Identification of Window of Opportunity for Chemical Dispersants on Gulf of Mexico Crude Oils

for:

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Executive Summary

Chemical dispersants are becoming a more accepted oil spill countermeasure. As a result, there is an increased need to know when dispersants will likely be effective on different oil types to assist in the dispersant-use decision-making process. Individual oils can be tested for their dispersibility while fresh, weathered and emulsified but such testing is costly and not practicable for the large number of different oils being produced and handled in the United States (US) and elsewhere.

The objective of this study was to develop best-fit correlations between readily available fresh oil properties and the window of opportunity for successful chemical dispersant use using data from Gulf of Mexico (GOM) crude oils.

Very detailed fresh and weathered oil property information was acquired from Environment Canada's oil property database and processed to derive the oil parameters required by the SL Ross Oil Spill Model (SLROSM) to complete detailed oil spill behavior modeling for each oil as a function of spill type and environmental conditions.

The results from the spill modeling were used to identify the time window for successful chemical dispersion of 1,000 and 10,000 barrel batch spills using average environmental conditions. The time that the model predicts that the oil's (or emulsion's) viscosity reaches 7,500 cP has been used as the maximum time-window for chemical dispersant use. Dispersant has also been deemed ineffective if the oil's pour point exceeds the ambient water temperature by 15ºC (60ºF). This criterion was applicable for only one of the oils studied (Mississippi Canyon Block 194).

The time windows identified using the spill behavior modeling have been correlated with the following independent fresh oil properties: API gravity, flash point, pour point, viscosity, boiling point distribution, wax content, asphaltene content, resin content, sulfur content, aromatic content and saturate content.

A commercially available statistical analysis program (Oakdale Engineering's "DataFit" package) was used to complete the data correlations. Various single- and multiple- parameter correlations were completed to identify the best-fit correlations between the commonly available fresh oil properties and the modeled time window for successful dispersant use.

The combination of sulfur, saturate and wax contents of the fresh oils correlated best with the time window for dispersant use for both the 1,000 and 10,000 barrel spill scenarios.

The best model identified for the 1,000 barrel spill is:

$$\text{Dispersant Time Window (hr)} = \exp^{(-1.997657*\text{Sulfur}+0.107833*\text{Saturate}-0.326005*\text{Wax}-1.35108)}$$

Coefficient of Multiple Determination (R^2) = 0.979, all input fresh oil property data in wt%)

The best model identified for the 10,000 barrel spill is:

$$\text{Dispersant Time Window (hr)} = \exp^{(-1.30926*\text{Sulfur}+0.05534*\text{Saturate}-0.28146*\text{Wax}+2.7153)}$$

(R^2 = 0.971, all input fresh oil property data in wt%)

It is recommended that these correlations be validated using oil property data from sources outside of the US Gulf of Mexico (US GOM) or from new analyses of additional oils from the US GOM to verify that the trends identified in this study are valid when applied to data independent from those used to develop the correlations.

Ideally, data on oil behavior and dispersibility of oils from large tank tests or field spills should be used to validate both the spill modeling results and the oil dispersibility criteria used in this study.

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1. Background

The use of chemical dispersants in United States (US) waters is achieving a similar status to that of conventional booming and skimming countermeasures. As chemical dispersant treatment operations become more common there is an increased need to know when dispersants will likely be effective on different oil types to assist in the dispersant-use decision-making process. Unfortunately, the old adage that "no two oils are alike" applies all too well when it comes to the prediction of the available time window for successful dispersant use. The major oil properties that determine if a dispersant will be effective on the oil are the viscosity, pour point and emulsification formation tendency of the oil (SL Ross 2000, NRC 2005). Without knowledge of these three properties and how they vary once the oil is spilled under various environmental conditions, it is difficult to predict if, or for how long after release, the oil can be chemically dispersed. The goal of the work was to determine if commonly available, fresh oil properties can be used to predict the time window for dispersibility of oils.

2. Objective

The objective of this research was to develop best-fit correlations between readily available fresh oil properties and the window of opportunity for successful chemical dispersant use on Gulf of Mexico (GOM) crude oils.

3. Study Approach

The following was undertaken to complete the study.

The very detailed fresh and weathered oil property information available in Environment Canada's oil property database (Env. Can. 2007) for 24 oils from the Gulf of Mexico Region of the United States Outer Continental Shelf (US OCS) were processed to derive the oil parameters required by the SL Ross Oil Spill Model (SLROSM) to complete detailed oil spill behavior modeling as a function of spill type and environmental conditions. The sources for the

algorithms used in the main fate and behavior processes in the SLROSM spill model can be found in the previous MMS TA&R report #349 (SL Ross 2000).

The results from SLROSM were used to identify the time window for chemical dispersibility for oil spill scenarios (1,000 and 10,000 barrel batch spills) using average environmental conditions for the US GOM; 23ºC (73ºF) water temperature and 6 m/s (13 miles/hr) wind speed (SL Ross 2000). This model requires an extensive oil property data set derived from both fresh and weathered oil properties measured at two temperatures. Extensive data sets of this type that allow this detailed oil fate modeling are not available for a large number of oils. The goal of the project was to use the SLROSM modeling results for those oils in the US GOM OCS where such oil properties do exist to identify time windows for successful chemical dispersion. This modeled time window has then been used to determine if more basic fresh oil properties that are available for a wide range of oils can be used to predict the time window available for successful dispersion. The time that the model predicts that the oil's (or emulsion's) viscosity reaches 7,500 cP has been used as the maximum time-window for chemical dispersant use. This viscosity has been chosen based on the results from large-scale dispersant effectiveness testing completed for the Minerals Management Service (MMS) at the National Oil Spill Response Test Tank Facility (Ohmsett) that suggest that dispersants will be effective on oils only when the oil (or emulsion) viscosity is less than about 6,000 to 8,000 cP (SLRoss 2005, 2006). Other researchers have identified viscosity cutoffs for effective chemical dispersion ranging between 2,000 and 20,000 cP for a range of oils and emulsions (Daling 1999). The 7,500 cP cutoff represents a reasonably conservative estimate of the upper viscosity limit after which chemical dispersants are unlikely to be significantly effective. The more viscous the oil or emulsion, the more difficult it is for the dispersant to penetrate and mix into the oil when sprayed onto a slick. If the dispersant does not mix quickly into the oil when applied it can be quickly washed away into the surrounding water. Dispersant will also be ineffective if the oil's pour point exceeds the ambient water temperature by about 15ºC (60ºF). If the oil's pour point reached 38ºC (100ºF) prior to the oil viscosity reaching 7,500 cP in the SLROSM modeling, the shorter time was used as the time window for successful dispersant use. This criterion was applicable for only one of the oils studied (Mississippi Canyon Block 194).

The time windows identified using the spill behavior modeling have been correlated with the independent fresh oil property variables shown in Table 1. General descriptions of these properties and the methods used to measure them can be found in Jokuty 1999. The first nine properties listed in Table 1 are those currently requested from deep-water operators by MMS as per NTL No. 2006-G14. The last two, total aromatics and saturates have also been included in the correlation analyses because they are commonly available in Environment Canada's oil property database, the source of the fresh oil properties used in the study.

Table 1. Fresh Oil Property Data for Correlation

Fresh Oil Property Data
Gravity (API)
Flash Point (ºC)
Pour Point (ºC)
Viscosity (Centipoise at 25ºC (77ºF))
Wax Content (wt %)
Asphaltene Content (wt %)
Resin Content (wt %)
Boiling Point Distribution (with %vol or %wt for each fraction)
Sulfur (wt %)
Aromatics (wt %)
Saturates (wt %)

Oakdale Engineering's "DataFit" software program (version 8.2.79) was used to complete the data correlations. Detailed information on this software program can be found at Oakdale Engineering's web site (http://www.oakdaleengr.com/datafit.htm). The following description of this software package is derived from information provided at this web site. "DataFit is a science and engineering tool that simplifies the tasks of data plotting, regression analysis (curve fitting) and statistical analysis. The version of Datafit used in this study has 298 two-dimensional and 242 three-dimensional nonlinear pre-defined regression models. The pre-defined nonlinear regression models are commonly used in scientific, statistical and engineering applications. Linear or non-linear regression can be performed on one model at a time chosen from a list, groups of models, or all of the models available. The pre-defined models are grouped together based on the number of parameters and the general shape of their curves. As regression models are solved, they are sorted automatically according to the goodness-of-fit criteria specified".

In this study, the group of non-linear regression models identified as “single term and intercept correlations” within Datafit were applied to the time window of opportunity for dispersant use data (as modeled using SLROSM) and each of the individual fresh oil properties (independent variables) to identify the basic fresh oil properties with the highest correlation to dispersant time window.

4. Results

4.1 Fresh Oil Properties

Table 2 shows the fresh oil properties taken from Environment Canada’s database for each of the oils used in the correlations. Not all fresh oil properties were available for all of the oils. When properties were missing for some oils, the regression analyses for that property were completed with less than 24 data points. Wax content was available for only sixteen of the oils studied. Only six of the sixteen fresh oil properties were available for the West Delta Block 143 oil. Four Gulf of Mexico oils in the Environment Canada database were rejected for use in this study because the oil samples that were analyzed had very high water contents (>10%) and the oil properties reported would be unreliable in modeling dispersant time window. These oils included Ship Shoal Block 239, South Pass Block 67, West Delta 30 and South Pass Block 93. Five of the oils used in the analysis did not have emulsion formation tendency and stability data but they were reported to have zero asphaltene content (Ship Shoal Block 269, Eugene Island Block 43, South Timbalier Block 130, Mississippi Canyon Block 194, and West Delta Block 97). It was assumed that these oils would not form an emulsion due to the absence of asphaltenes in their composition (Bobra 1992, Walker1993).

