NC	NC
Toluene/Methylcyclohexane	10.8		98.23	99.39	99.37	97.81	99.12
Biodegradation							
3-Methylhexane/n-Heptane	1.6		NC	NC	NC	NC	NC
Methylcyclohexane/n-Heptane	0.6		-30.27	-42.94	-46.54	-2728.48	-312.87

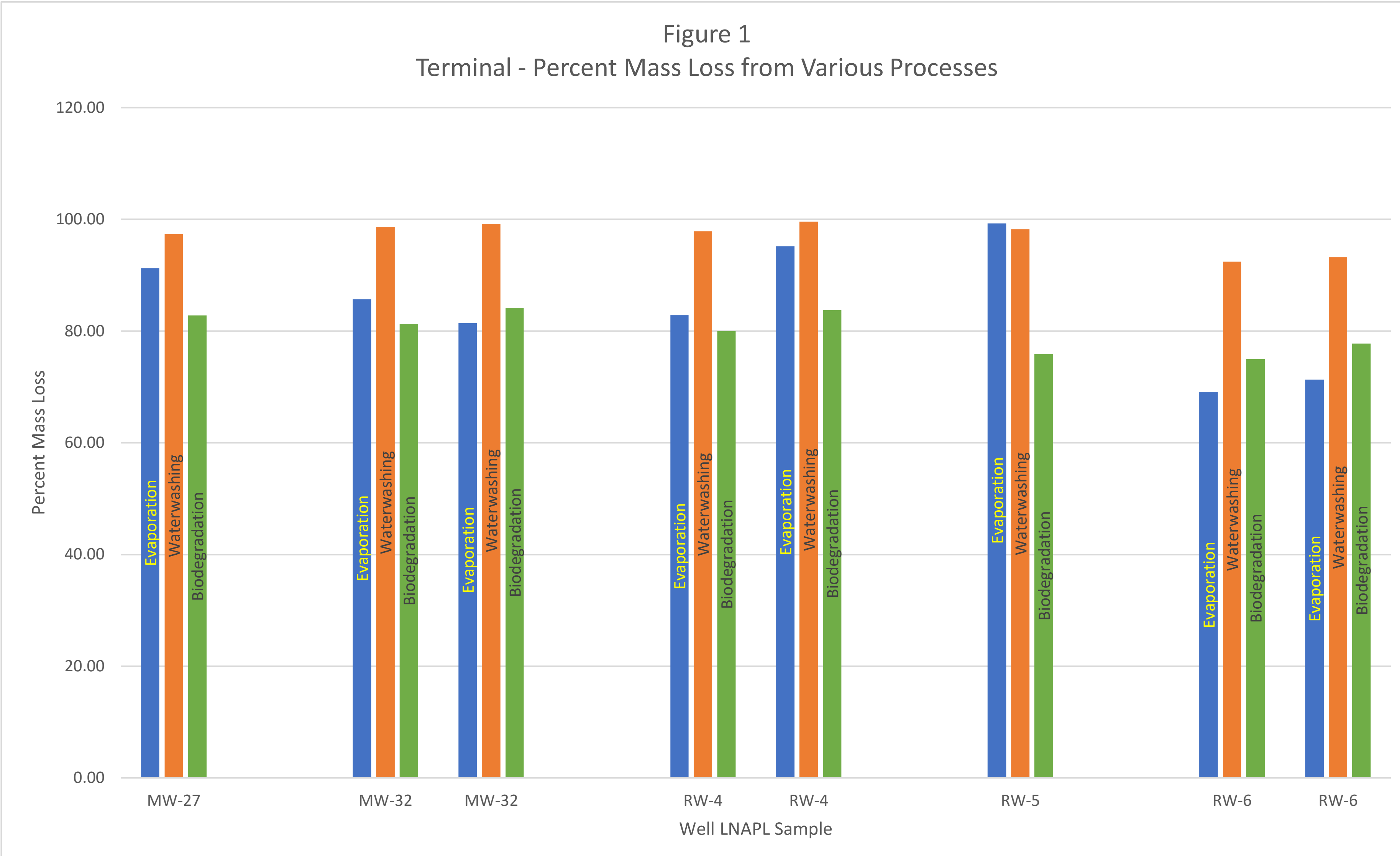


Figure 1
Terminal - Percent Mass Loss from Various Processes
Percent Mass Loss
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Evaporation
Waterwashing
Biodegradation
MW-27
MW-32
MW-32
RW-4
RW-4
RW-5
RW-6
RW-6
Well LNAPL Sample

