

MEMO

To:
Michael Schmoller
Wisconsin Department of Natural Resources
(WDNR)

Copies:

From:
Dave Lipson, Mike LeFrancois, Jennine Trask

Date:
April 16, 2014

ARCADIS Project No.:
WI001368.0009

Subject:
Evaluation of Plume Stability and Fate and Transport Modeling for PCE in Bedrock
Groundwater, Madison Kipp Corporation, Madison, Wisconsin

Introduction

ARCADIS U.S., Inc. (ARCADIS) evaluated the stability of a dissolved-phase tetrachloroethene (PCE) plume present in bedrock groundwater beneath the Madison Kipp Facility located at 201 Waubesa Street, Madison, Wisconsin (site, Figure 1). The evaluation consisted of two parts:

1. Analysis of PCE concentration trends at 22 site groundwater monitoring wells located within the PCE plume and at the plume margin, where data have been collected in some cases since 1995 and in most cases quarterly since 2012. The 22 site groundwater monitoring wells used in this analysis screen the shallow, intermediate, and deep bedrock zones to a maximum depth of 240 feet below ground surface (ft bgs).
2. Calibration of a discrete-fracture groundwater fate and transport model that simulates PCE transport subject to mechanisms including: groundwater flow in a bedrock fracture network, dispersion, molecular diffusion and storage in bedrock matrix blocks, hydrophobic sorption, and chemical degradation due to both biotic and abiotic degradation processes. The purpose of the fate and transport model was to provide a quantitative framework for understanding trends in the site groundwater monitoring data and PCE plume stability.

As discussed in greater detail below, the empirical data show that PCE concentration trends in groundwater samples collected at monitoring wells within the PCE plume and at the plume margin are decreasing or stable over time, which indicates that the PCE plume has stabilized and is no longer expanding. The primary mechanisms contributing to PCE plume stability are molecular diffusion and

storage of PCE in low-permeability bedrock matrix blocks, as well as naturally-occurring in-situ abiotic and biotic degradation processes that either result in PCE mineralization or facilitate dechlorination to daughter products, respectively.

The remainder of this memorandum discusses in greater detail the site conceptual model, empirical data, data analysis methods, and fate and transport modeling techniques used in this evaluation.

Site Conceptual Model Summary

The Site is located at 201 Waubesa Street in the city of Madison, Dane County, Wisconsin, on the isthmus between Lake Mendota and Lake Monona (Figure 1). Regional hydrogeology near the site has been investigated by the Wisconsin Geological Natural History Survey (WGNHS) and documented in publications such as Bradbury et al (1999) and Krohelski et al (2000). Site-specific hydrogeology at the site has been investigated by Madison Kipp and documented in the March 2013 Site Investigation and Interim Actions Report (ARCADIS, 2013). The remainder of this section summarizes key elements of the site conceptual model relevant to evaluating PCE plume stability.

Surface water elevations in Lake Mendota are controlled by a lock and dam system and remain approximately four feet higher than surface water elevations in Lake Monona, resulting in a regional hydraulic gradient across the site of approximately 0.0014 feet per foot (ft/ft) oriented northwest to southeast (Figure 1).

Municipal Unit Well 8 (Unit Well 8) is located approximately 1,400 feet southeast of the site (Figure 1). The intake portion of Unit Well 8 is screened from approximately 280 to 774 ft bgs within the Mount Simon Formation. Unit Well 8 is currently not being utilized for water supply.

Figure 2 maps the horizontal extent of the PCE plume in bedrock groundwater at the site and was interpreted based on groundwater samples collected in October 2013, from wells screened in the Upper Wonewoc Formation. The Wonewoc Formation is present beneath the site at depths between approximately 75 and 220 ft bgs and site monitoring wells are screened at discrete intervals throughout this formation. The extent of PCE is larger in the Upper Wonewoc Formation compared to other formations beneath the site, which is why it was selected for Figure 2. As shown, the interpreted PCE plume is approximately 2,400 feet long and 1,550 feet wide. Monitoring well cluster MW-25 contains one monitoring well designated as MW-25D screened at a depth of approximately 120 ft bgs and a second monitoring well designated as MW-25D2 screened at a depth of approximately 160 ft bgs. These monitoring wells: (1) delineate the downgradient extent of the PCE plume in bedrock groundwater; and (2) are located between the PCE plume and Unit Well 8 potentially serving as “sentinel wells” and providing early-warning detection capabilities in the unlikely event of future PCE plume expansion. There is approximately 800 feet of horizontal separation between the PCE plume and Unit Well 8.