Table 2. Fresh Oil Properties from Environment Canada's Oil Property Database & Dispersant Use Time Window of Opportunit

Oil Filename	Fresh Oil Properties																Time Window (hr)	
	API Gravity	Sulfur (wt %)	Flash point (°C)[1]	Pour Point (°C)	Viscosity (cP)	Saturates (wt %)	Aromatics (wt %)	Resin (wt %)	Asphaltenes (wt %)	Wax (wt %)	BP<200 °C (wt %)	BP<250 °C (wt %)	BP<300 °C (wt %)	BP<350 °C (wt %)	BP < 400 °C (wt %)	BP<450 °C (wt %)	1,000 Barrel	10,000 Barrel
Green Canyon Block 65	19.5	1.9	-4	-28	102	38	40	14	8	1	11	18	26	34	43	52	5.2	6
West Delta Block 143	29.1				20	61	27	9	3.6								9.1	13.6
Morpeth Block EW921	25.1	1.73	-10	-65	30	71	17	8	4	0.7	14	20	26	34	40	48	12.1	16.7
Garden Banks Block 386	29.5	1.52	-28	-39	19	53	36	10	1		17	24	33	43	53	62	16.2	23.6
Viosca Knoll Block 826	31.6	0.29	-2	-4	11	66	26	6	2		19	29	40	51	62	72	20.2	30
Mississippi Canyon Block 72	32	0.39	-5	-28	12	64	27	7	2		20	29	39	49	59	68	27	46
Green Canyon Block 109	27	1.89	0	-36	25	51	39	9	1	2	15	22	30	39	48	57	30	46.5
Mars TLP (2004)	27.6	2.1	-26	-28	24	60	24	11	5.5	1.5	11	16	22	28	35	42	31.5	53
South Pass Block 60	35.8	0.28	-4	-9	5	71	20	8	1	7	27	39	51	62	71	79	50	82.6
Eugene Island Block 43	36.8	0.18	12	0	7	81	16	3	0	8	16	27	43	58	71	83	60.6	87
Garden Banks Block 426	40.8	0.94	-24	-22	5	70	24	5	1		29	39	49	59	67	75	65.6	109
Mississippi Canyon Block 807	27.5	2.2	-35	-34	29	47	35	12	6		21	28	36	45	53	62	76.5	146
Mississippi Canyon Block 194	35.2	0.21	-6	-40	5	71	25	4	0	5	23	37	52	66	75	84	102	169
Green Canyon Block 200	33.9	0.87	0	-10	11.4	82	10	6.9	0.8	1.7	27	35	44	53	61	69	177	296
Viosca Knoll Block 990	38.1	0.22	-17	-32	5	73	22	4	1	2.2	26	36	46	57	66	74	200.4	335
Petronius Block VK87A	30	0.34	-10	-19	20	84	9	6	1.6	2.7	17	25	34	44	53	61	473	473
Eugene Island Block 32	36.9	0.02	21	7	6	84	14	2	1		10	23	46	69	82	91	1000	1000
Green Canyon Block 184	39.4	0.94	-18	-44	4	69	24	6	1		29	39	48	58	66	74	1000	1000
South Louisiana Crude	34.5	0.45	-11	-28	5	73	21	4	1	4	21	33	46	59	69	78	1000	1000
Main Pass Block 306	32.8	0.28	-35	-53	7	65	29	5	1	3	26	37	49	60	70	79	1000	1000
Main Pass Block 37	33	0.16	-6	-3	4	73	21	5	1	8	29	41	53	65	74	83	1000	1000
Ship Shoal Block 269	38.7	0.41	-7	-42	4	79	15	6	0	5	30	43	56	68	77	84	1000	1000
South Timbalier Block 130	35.1	0.32	5	-27	5	78	16	5	0	4	25	39	54	66	76	84	1000	1000
West Delta Block 97	50.2	0.07	-35	-27	1	92	7	1	0	4	55	72	86	95	99	100	1000	1000

[1] ºC *(9/5)+32 = ºF

4.2 Spill Scenario Modeling Results

The time windows for dispersant use, as estimated using the SLROSM spill model, for each of the oils for the 1,000 and 10,000 barrel batch spill scenarios are shown in the last two columns of Table 2. Eight of the oils dispersed naturally, within 6 to 30 hours, under the prevailing environmental conditions (23°C (73ºF) temperatures and 6 m/s (13 miles/hr) wind speed). These oils never reached the viscosity cutoff that would limit dispersant use. The spill scenarios involving these eight oils were re-run with natural dispersion turned off to allow evaporation to proceed in hopes of reaching the viscosity cutoff. The oil continued to evaporate slowly in these scenarios up to 720 hours of simulation but the oil viscosities never reached the 7,500 cP cutoff that would preclude dispersant use. A time window of 1,000 hours was entered for these oils for use in the correlations of time window to fresh oil properties. For all of the other oils, the time for the oil or emulsion to reach a viscosity of 7,500 cP, as predicted by SLROSM, was used in the regression analyses.

4.3 Fresh Oil Property – Time Window Correlations

Two sets of time window / fresh oil property correlations were completed for each oil property. One set utilized the data from all oils and one used only the data for the persistent oils. The correlations were completed for the persistent oil subset when it was found that poor correlations resulted when the full data set was used. The persistent oils are the first sixteen oils in Table 2. These oils all have predicted time windows for dispersant application of less than 1,000 hours (see last two columns in Table 2).

4.3.1 Full Data Set Correlations

Tables 3 and 4 provide results from single independent parameter (fresh oil property) correlations with time window for dispersibility for the 1,000 barrel and 10,000 barrel spill scenarios for all oils. The full group of “single term and intercept” non-linear regression correlations available in the Datafit software was applied to each fresh oil property / dispersant time window combination. The forms of the regression models that provided the best-fit correlations and the best “simple” correlations (those without logarithmic or exponential terms)

are provided in Tables 3 and 4. The simple correlations have been included to reveal if the more complex correlations are justifiable given a comparison of the R^2 values for the simple and complex regressions. The Coefficients of Multiple Determination (R^2) are provided in each table to show the goodness of the fit of each equation. This value can be interpreted as the fraction of the variance in the data that is explained by the data model. R^2 approaching 1.0 indicates a very good fit, values below 0.7 are poor fits. When all of the data (persistent and non-persistent oils) are used in the correlations, there is no fresh oil property that correlates well with the time window for dispersant use. The results suggest that there is no way to predict time window of opportunity for dispersant effectiveness using basic fresh oil properties for the full range of non-persistent and persistent oils. The highest R^2 recorded is less than 0.5 for both the 1,000 and 10,000 barrel spills. No attempt was made to correlate multiple independent variables to time window for dispersant use using the full oil property dataset because of the poor individual correlations with the full dataset.

Table 3. 1,000 Barrel Time Window (Y) - Fresh Oil Property (x) Correlations: All Oils

Fresh Oil Property (x)	Form of Best Fit Equation (Y=)	R^2	Simpler Best Fit Eq'n	R^2
BP<400	a+b*x^1.5	0.428057		
BP<350	a+b*x/log(x)	0.422548	a+b*x^.5	0.418323
BP<450	a+b*x^2.5	0.419391	a+b*x^3	0.418934
BP<300	a+b*log(x)^2	0.386318	a+b*x^.5	0.38629
Viscosity	a+b/x^.5	0.38625		
Resins	a+b*x^.5	0.336451		
BP<250	a+b*log(x)^2	0.294311	a+b*x^.5	0.293947
Waxes	a+b*exp(-x)	0.291931	a+b/x^.5	0.238406
Saturates	a+b*x^2.5	0.282478	a+b*x^2	0.281461
Sulfur	a+b*x^.5	0.273354		
API Gravity	a+b*x^.5*log(x)	0.267872	a+b*x^.5	0.26734
Asphaltenes	a+b*x^.5	0.220641		
BP<200	a+b*x*log(x)	0.20501	a+b*x^1.5	0.200257
Aromatics	a+b*x*log(x)	0.198093	a+b*x^1.5	0.197158
Flash point	a+b*exp(x)	0.081368	a+b*x^2	0.028187
Pour Point	a+b*exp(x)	0.081305	a+b*x^2	0.000873

Note: constants a, b, c, d and e shown in the "best fit" equations in this report are curve-fitting values determined by Datafit. Values for these constants are provided only for the final best-fit correlations in Tables 8 and 10.

Table 4. 10,000 Barrel Time Window (Y) - Fresh Oil Property (x) Correlations: All Oils

Fresh Oil Property (x)	Form of Best Fit Equation (Y=)	R^2	Simpler Best Fit Eq'n	R^2
BP<400	a+b*x^1.5	0.448466		
BP<350	a+b*x*log(x)	0.44771	a+b*x^.5	0.44523
BP<300	a+b*log(x)^2	0.415651	a+b*x^.5	0.414022
Viscosity	a+b/x^.5	0.404611		
Resins	a+b*x^.5*log(x)	0.356095	a+b*x^.5	0.356032
BP<250	a+b*log(x)^2	0.323014	a+b*x^.5	0.320978
Waxes	a+b*log(x)/x	0.313216	a+b/x^.5	0.251378
Saturates	a+b*x^2*log(x)	0.301624	a+b*x^2	0.301089
API Gravity	a+b*x^.5*log(x)	0.295422	a+b*x^.5	0.295318
Sulfur	a+b*x^.5	0.287223		
Asphaltenes	a+b*x^.5	0.236481		
BP<200	a+b*x/log(x)	0.225585	a+b*x^.5	0.218543
Aromatics	a+b*x*log(x)	0.213755	a+b*x^2	0.208341
Flash point	a+b*exp(x)	0.079918	a+b*x^2	0.029492
Pour Point	a+b*exp(x)	0.079854	a+b*x^2	0.000306

4.3.2 Persistent Oil Data Set Correlations

Tables 5 and 6 provide the results from the single independent parameter correlations for the 1,000 barrel and 10,000 barrel spill scenarios for the persistent oils (i.e, excluding the eight oils assigned a time window of 1,000 hours). The full group of "single term and intercept" correlations available in Datafit was applied to each fresh oil property / time window correlation. The best-fit correlation and the best "simple" correlation (not log or exponential) are provided in Tables 5 and 6. When only the persistent oil data is used in the correlations, the percentage of aromatics, saturates and fraction lost below 400 °C in the distillation of the fresh oil show significant correlation to the time window for dispersant use in the 1,000 barrel spill scenarios. Coefficients of Multiple Determination (R^2) of about 0.8 were achieved in these data fits. The other fresh oil properties do not show any significant correlation to dispersant time window and have R^2 values of less than 0.2. The percentages of aromatics and saturates also have the highest correlations with the time window for the 10,000 barrel spill scenarios, although the R^2 values are only about 0.6 as seen in Table 6. It is believed that the reduced R^2 for the 10,000 barrel spills is related to the slower evaporation rate for the larger (and thicker) spills. This extends the time before the oil emulsifies and may be increasing the scatter in the cut off times for dispersant application. Plots of the significant data models can be viewed by clicking the active links in the

"Form of Best Fit Equations" columns of Tables 5 and 6. Considerable scatter is evident in the data even for the better correlations identified.