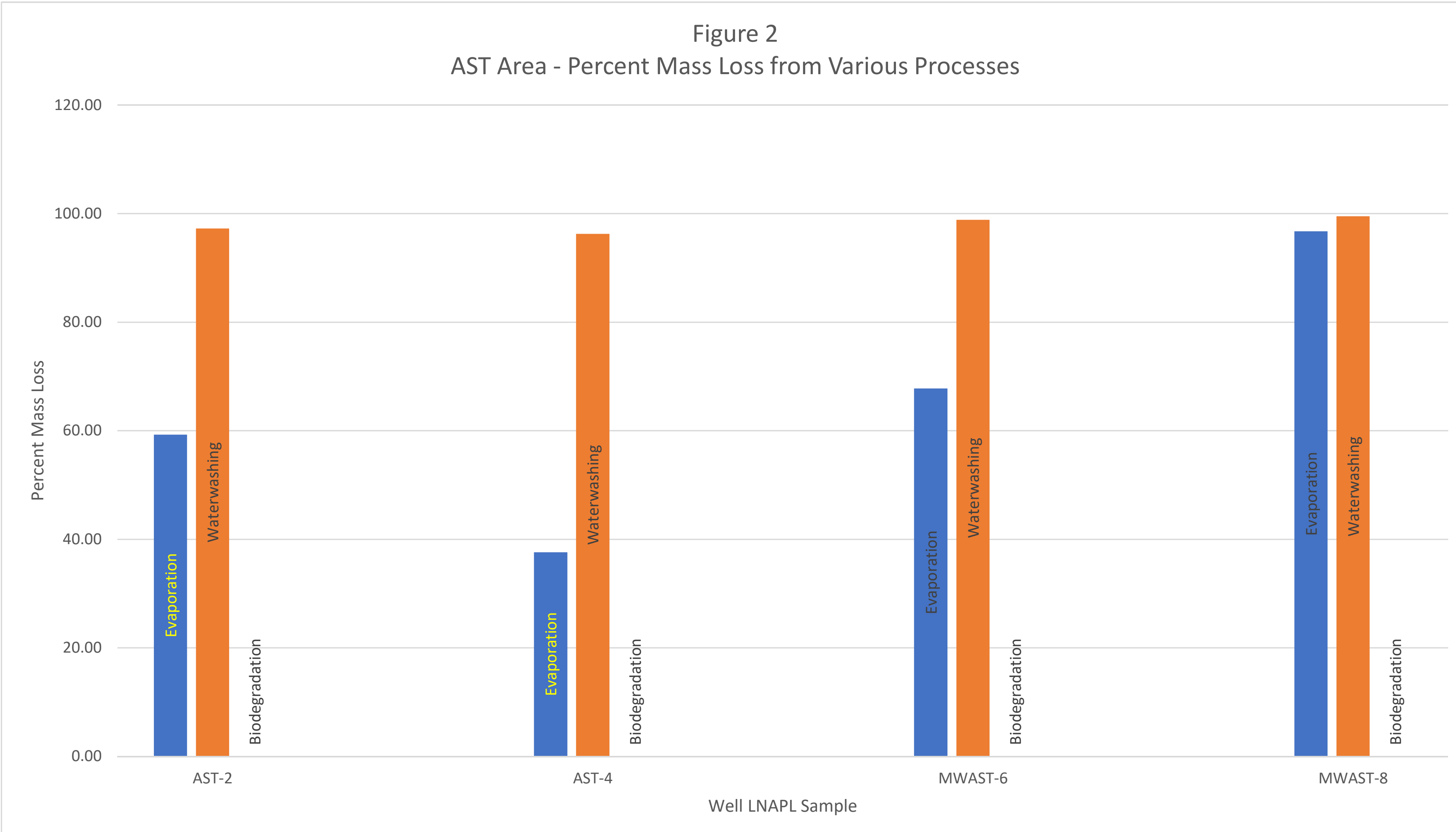


Figure 2
AST Area - Percent Mass Loss from Various Processes
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Percent Mass Loss
Evaporation
Waterwashing
Biodegradation
AST-2
AST-4
MWAST-6
MWAST-8
Well LNAPL Sample