Figure 3 maps the vertical extent of the PCE plume in bedrock groundwater at the site onto a geologic cross section. As shown, the vertical extent of the PCE plume has been delineated to a depth of approximately 170 ft bgs beneath the site. Additionally, the site and the PCE plume are underlain by a regionally-extensive, well-documented shale layer present within the Eau Claire Formation with an estimated vertical hydraulic conductivity of approximately 0.0006 feet per day (ft/day) (Krohelski, 2000). In contrast, the horizontal hydraulic conductivity of the Wonewoc Formation has been estimated between approximately 5 and 6 ft/day (ARCADIS, 2013; Krohelski, 2000), suggesting that the vertical hydraulic conductivity of the Eau Claire shale is roughly four orders of magnitude lower than the horizontal hydraulic conductivity of the Wonewoc Formation (i.e., the horizontal to vertical anisotropic permeability ratio may be as high as 10,000). Because of this, the Eau Claire shale strongly resists vertical groundwater flow and transport and forces predominantly horizontal groundwater flow near the site. This is evidenced by the shape of the PCE plume which is roughly 10 times longer than it is deep.

When pumping, Unit Well 8 could possibly be vulnerable to PCE impacts because, even with Unit Well 8 screened below the protective Eau Claire shale and approximately 110 feet of vertical separation and approximately 800 feet of horizontal separation between the PCE plume and the Unit Well 8 intake, the city of Madison completed a "Test Hole" within approximately five feet of Unit Well 8 that is open across the Eau Claire shale (Figure 3). The Unit Well 8 Test Hole provides the only hypothetically plausible pathway for relevant quantities of shallow groundwater containing PCE to migrate vertically downward and impact Unit Well 8. The potential created by the Unit Well 8 Test Hole for shallow groundwater containing PCE to migrate vertically downward is one reason for completion of the PCE plume stability evaluation documented in this memorandum. As has been discussed with the city of Madison, it would be prudent to properly plug and abandon the Unit Well 8 Test Hole.

Analysis of Site Groundwater Monitoring Data

The first part of the PCE plume stability evaluation involved analyzing empirical groundwater monitoring data in accordance with standard environmental guidance documents (e.g., WDNR, 2014; USEPA, 1998; USEPA, 2004). One thing common to all of these documents is that the primary line of evidence for plume stability is chemical concentration trends over time in monitoring wells. The following general definitions of plume stability are useful:

- *Receding Plume*: Decreasing chemical concentration trends within the plume and a stable plume margin.
- *Stable Plume*: Stable chemical concentration trends within the plume and a stable plume margin.
- *Advancing Plume*: Chemical concentration trends that increase over two or three consecutive monitoring events.

In accordance with these guidance documents and their general framework for evaluating plume stability, we analyzed site groundwater monitoring data for trends in PCE concentrations over time at select wells within both the PCE plume and at the margins (Figure 2). The data used to perform this analysis and resulting trends are shown in Appendix A. The methods are summarized below.

To evaluate PCE concentration trends in groundwater samples collected at the monitoring wells shown on Figure 2, we used a combination of quantitative and qualitative statistical methods, depending on the nature of the dataset. The quantitative statistical method involved linear regression analysis using natural log-normalized concentration data to evaluate trend direction and statistical significance (USEPA, 2002). This quantitative statistical method was used to evaluate PCE concentration trends when the following conditions were present:

- Sufficient data points were available (i.e., more than eight data points in a dataset); and
- PCE concentrations were not influenced by the December 2012 in-situ chemical oxidation pilot testing activities.

For monitoring locations that did not fulfill the above criteria, qualitative methods were used which involved visually identifying the trend direction and identifying a best-fit line through the data.