Table 5. 1,000 Barrel Time Window (Y) - Fresh Oil Property (x) Correlations: Persistent Oils

Fresh Oil Property (x)	Form of Best Fit Equation (Y=)	Figure # in Appendix A	R^2	Simpler Best Fit Eq'n (Y=)	R^2
Aromatics	a+b*exp(-x)	Figure A1	0.831283	a+b/x^2	0.690272
Saturates	a+b*exp(x)	Figure A2	0.812618	a+b*x^3	0.441491
BP<400	a+b*exp(x)	Figure A3	0.791651	a+b*x^3	0.619175
Waxes	a+b*log(x)/x	Figure A4	0.179121	a+b/x^2	0.127023
Sulfur	a+b*x^.5*log(x)		0.155648	a+b*x^1.5	0.150981
Resins	a+b*x/log(x)		0.13833	a+b*x^1.5	0.132897
Asphaltenes	a+b*x^1.5	Figure A5	0.078329	a+b*x^2	0.073155
BP<200	a+b/x^2		0.07294		
API Gravity	a+b/x^2		0.06544		
BP<250	a+b/x^2		0.064703		
Pour Point	a+b*x^2		0.058445		
BP<300	a+b/x^2		0.055904		
BP<350	a+b/x^2		0.053339		
Viscosity	a+b*x*log(x)		0.040332	a+b*x^1.5	0.039279
BP<450	a+b/x^2		0.035459		
Flash point	a+b*x^3		0.016065		

Table 6. 10,000 Barrel Time Window (Y) - Fresh Oil Property (x) Correlations: Persistent Oils

Fresh Oil Property (x)	Form of Best Fit Equation (Y=)	Figure # in Appendix A	R^2	Simpler Best Fit Eq'n (Y=)	R^2
Aromatics	a+b*exp(-x)	Figure A6	0.619229	a+b/x^2	0.601151
Saturates	a+b*exp(x)	Figure A7	0.54533	a+b*x^3	0.457886
Sulfur	a+b*x^.5*log(x)	Figure A8	0.287223	a+b*x^.5	0.166996
Waxes	a+b*log(x)/x	Figure A9	0.252561	a+b/x^2	0.18018
Resins	a+b*x/log(x)		0.188085	a+b*x^.5	0.176383
BP<200	a+b*log(x)/x		0.171499	a+b/x^.5	0.171481
BP<250	a+b/x^1.5		0.149203		
API Gravity	a+b*log(x)/x		0.137313	a+b*x^.5	0.133423
BP<300	a+b/x^2		0.125907		
BP<350	a+b/x^2		0.113954		
Asphaltenes	a+b*x^1.5		0.104252	a+b*x^2	0.094
BP<400	a+b/x^2		0.100365		
Viscosity	a+b*log(x)^2		0.090309	a+b*x^.5	0.09028
Pour Point	a+b*x^3		0.068341		
Flash point	a+b*exp(x)		0.006835	a+b*x^3	0.005636

A number of multiple independent variable correlations were completed using the "best fit" fresh oil parameters from the single parameter correlations. Tables 7 through 10 show these results of these multiple parameter correlations. Plots of the significant data models can be viewed by clicking the active links in the "Form of Best Fit Equations" columns of these Tables. These plots show a comparison of the modeled time window with the dependent value.

Two and three parameter correlations with aromatics, saturates and BP <400 (the three highly correlated single independent parameters) did not provide any improvement in correlations for the 1,000 barrel spills as seen from the R^2 values in Table 7 (all R^2 values less than 0.75). Three parameter correlations of aromatics and saturates with sulfur, resins or asphaltenes did not generate any significant fits. However, the correlation of aromatics, saturates and waxes with the time window resulted in a dramatic improvement in the goodness-of-fit. An R^2 of 0.932 was achieved with this three-parameter correlation. The wax parameter is available for only 10 of the 16 persistent oils. When it is included in a regression analysis the sample size used in the regression analysis is reduced. It was considered a possibility that the improved fit, when wax was included, might be due to the reduced sample size rather than the inclusion of the wax parameter. A number of additional three parameter correlations were completed to test this possibility using only the sub-set of data where wax content is available. The correlations with the reduced sample size resulted in lower R^2 values than those where wax was included (see bottom three rows of Table 7) thus indicating that the sample size was likely not the reason for the improved fit but rather the inclusion of the wax content in the correlation. A four-parameter correlation was completed using saturates, aromatics, BP<400 and waxes. The resulting R^2 of 0.953 is only marginally better than the 0.932 R^2 associated with the aromatics, saturate and wax correlation. A final three-parameter correlation was completed using sulfur, saturates and waxes. This correlation was added because this combination was found to provide the best correlation in the 10,000 barrel spill analysis. This combination of sulfur, saturates and waxes resulted in the best fit for the 1,000 barrel spill, as well, with an R^2 value of 0.979. The three best-fit equations for the 1,000 barrel spill correlations are provided in Table 8.

Table 7. Multiple Independent Variable (xi) Correlations:1,000 Barrel Spills

Independent Variables (xi)	Form of Best Fit Equation (Y=)	Figure # in Appendix A	R^2
SatBP<400	a*b^x1*x2^c		0.722373
AroSat	a*b^x1*x2^c		0.704566
AroBP<400	a+b/x1+c/x2		0.313172
AroSatBP<400	exp(a*x1+b*x2+c*x3+d)	Figure A10	0.677938
SulSatWax	exp(a*x1+b*x2+c*x3+d)	Figure A11	0.976245
AroSatWax	exp(a*x1+b*x2+c*x3+d)	Figure A12	0.932368
AroSatSulfur	exp(a*x1+b*x2+c*x3+d)		0.785066
AroSatAsphaltenes	exp(a*x1+b*x2+c*x3+d)		0.741935
AroSatResin	exp(a*x1+b*x2+c*x3+d)		0.694360
AroSatBP<400Wax	exp(a*x1+b*x2+c*x3+d*x4+e)	Figure A13	0.95279
AroSatBP<400#	exp(a*x1+b*x2+c*x3+d)		0.75796
AroSat#	a*b^x1*x2^c		0.695774
AroSatResin#	exp(a*x1+b*x2+c*x3+d)		0.445539
# using only data where wax data also exists			

The Prob(t) numbers in Tables 8 and 10 provide an indication of the importance of the independent variable in the correlation. The smaller the value of Prob(t), the less likely the parameter is zero and the more likely the parameter is important in the correlation. For example, if Prob(t) = 0.01, there is a 1% chance that the parameter is zero. If Prob(t) = 0.95, there is a 95% chance that the parameter value is zero and can usually be removed from the model without affecting the regression accuracy.

Table 8. Best-Fit Equations for 1,000 Barrel Spill

Model (Y=)	Figure # in Appendix A	Parameters		Independent Variables (xi)		Prob(t)
SulSatWax: R^2 0.979		a	-1.997657	x1	sulfur	0.00043
exp(a*x1+b*x2+c*x3+d)	Figure A11	b	0.107833	x2	saturates	0.00008
		c	-0.326005	x3	waxes	0.00082
		d	-1.351080			0.1874
AroSatWax : R^2 0.932		a	1.67416	x1	saturates	0.00804
exp(a*x1+b*x2+c*x3+d)	Figure A12	b	1.30981	x2	aromatics	0.01007
		c	-1.12801	x3	waxes	0.0078
		d	-143.22522			0.00989
AroSatBP<400Wax : R^2 0.953		a	0.72856	x1	saturates	0.01992
exp(a*x1+b*x2+c*x3+d*x4+e)	Figure A13	b	0.60839	x2	aromatics	0.01889
		c	-0.07188	x3	BP<400	0.04602
		d	-0.47719	x4	waxes	0.03527
		e	-55.42860			0.03687

The two parameter correlations using aromatics and saturates for the 10,000 barrel spills (the highest correlated single independent parameters as seen in Table 6) generated an R^2 value of only about 0.6 as shown Table 9. Additional two-parameter correlations were also completed using various combinations of aromatics, saturates, waxes and sulfur. These correlations generated R^2 values between 0.6 and 0.8.

The three-parameter correlation of aromatics, saturates and waxes with the time window resulted in a dramatic improvement in the goodness-of-fit similar to that observed with the 1,000 barrel spill scenarios. An R^2 of 0.905 was achieved with this three-parameter correlation. The improved fit was not due to the reduced sample size caused by the use of the wax parameter. A number of multiple parameter correlations were completed to test this possibility using only the sub-set of data where wax content is available. The correlations with the reduced sample size did not result in fits as good as the ones in which wax was included (see bottom three rows of Table 9) thus indicating that the sample size was not the reason for the improved fit but rather the inclusion of the wax content in the correlation. Three parameter correlations of aromatics and saturates with sulfur or resins did not generate significant correlations ($R^2 < 0.6$).

A four-parameter correlation of saturates, aromatics, resins and asphaltenes (SARA) resulted in a poor fit (R^2 = 0.641). The five-parameter correlation of SARA plus waxes to time window generated a good fit (R^2 = 0.97) but the complexity of this model is not warranted since simpler models have been identified with a similar fit.

A four parameter correlation was completed using saturates, aromatics, sulfur and waxes (the highest four single parameter correlations in Table 6). The resulting R^2 of 0.971 is better than the 0.905 R^2 associated with the aromatics, saturate and wax correlation. The high prob(t) value for aromatics shown in Table 10 for this four-parameter model indicate that the aromatics parameter is not significantly contributing to the correlation. When it is removed from the correlation the three-parameter fit is as good as the four parameter model and the resulting prob(t) values are all very low indicating that all parameters are required in the correlation. The best-fit equations for the two models are provided in Table 10 along with the aromatics, saturates, and wax correlation.