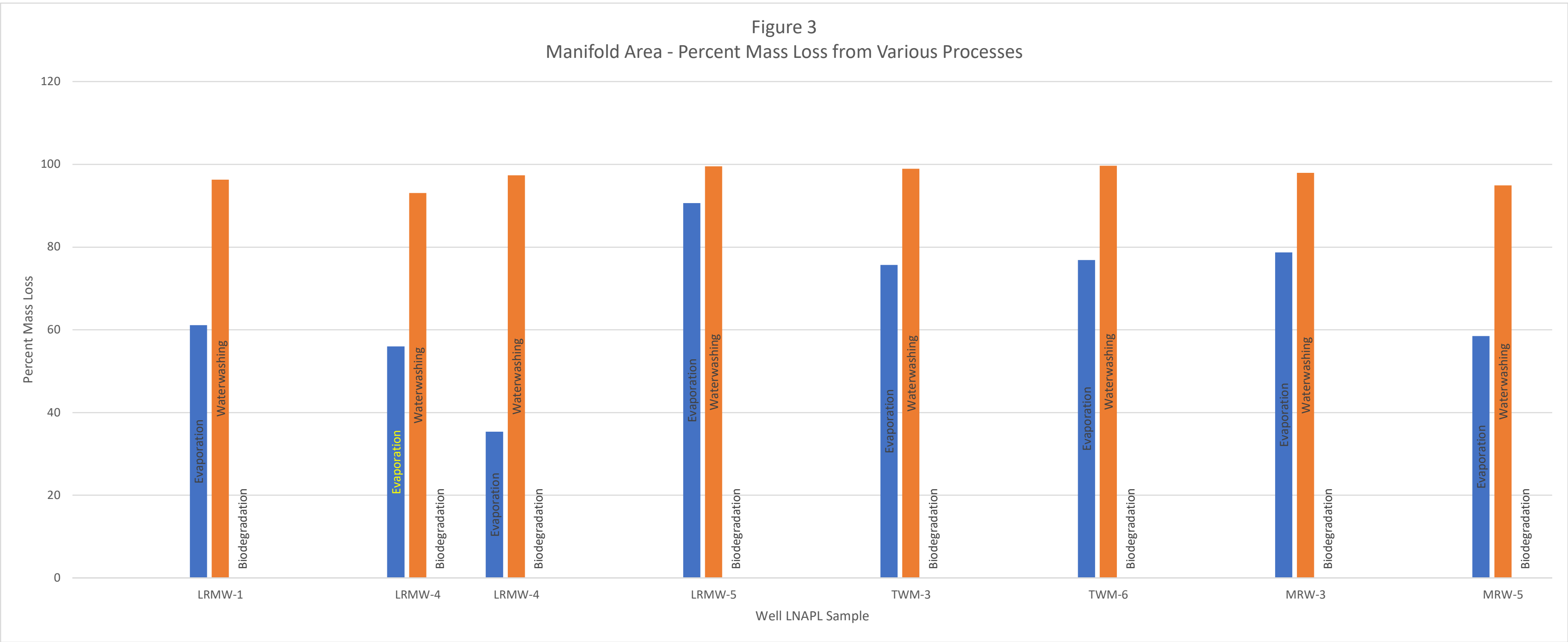


Figure 3
Manifold Area - Percent Mass Loss from Various Processes
Percent Mass Loss
0
20
40
60
80
100
120
Evaporation
Waterwashing
Biodegradation
LRMW-1
LRMW-4
LRMW-4
LRMW-5
TWM-3
TWM-6
MRW-3
MRW-5
Well LNAPL Sample