Results of the quantitative statistical analyses are provided in Appendix A and summarized in Table 1, including both the p-value and the coefficient of determination, also known as the R^2 value. The p-value provides a measure of the significance of the slope, or the correlation between the x and y variables. Correlations were accepted as statistically significant at the 90 percent confidence level which is indicated by a p-value of 0.10 or less. The R^2 value measures the overall fit of linear regression to the data set; values close to one are considered to be a good fit, while values close to zero are considered poor.

Results show that 12 of 22 monitoring wells tested had a sufficient amount of data to support quantitative statistical analysis and, of those, seven showed statistically significant evidence of decreasing PCE concentration trends over time (i.e., their p-values were less than 0.1). For the remaining five monitoring wells with a sufficient amount of data for quantitative analysis, there is a clear decreasing or stable PCE concentration trend over time but too much scatter in the data to be statistically significant. The one exception is Monitoring Well MW-4S which had a sufficient amount of data to support quantitative statistical analysis, but showed an increasing trend that was statistically insignificant. All of the PCE concentrations measured in groundwater samples collected at Monitoring Well MW-4S were below the maximum contaminant level (MCL) for PCE of 5 micrograms per liter ($\mu\text{g/L}$). 10 of the 22 monitoring wells had insufficient data to support quantitative statistical analyses and were analyzed qualitatively. Of these wells, all showed evidence of decreasing or stable PCE concentration trends over time.

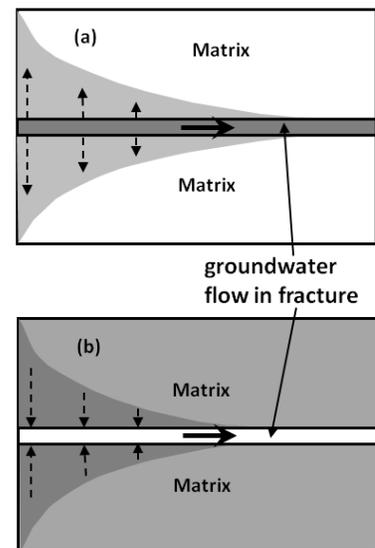
In summary, results of the statistical analysis indicate that all of the monitoring wells tested within the PCE plume or at the plume margin showed decreasing or stable PCE concentration trends over time. The exception is for Monitoring Well MW-4S which showed a slightly increasing trend, but all of the historical PCE concentrations detected in groundwater samples collected at Monitoring Well MW-4S have been below the MCL. This information demonstrates that the PCE plume in bedrock groundwater beneath the site is stable or shrinking over time, likely due to a combination of naturally-occurring fate and transport processes. Reasons for plume stabilization are explored in greater detail below.

Fate and Transport Modeling

The second part of the evaluation of PCE plume stability in site groundwater involved calibrating a mathematical PCE fate and transport model using methods described in Lipson et al (2005). This approach uses a discrete-fracture groundwater fate and transport model that simulates PCE transport subject to mechanisms including groundwater flow in bedrock fractures, dispersion, molecular diffusion in bedrock matrix blocks (also known as matrix diffusion), hydrophobic sorption, and chemical degradation due to both biotic and abiotic degradation processes. The purpose of the fate and transport model was to provide a quantitative framework for understanding trends in the site groundwater monitoring data and PCE plume stability.

Theory

Matrix diffusion refers to the transport process whereby solutes such as PCE dissolved in groundwater diffuse either from open bedrock fractures into the bedrock matrix, or from the matrix into open fractures (Pankow and Cherry, 1996). The direction of diffusion depends on the direction of the concentration gradient. For example, when solutes are initially introduced into fractures (figure a), a strong concentration gradient exists from the open fractures to the initially un-impacted rock matrix, resulting in diffusion of solutes from the fractures into the matrix. This forward diffusion process continues until either the solute storage capacity of the rock matrix has been reached, or the solute concentration in the fractures is equal to that in the matrix. Once the solute source is removed from the fractures (figure b), the concentration gradient reverses resulting in back diffusion of solutes from the rock matrix into the fractures. One implication of matrix diffusion is that the majority of the solute mass in fractured rock may be located within the rock matrix and not in open fractures. While open bedrock fractures can be considered the primary pathways for flow and transport, the rock matrix can be considered the primary reservoir for solute storage. A second implication of matrix diffusion is that the average rate of plume migration in fractured rock may be



(a) When concentrations are higher in the fracture, solutes diffuse from the fracture into the matrix. (b) When concentrations are higher in the matrix, solutes diffuse from the matrix into the fracture.

significantly less than the rate of groundwater flow. The rock matrix acts as a solute sink, continuously removing solute from groundwater flowing through fractures as the plume advances. This plume attenuation process manifests itself in a manner similar to what would occur due to solute sorption to grain surfaces.