Table 9. Multiple Independent Variable (xi) Correlations:10,000 Barrel Spills

Independent Variables (xi)	Form of Best Fit Equation (Y=)	Figure # in Appendix A	R^2
AroSat	a*b^x1*x2^c		0.598969
SulWax	a+b*x1+c*x2		0.789128
SatWax	a*x1^b*c^x2		0.666551
AroWax	a+b/x1+c/x2		0.620339
AroSatWax	exp(a*x1+b*x2+c*x3+d)	Figure A14	0.905291
AroSatSul	exp(a*x1+b*x2+c*x3+d)		0.596224
AroSatRes	exp(a*x1+b*x2+c*x3+d)		0.569753
SatSulWax	exp(a*x1+b*x2+c*x3+d)	Figure A16	0.971208
AroSatSulWax	exp(a*x1+b*x2+c*x3+d*x4+e)	Figure A15	0.971474
SARA[1]	exp(a*x1+b*x2+c*x3+d*x4+e)		0.616519
SARA+wax	exp(a*x1+b*x2+c*x3+d*x4+e*x5+f)		0.970179
AroSat*	a*b^x1*x2^c		0.596326
AroSatSul*	exp(a*x1+b*x2+c*x3+d)		0.642766
SARA*	exp(a*x1+b*x2+c*x3+d*x4+e)		0.64111
*only data used where wax data also exists			

[1] Saturates, Aromatics, Resins and Asphaltenes (SARA)

Table 10. Best-Fit Equations for 10,000 Barrel Spill

Model (Y=)	Model Parameters		Independent Variables (xi)		Prob(t)
AroSatWax: R^2 0.905	a	0.64470	x1	saturates	0.05906
exp(a*x1+b*x2+c*x3+d)	b	0.50826	x2	aromatics	0.06703
	c	-0.52885	x3	waxes	0.02451
	d	-51.22984			0.08482
AroSatSulWax: R^2 0.971	a	0.03817	x1	saturates	0.64241
exp(a*x1+b*x2+c*x3+d*x4+e)	b	-0.01545	x2	aromatics	0.83244
	c	-1.36210	x3	sulfur	0.00943
	d	-0.27811	x4	waxes	0.00243
	e	4.30946			0.57479
SatSulWax: R^2 0.971	a	0.05534	x1	saturates	0.00114
exp(a*x1+b*x2+c*x3+d)	b	-1.30926	x2	sulfur	0.00075
	c	-0.28146	x3	waxes	0.00072
	d	2.71530			0.01191

The “saturates, sulfur and wax” correlation provides the best prediction of time window for dispersant use for the larger spill volume with the smallest number of independent variables.

5. Conclusions and Recommendations

Two distinct groups of oils were identified with respect to dispersant use time window; persistent and non-persistent oils. The non-persistent oils are those that do not form water-in-oil emulsions and are amenable to dispersant use over the entire time that they are present on the water surface. If natural dispersion were not occurring, these oils would be dispersible for at least 20 days after being spilled. However, it is likely that they will disperse naturally within 6 to 30 hours of being spilled under average environmental conditions based on the modeling completed in this study. The persistent oils are those that form stable water-in-oil emulsions at some point with a subsequent increase in bulk viscosity and a reduction in dispersion. In most cases, oil can be categorized into the two groups by its asphaltene content. If there are no asphaltenes present in the oil then the oil is unlikely to emulsify (Bobra 1992, Walker 1993) and will be chemically dispersible while on the water surface as long as the parent oil viscosity remains below the threshold for successful dispersion. In the absence of emulsification most oils will remain below

this viscosity for long periods. Oils with small quantities of asphaltene (1% or less) may or may not form a stable emulsion and it is impossible to categorize these oils without detailed fresh and weathered oil property testing. Oils with asphaltene contents of 1% or more and asphaltene/resin concentrations of 3% or more will likely emulsify at some point after spilled (Bobra 1992, Walker 1993).

Correlations of fresh oil properties with maximum time window for dispersant use for the persistent US GOM oils studied have identified predictor models for 1,000 and 10,000 barrel spills. The correlation of fresh oil sulfur, saturate and wax contents with the time window generated the best model for prediction of dispersant time window for both the 1,000 and 10,000 barrel spill scenarios. The best model identified for the 1,000 barrel spill is:

$$\text{Dispersant Time Window (hr)} = \exp^{(-1.997657*\text{Sulfur}+0.107833*\text{Saturate}-0.326005*\text{Wax}-1.35108)}$$

($R^2 = 0.979$, all input fresh oil property data in wt% as per Table 2)

The best model identified for the 10,000 barrel spill is:

$$\text{Dispersant Time Window (hr)} = \exp^{(-1.30926*\text{Sulfur}+0.05534*\text{Saturate}-0.28146*\text{Wax}+2.7153)}$$

($R^2 = 0.971$, all input fresh oil property data in wt% as per Table 2)

The quantity of wax in the fresh oil has a significant effect in all of the correlations in this study. The use of wax content in the "persistent oil only" correlations reduces the sample size to 10. It may be prudent to complete additional correlations using oil property data from sources outside of the US Gulf of Mexico (US GOM) or from new analyses of additional oils from the US GOM to verify that the trends identified in this study are valid when applied to data independent from those used to develop the correlations.

Ideally, data on oil behavior and dispersibility of oils from large tank tests or field spills should be used to validate both the spill modeling results and the oil dispersibility criteria used in this study.

6. References

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7. Appendix A. Data Correlation Plots