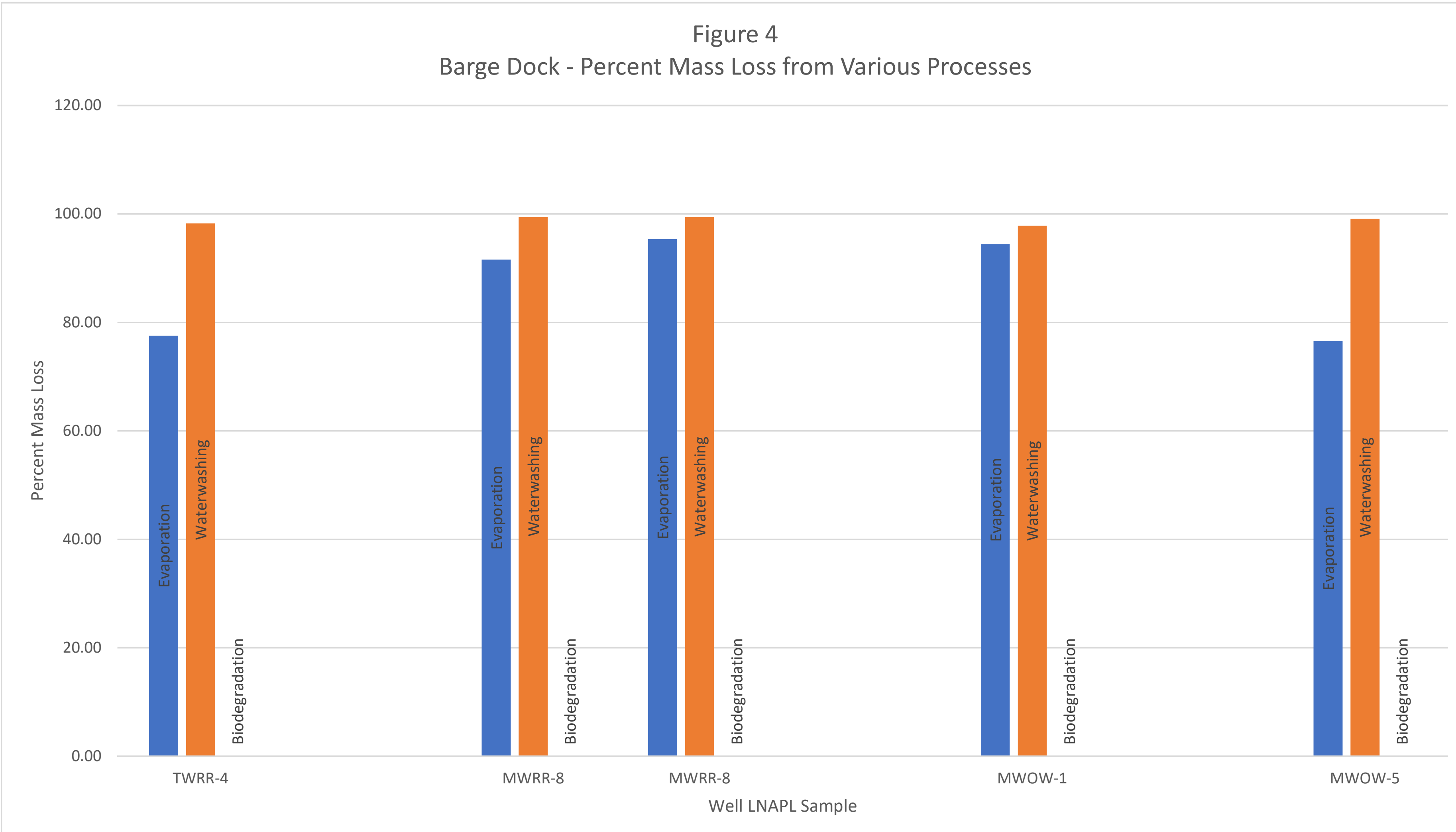


Figure 4
Barge Dock - Percent Mass Loss from Various Processes
120.00
100.00
80.00
60.00
40.00
20.00
0.00
Percent Mass Loss
Evaporation
Waterwashing
Biodegradation
TWRR-4
MWRR-8
MWRR-8
MWOW-1
MWOW-5
Well LNAPL Sample