Another important mechanism that is well-known to influence the fate and transport of PCE in groundwater is degradation. PCE can be degraded in groundwater via both chemical (i.e., abiotic) and microbiological degradation reactions (Pankow and Cherry, 1996). In-situ biodegradation of PCE in groundwater typically involves biologically-mediated reductive dechlorination, in which naturally occurring groundwater microorganisms use PCE as an electron acceptor while metabolizing alternative organic carbon substrates. Biologically-mediated reductive dechlorination of PCE in groundwater has been thoroughly documented in the scientific literature (e.g., Pankow and Cherry, 1996; USEPA, 1998) and is commonly used to remediate sites either under natural or enhanced conditions. Abiotic dechlorination can also be an important naturally occurring mechanism that degrades PCE in groundwater, and occurs in the presence of naturally occurring metals such as iron or manganese, sulfide minerals, or green rusts. Both biologically-mediated and abiotic degradation reactions can be important and contribute to plume stabilization if the overall degradation rate exceeds the groundwater transport rate.

Mathematical Model

The mathematical fate and transport model used in this evaluation is an analytical solution to the one-dimensional (1D) dual-porosity advection-dispersion-diffusion equation developed by Sudicky and Frind (1988) that has been programmed into a FORTRAN software program referred to as CRAFLUSH. CRAFLUSH simulates transport of dissolved organic chemicals in fractured bedrock, including advection within the fracture network, dispersion within the fracture network, diffusive exchange of chemicals between bedrock fractures and matrix, storage of groundwater and chemicals in the bedrock matrix, hydrophobic sorption in the rock matrix and along fracture walls, and first-order degradation reactions.

The conceptual model underlying CRAFLUSH assumes unidirectional, steady-state groundwater flow in parallel planar fractures with no advective flow in the bedrock matrix. This model approximates the structure of the Wonewoc Formation, which is horizontally-deposited, fine to coarse-grained sandstone with numerous horizontal to sub-horizontal bedding plane fractures that may extend for hundreds and possibly thousands of feet (Figure 4). It is recognized that some steeply-dipping or even vertical fractures may exist in the Wonewoc Formation that can cross-connect the horizontal bedding plane fractures and provide transport pathways for downward vertical migration (e.g., Bradbury et al., 2013). Tortuosity along a flow-path can be accounted for mathematically in CRAFLUSH through use of a tortuosity factor.

Model Parameters

Model parameters are shown in Table 2 and include source information, geologic media-specific values derived from site data, boundary values, and chemical-specific values. Parameters used in this evaluation fall into three categories:

1. Parameters constrained by site investigation data, for example hydraulic conductivity, hydraulic gradient, fracture spacing, rock matrix porosity, rock matrix fraction of organic carbon, rock matrix bulk density, and PCE source concentration.
2. Parameters obtained from scientific literature sources, such as PCE organic-carbon partition coefficient and PCE pure-water diffusion constant.
3. Parameters estimated during model calibration, including matrix tortuosity and PCE half-life.

These parameters are discussed in greater detail below.

Average linear groundwater velocity in the fracture network was estimated using a form of Darcy’s Law as follows:

$$v = \frac{e^2 \rho g}{12\mu} \Delta h$$

where *v* is average linear groundwater velocity, *e* is average hydraulic aperture in the fractures, *ρ* is groundwater density, *g* is acceleration due to gravity, *μ* is groundwater viscosity, and *Δh* is hydraulic gradient across the fracture network.

A hydraulic gradient of 0.0014 ft/ft was used in the model based on the regional hydraulic gradient between Lakes Mendota and Monona. This value is within the range of hydraulic gradients measured at the site groundwater monitoring well network (ARCADIS, 2013).