Figure A1. Aromatics vs Dispersant Time Window: 1,000 Barrel Spills

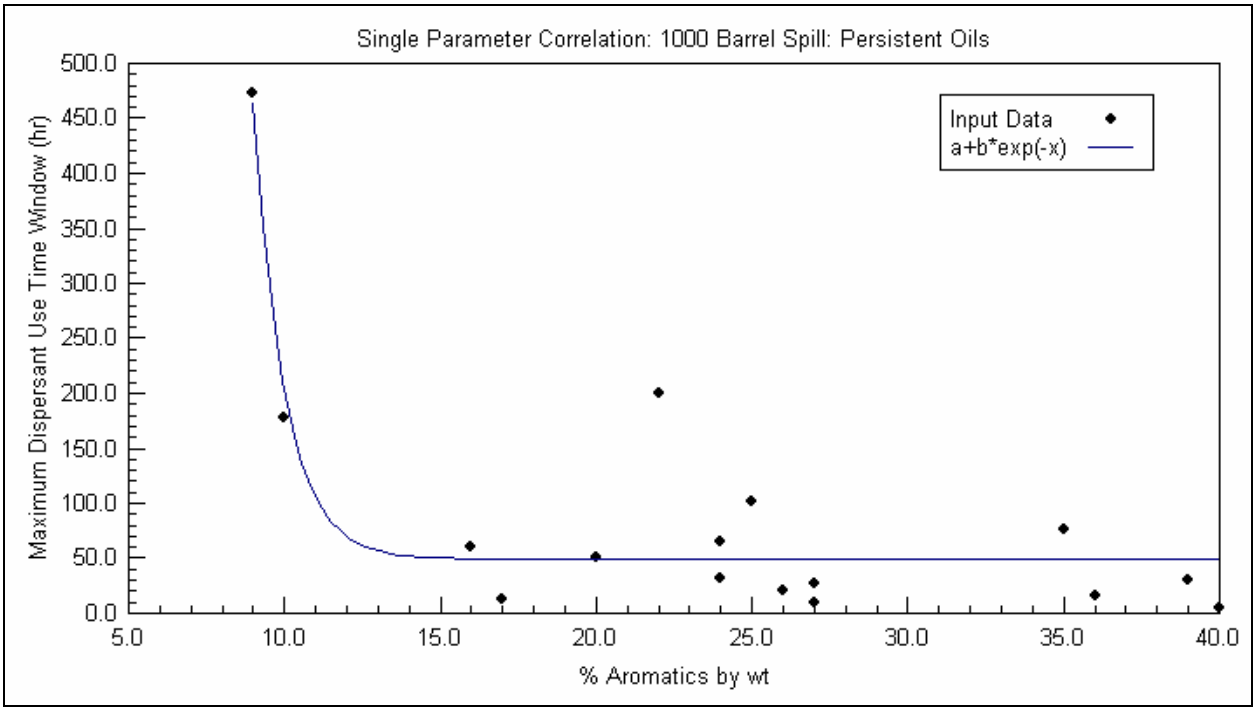

Figure A2. Saturates vs Dispersant Time Window: 1,000 Barrel Spills

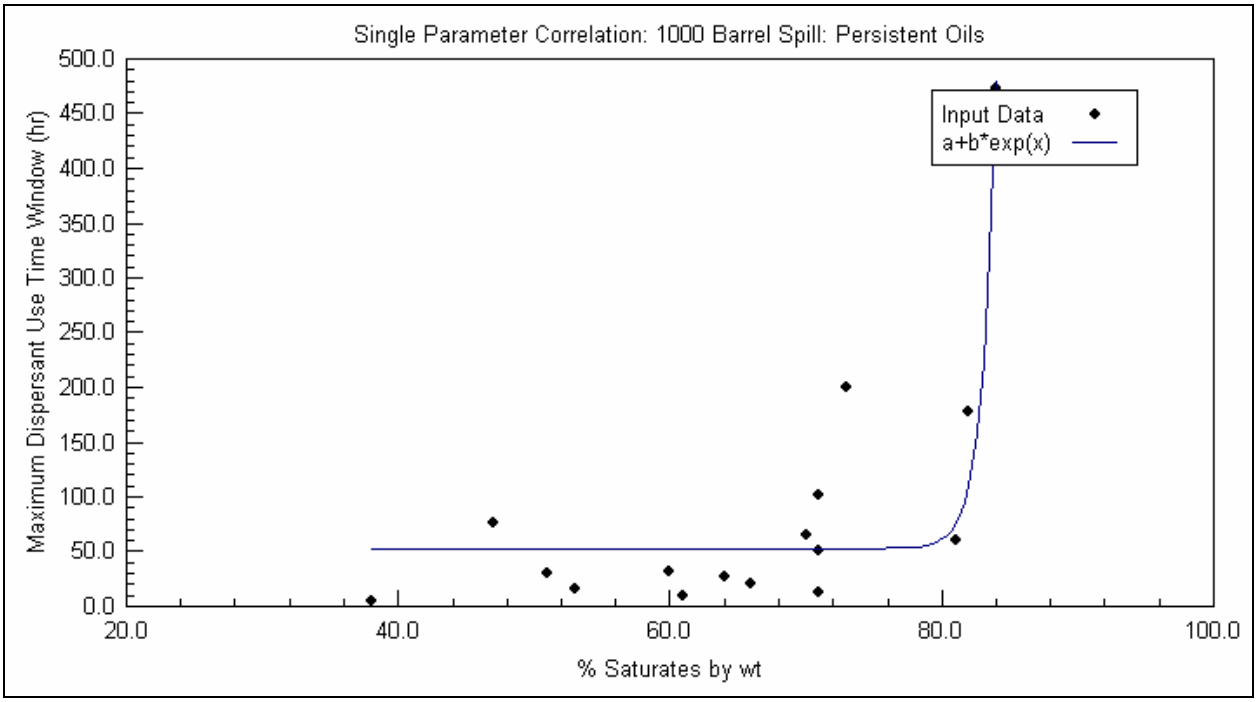

Figure A3. BP<400 vs Dispersant Time Window: 1,000 Barrel Spills

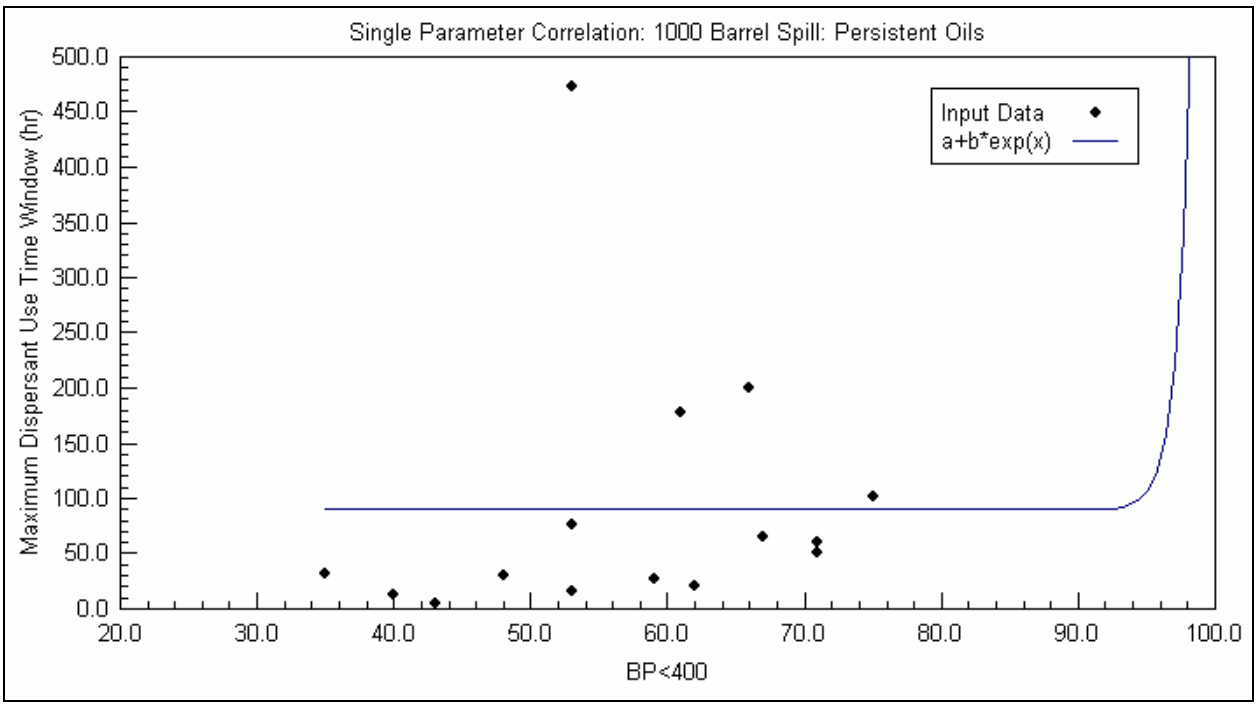

Figure A4. Wax vs Dispersant Time Window: 1,000 Barrel Spills

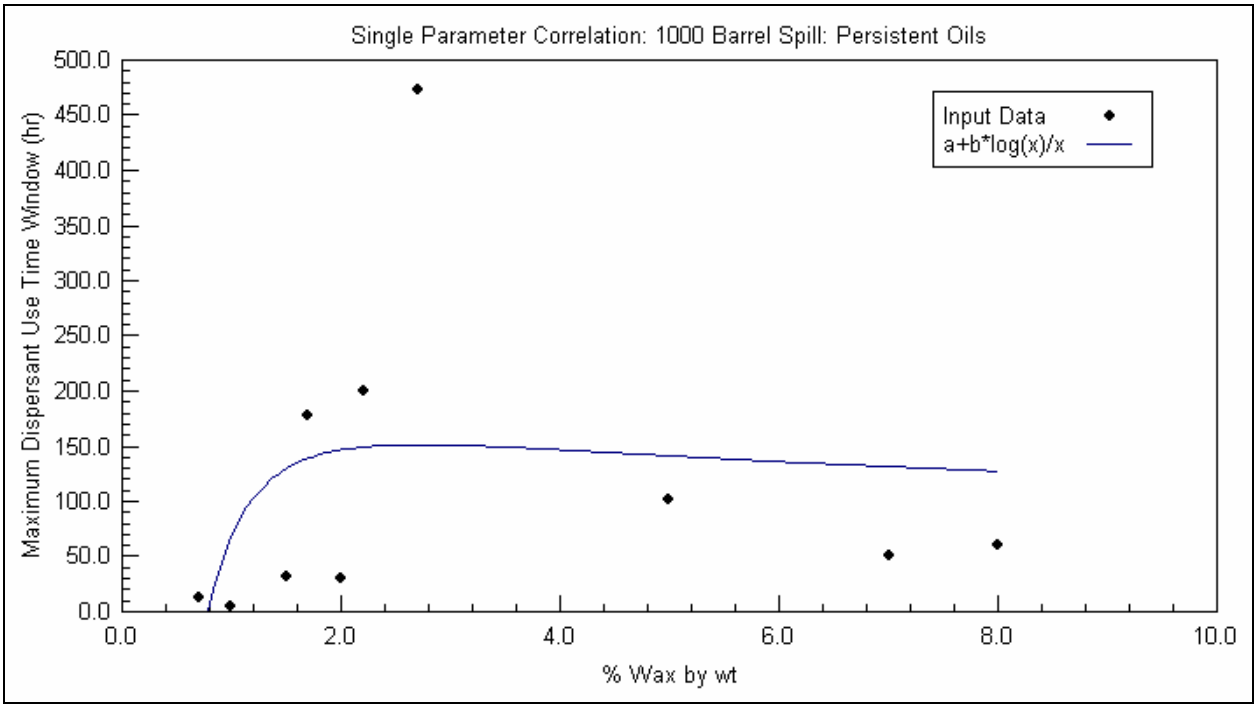

Figure A5. Asphaltene vs Dispersant Time Window: 1,000 Barrel Spills

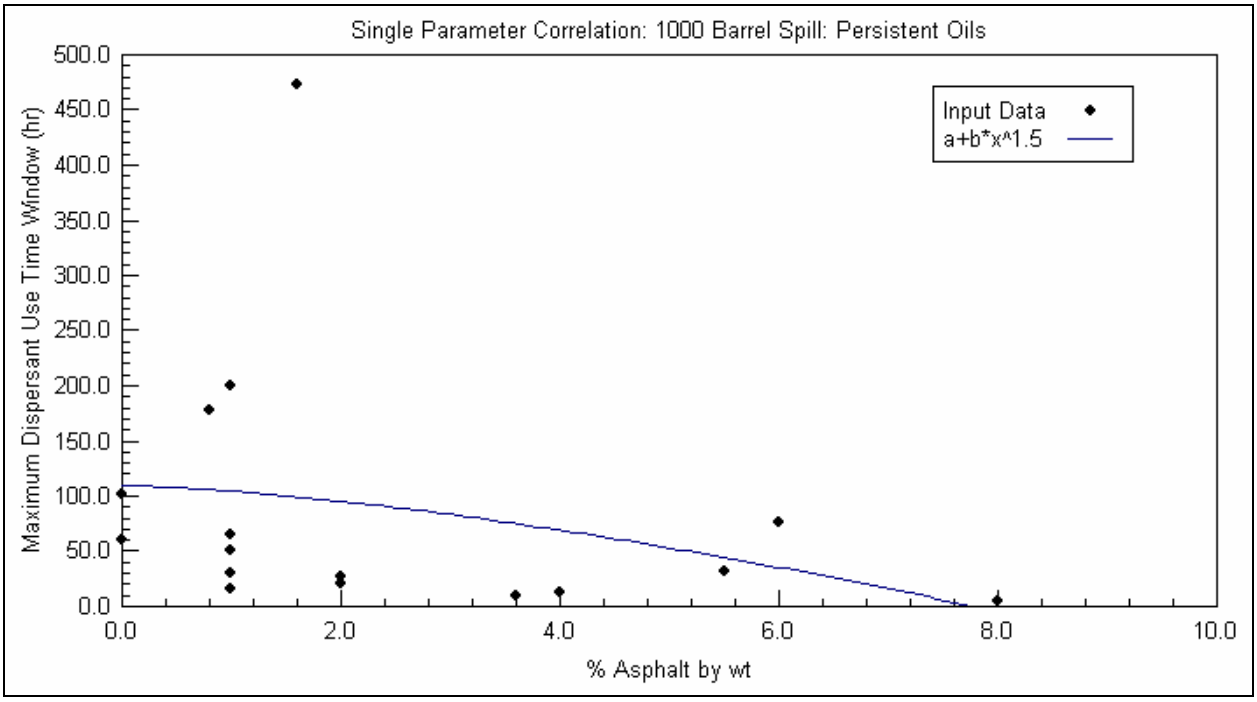

Figure A6. Aromatics vs Dispersant Time Window: 10,000 Barrel Spills

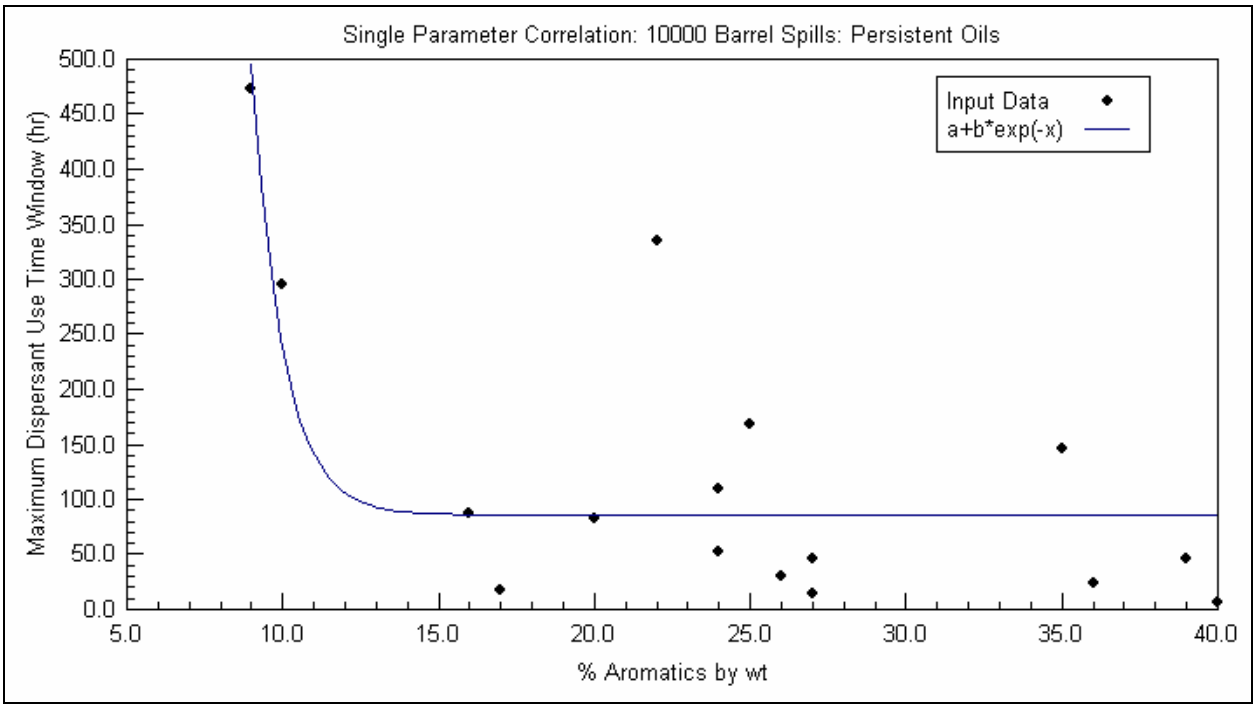

Figure A7. Saturates vs Dispersant Time Window: 10,000 Barrel Spills

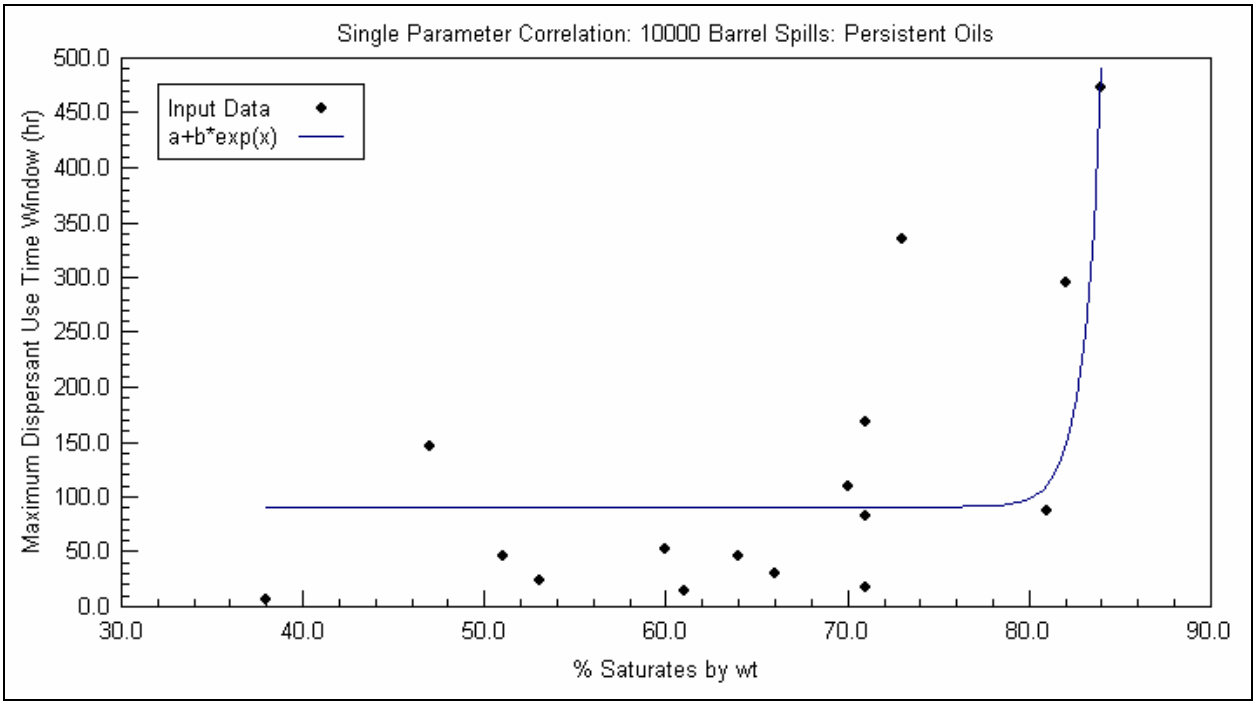

Figure A8. Sulfur vs Dispersant Time Window: 10,000 Barrel Spills

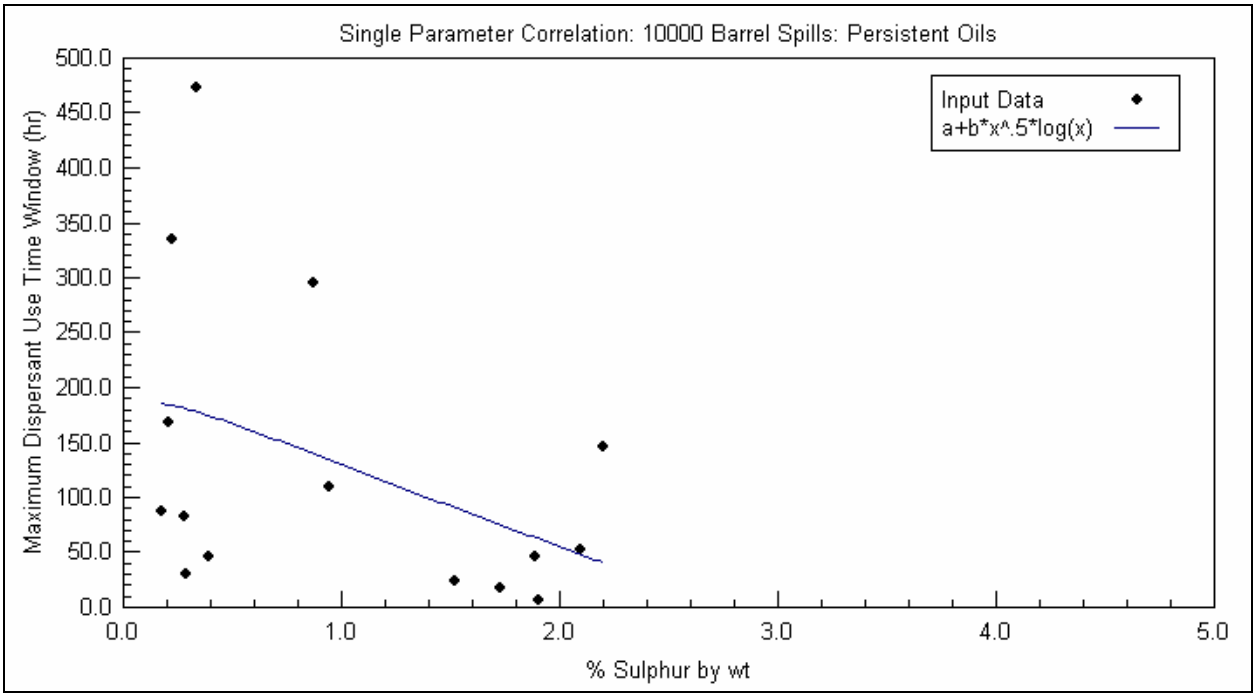

Figure A9. Waxes vs Dispersant Time Window: 10,000 Barrel Spills

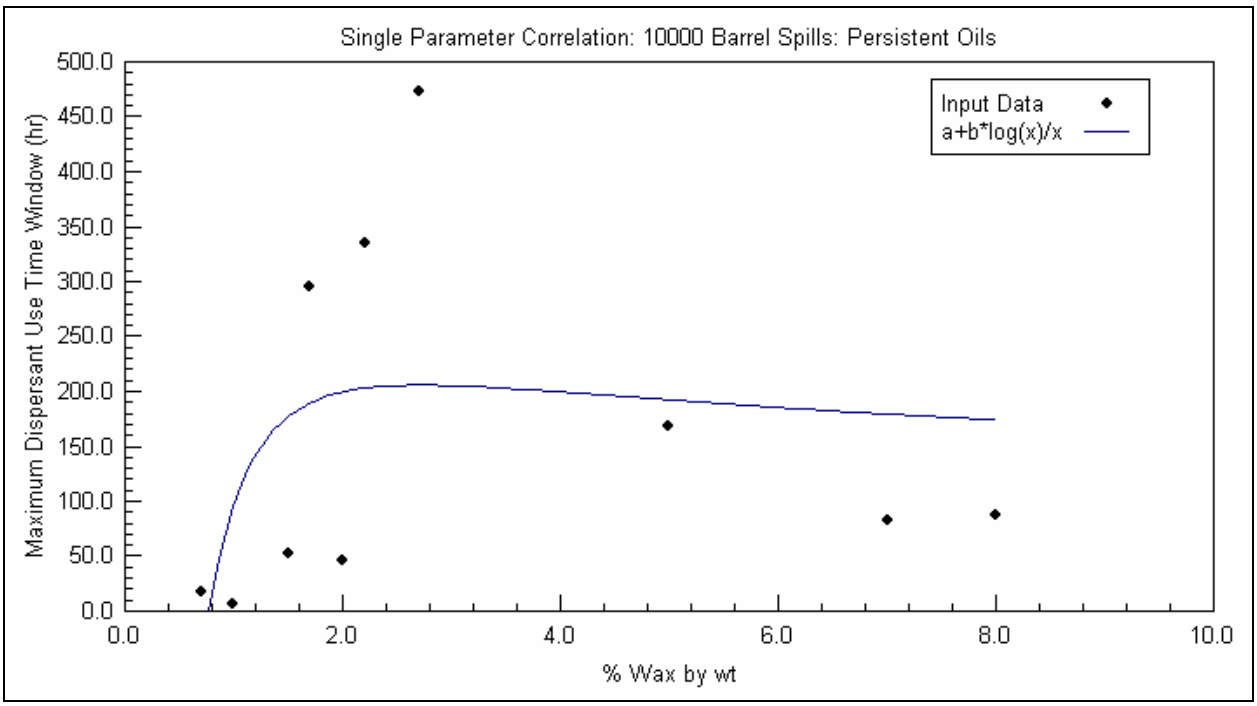