A range of fracture hydraulic aperture values was estimated throughout the site (Table 2) based on 75 hydraulic conductivity tests completed in isolated sections of bedrock during the vertical aquifer profiling phase of site investigation activities (ARCADIS, 2013). Results show the bulk hydraulic conductivity of fractured bedrock beneath the site varied between 0.8 and 13 ft/day and averaged 6 ft/day (geometric mean), which is consistent with a hydraulic conductivity value of 5 ft/day used to simulate the Wonewoc Formation in the WGNHS regional groundwater flow model (Krohelski et al, 2004). Fracture apertures were estimated by dividing bulk hydraulic conductivity of the bedrock by fracture spacing in accordance with Freeze and Cherry (1979).

A range of fracture spacing values was estimated based on down-hole geophysical measurements collected at six open boreholes prior to completion of bedrock monitoring wells, spanning a total vertical distance of approximately 600 linear feet to a total depth of approximately 230 ft bgs (Table 2). The geophysical measurements were made using optical and acoustic televiewers, which identified and measured the orientation of 617 planar features intersecting boreholes interpreted to be open, flowing fractures. The primary purpose of this investigation was to identify transmissive groundwater-bearing zones targeted for monitoring (ARCADIS 2013).

In addition to fracture network characterization, bedrock matrix properties including rock porosity, fraction of organic carbon, and bulk density were measured on 21 undisturbed bedrock samples collected during drilling to a total depth of 235 ft bgs (Table 2). These measurements were made in an analytical laboratory using standard geotechnical methods (ARCADIS, 2013).

Source area PCE concentration and other flow-path PCE concentrations were developed using averages of site investigation data. A constant PCE concentration of 7,900 $\mu\text{g/L}$ was assigned as a boundary condition at the fracture origin, and initial concentrations in the fractures and bedrock matrix were assumed to be zero.

PCE sorption to solid organic carbon in the bedrock matrix was accounted for by estimating a matrix retardation factor of 1.4 using standard groundwater calculations (e.g., Freeze and Cherry, 1979). PCE sorption to bedrock fracture walls was assumed to be negligible.

In terms of source timing, it was assumed that PCE first penetrated bedrock beneath the site in June 1965. This results in a PCE plume residence time of approximately 48 years.

Model Calibration and Results

The fate and transport model was calibrated by assigning average or reasonable values to parameters constrained by site investigation data and scientific literature, and adjusting the only two remaining uncertain parameters, namely (1) matrix tortuosity and (2) PCE degradation rate, until modeled PCE concentrations were consistent with measured PCE concentrations at calibration target locations along a conceptual flow-path (Figure 2).

Matrix tortuosity is an uncertain parameter that accounts for tortuous diffusion pathways through complex pore geometries in the bedrock matrix porosity, and is very difficult to measure in the field. The PCE pure-water diffusion coefficient, a highly constrained literature value, is valid in open water where diffusion may occur relatively unimpeded. However, chemicals diffusing through bedrock must follow sinuous pathways around solid rock particles. This results in flow-path lengthening during diffusive transport, and is accounted for mathematically by multiplying the free-water diffusion coefficient by a tortuosity factor which ranges between zero and one.

Calibration targets consisted of average PCE concentrations measured at monitoring wells located on and near the conceptual flow-path (Table 3, Figure 2). The period of PCE concentration averaging for calibration purposes was January through May 2013. Calibration targets were selected as those monitoring wells screened in the Upper Wonewoc Formation (Figure 3) because the extent of PCE is larger in this formation compared to other geologic formations beneath the site.