Figure A10. Aromatics, Saturates and BP<400 vs Dispersant Time Window: 1,000 Barrel Spills

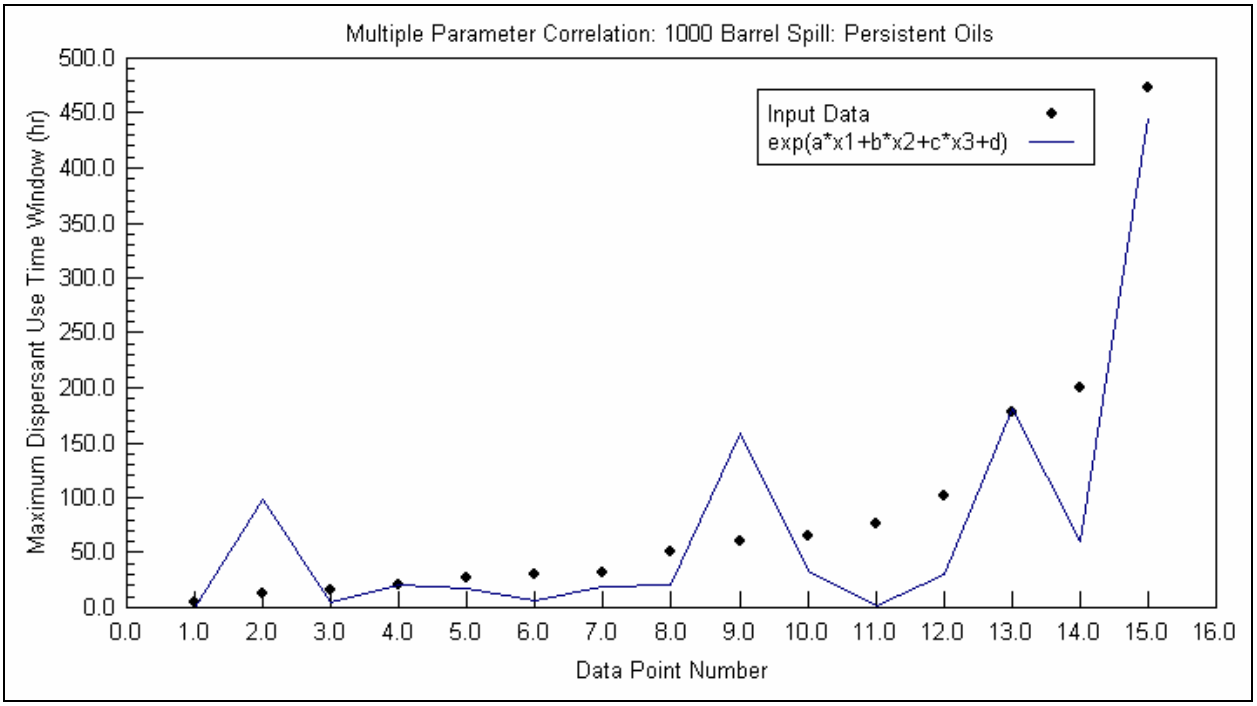

Figure A11. Sulfur, Saturates and Waxes vs Dispersant Time Window: 1,000 Barrel Spills

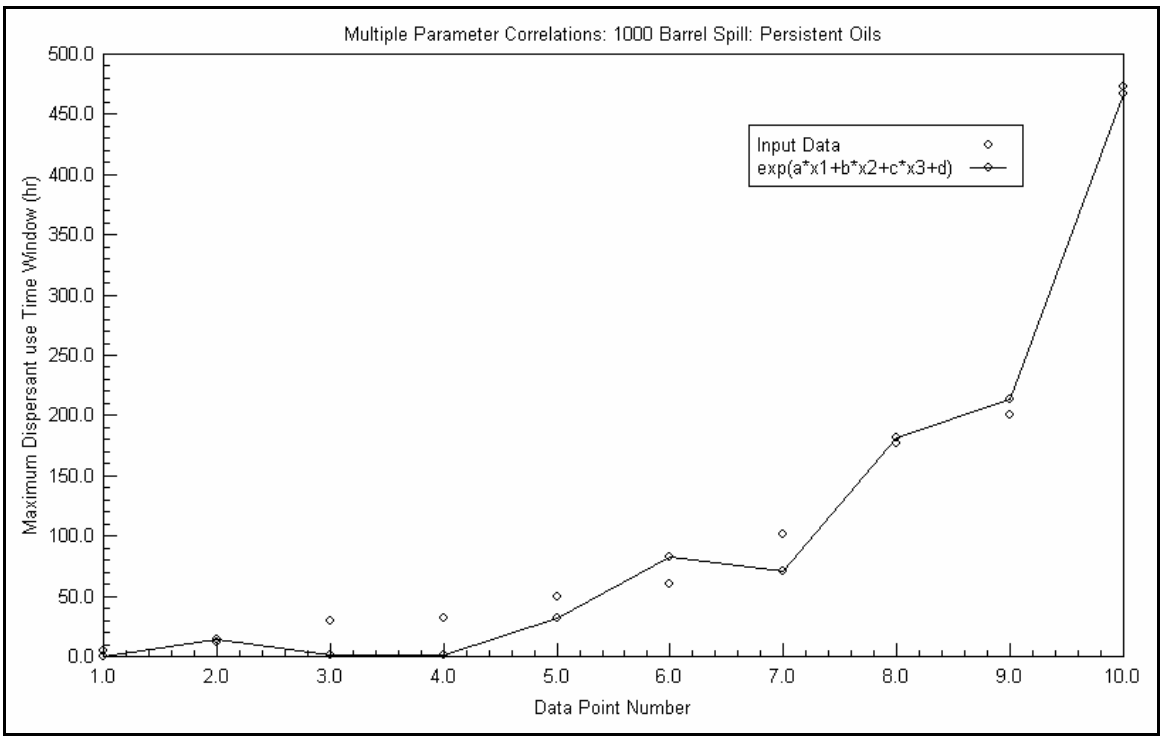

Figure A12. Aromatics, Saturates and Waxes vs Dispersant Time Window: 1,000 Barrel Spills

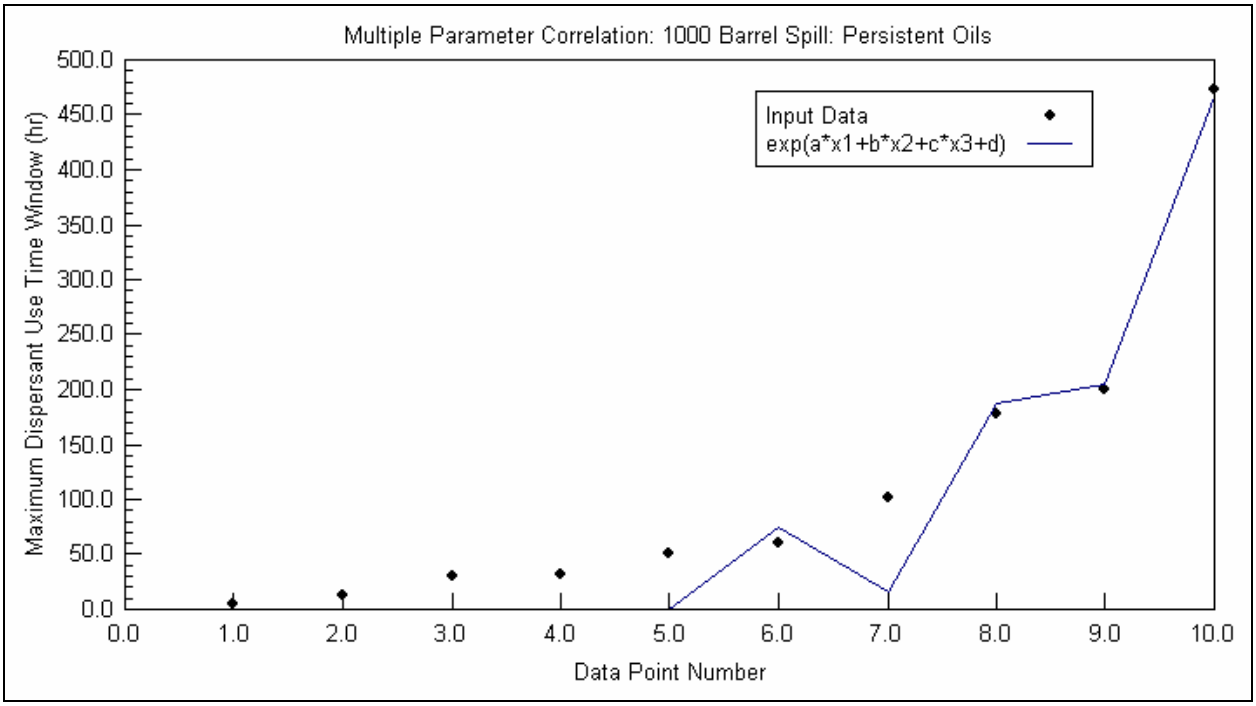

Figure A13. Aromatics, Saturates, BP<400 and Waxes vs Time Window: 1,000 Barrel Spills