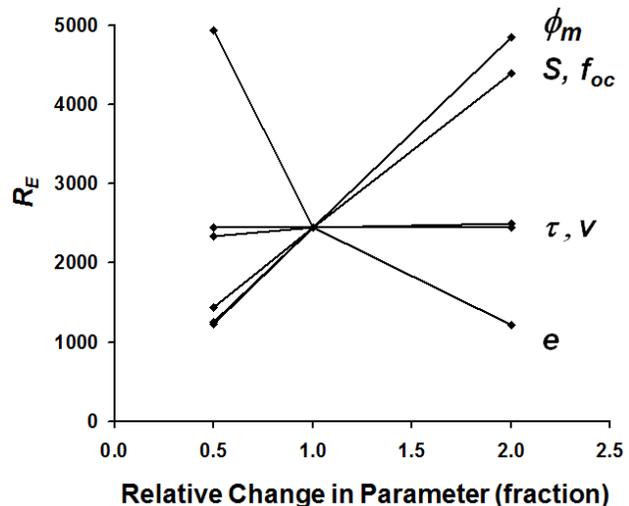
The calibration procedure involved holding all parameters steady at their estimated values, and iteratively adjusting matrix tortuosity and PCE degradation rate (expressed as half-life) until modeled PCE concentrations were consistent with measured concentrations. The degree of model calibration was quantitatively evaluated using the coefficient of determination (i.e., R^2 value) between modeled and measured PCE concentrations. The model was considered calibrated when the R^2 value reached its maximum.

Modeling results are shown on Figure 5, which plots modeled and measured PCE concentrations over distance in bedrock groundwater along the conceptual flow-path after 48 years of transport. As shown, model results were consistent with measured results and the two datasets have a coefficient of determination of 0.66, which indicates the fate and transport model simulates PCE transport in bedrock beneath the site with a good degree of accuracy.

Parameters estimated through model calibration are shown in Table 2. As shown, the final estimated value for matrix tortuosity was 0.10, which is well within the range of published literature values for tortuosity of sandstone and is therefore a reasonable result. Also, as shown, the final estimated value for PCE half-life was 1,775 days (4.9 years), which is well within the range of published literature values for in-situ PCE degradation under natural conditions and is therefore a reasonable result. Based on these results, we consider the fate and transport model to be reasonably calibrated within a sufficient degree of accuracy to achieve its stated purpose.

Parameter Sensitivity

Sensitivity of model parameters used in CRAFLUSH was thoroughly investigated by Lipson et al (2005). A copy of their results is shown in the adjacent figure. In this analysis, sensitivity of CRAFLUSH parameters was evaluated using an R_E factor, which is a matrix-diffusion derived plume retardation factor that indicates the degree to which plume velocity is slowed down due to the matrix diffusion effect relative to the average linear groundwater velocity. In this case, results showed that plume



velocity was most sensitive to rock matrix porosity (ϕ_m), rock matrix fraction of organic carbon (foc), fracture aperture (e), and fracture spacing (S), and it was least sensitive to bedrock matrix tortuosity factor (τ). Because CRAFLUSH uses the same mathematical formulation regardless of which parameter set is used, these results are valid for the site fate and transport model. Knowledge of the sensitivity of these parameters helped inform the site investigation strategy so that some site-specific data were collected to help constrain the most sensitive model parameters.

Predictive Scenarios

The calibrated site-specific PCE fate and transport model was run for timeframes 5, 10, and 20 years longer than 48 years (i.e., totals of 53, 58, and 68 years) to predict potential plume migration 5, 10, and 20 years into the future, also known as a forecasting scenario. Results show that the PCE plume is currently stable and no longer migrating. Results demonstrate that the primary mechanism controlling the PCE plume length is matrix diffusion and the primary mechanism controlling plume stability is the PCE degradation rate.

In an effort to predict when the PCE plume reached steady-state, the model was run at a variety of timeframes shorter than 48 years, also known as a hind-casting scenario. Results show that the PCE plume expanded rapidly during the initial several years after PCE first penetrated bedrock, and then the PCE plume migration rate gradually decreased over time until a stabilized condition was reached after approximately 45 years of transport.

Summary and Conclusions

In summary, the PCE plume in bedrock groundwater beneath the site is stable and no longer expanding as demonstrated by empirical site groundwater monitoring data. The most probable mechanisms controlling the extent and stability of the PCE plume in site groundwater are matrix diffusion (i.e., diffusive transfer and storage of PCE into low-permeability bedrock matrix zones) and in-situ PCE degradation, respectively. Results of the modeling analysis indicate that the PCE plume stabilized after approximately 45 years of transport, approximately three years ago. These results suggest that Unit Well 8 will likely not be impacted by PCE in groundwater at the site if Unit Well 8 were to become operational in the future. This conclusion is further supported by the following:

- The vertical extent of PCE has been delineated at the site and is limited to a depth of approximately 170 ft bgs.
- The intake portion of Unit Well 8 starts at approximately 280 ft bgs and, therefore, there are at least 110 feet of vertical separation between the bottom of the PCE plume and the top of the intake screen of Unit Well 8, as well as approximately 800 feet of horizontal separation.