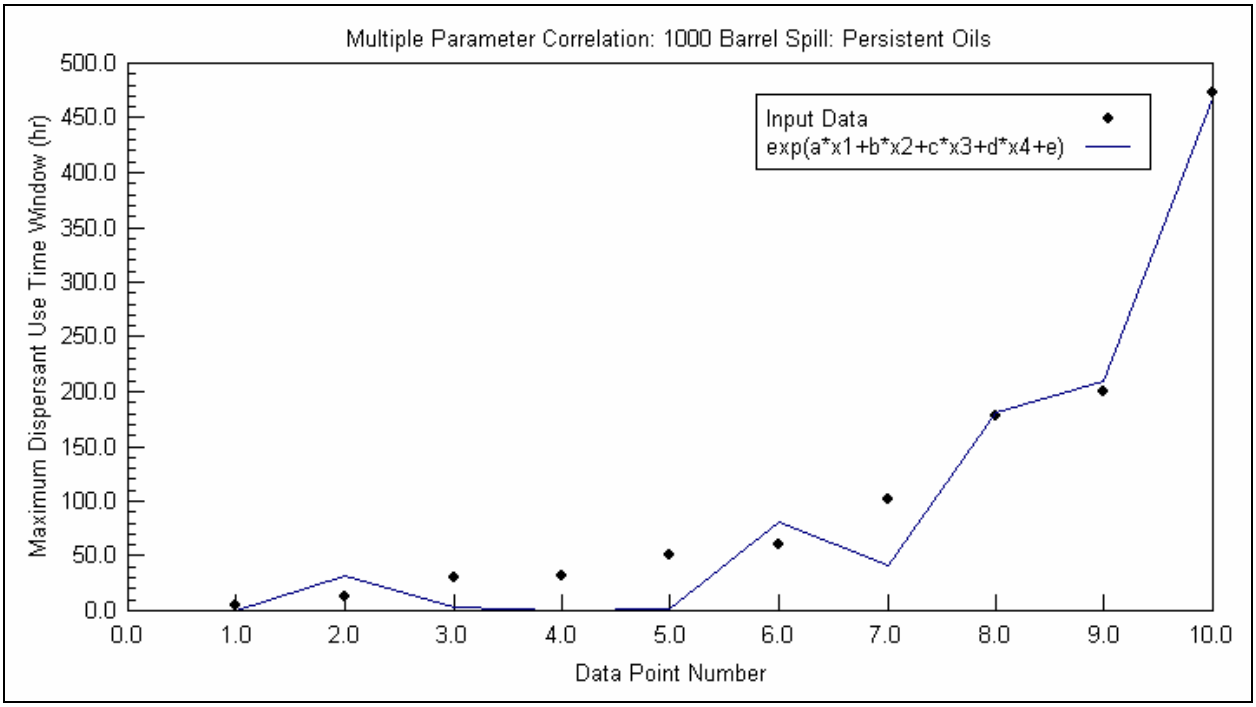

Figure A14. Aromatics, Saturates, Waxes vs Dispersant Time Window: 10,000 Barrel Spills

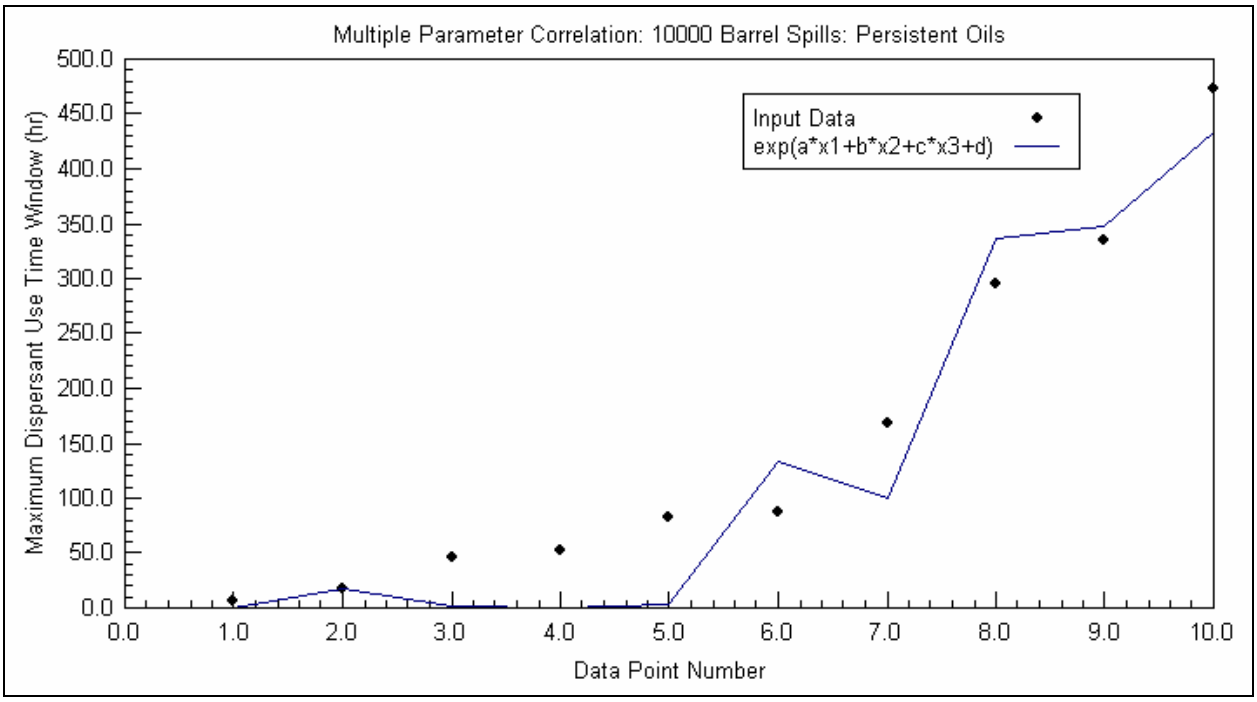

Figure A15. Aromatics, Saturates, Sulfur, and Waxes vs Time Window: 10,000 Barrel Spills

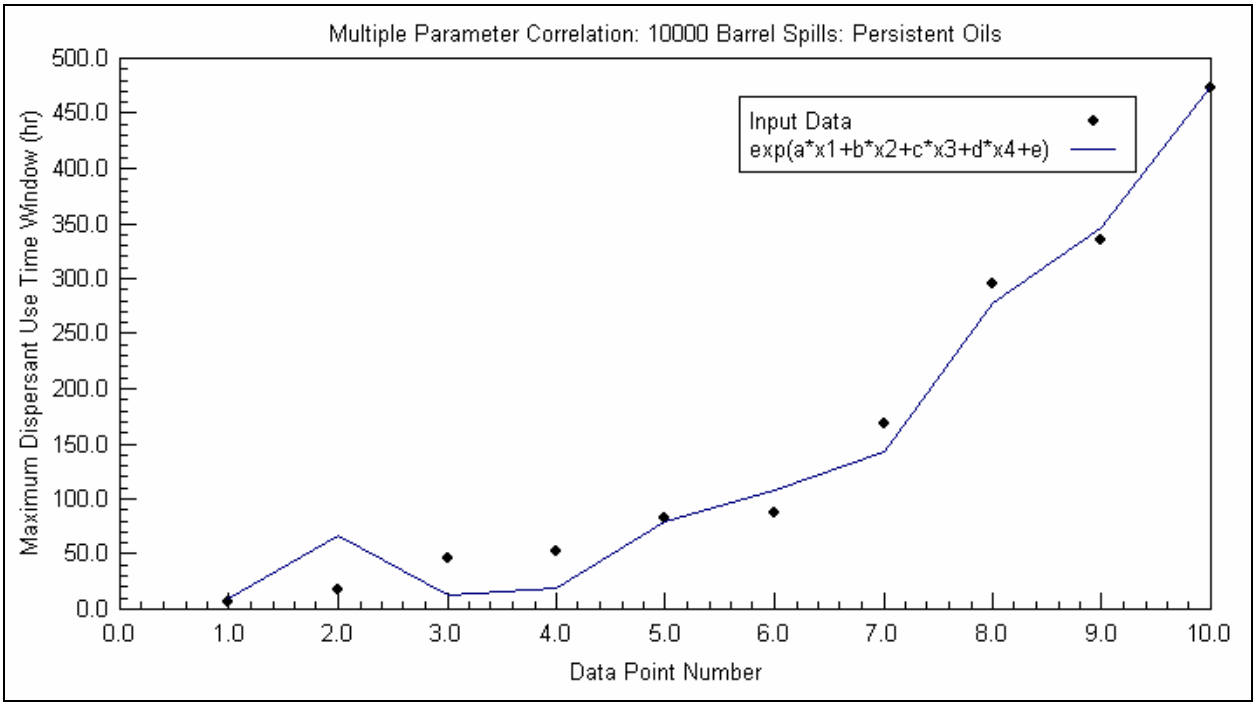

Figure A16. Saturates, Sulfur, and Waxes vs Dispersant Time Window: 10,000 Barrel Spills