- The intake portion of Unit Well 8 is screened below the Eau Claire shale which is regional in extent, has a very low vertical hydraulic conductivity (0.0006 ft/day), and strongly restricts vertical groundwater flow and transport above the confining layer from migrating vertically downward and into the deeper aquifer in which Unit Well 8 is screened.
- Pumping at Unit Well 8 for water supply purposes will result in radial flow of groundwater from all directions toward Unit Well 8 to the extent that the vast majority (e.g., ~90%) of groundwater entering Unit Well 8 will be from other areas not associated with the site.
- The PCE source area at the site (i.e., the zone with the highest PCE concentrations) will be hydraulically contained by Madison Kipp's proposed groundwater extraction system.
- The PCE plume at the site has stabilized and is no longer expanding. The key controlling factors on plume stabilization are matrix diffusion and biodegradation.

Moreover, monitoring well cluster MW-25 is located between the PCE plume and Unit Well 8, and can serve as a sentinel well for early-warning detection in the unlikely event that the PCE plume begins to migrate.

Recommendations

We continue to recommend that additional evaluation should be completed by the city of Madison to determine the extent to which the original Test Hole is or is not connected to Municipal Unit Well 8. If a connection exists, it is recommended that the city abandon the Test Hole as a conservative measure to protect Unit Well 8.

It is also recommended that groundwater monitoring be completed by Madison Kipp as presented in the 2013 Annual Report (ARCADIS, 2014).

References

ARCADIS. March 2014. 2013 Annual Report, Madison-Kipp Corporation.

ARCADIS. March 2013. Site Investigation and Interim Actions Report, Madison-Kipp Corporation.

Bradbury, K. R., Swanson, S.K., Krohelski, J.T., and Fritz, A.K., 1999, Hydrogeology of Dane County, Wisconsin. Wisconsin Geological and Natural History Survey Open-File Report 1999-04.

Bradbury, K. R., M.A. Borchardt, M. Gotkowitz, S.K. Spencer, J. Zhu, and R.J. Hunt. 2013. Source and Transport of Human Enteric Viruses in Deep Municipal Water Supply Wells. *Environ. Sci. Technol.*, 47, 4096-4103.

Freeze, R.A. and J.A. Cherry. 1979. *Groundwater*. Prentice-Hall, Inc.: Englewood Cliffs, NJ.

Krohelski, J.T., K.R. Bradbury, R.J. Hunt, and S.K. Swanson. 2000. Numerical Simulation of Groundwater Flow in Dane County Wisconsin. Wisconsin Geological and Natural History Survey. Bulletin 98.

Lipson, D., Kueper, B., Gefell, M., 2005, Matrix Diffusion-Derived Plume Attenuation in Fractured Bedrock, *Ground Water*, Vol. 34, No. 1, pp. 30-39.

Pankow, J.F. and J.A. Cherry. 1996. *Dense Chlorinated Solvents and Other DNAPLs in Groundwater*. Waterloo Press: Portland, Oregon.

Sudicky, E.A., 1988, *CRAFLUSH, Programmer's Guide*. Waterloo Centre for Ground-water Research, University of Waterloo, Waterloo, Ontario, Canada, 12p.

United States Environmental Protection Agency (USEPA). 1998. Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water. Office of Research and Development. EPA/600/R-98/128.

USEPA. 2002. Calculation and Use of First-Order Rate Constants for Monitored Natural Attenuation Studies. EPA/540/S-02/500.

USEPA. 2004. Performance Monitoring of MNA Remedies for VOCs in Ground Water. National Risk Management Research Laboratory. EPA/600/R-04/027.

Wisconsin Department of Natural Resources (WDNR). 2014. Guidance on Natural Attenuation for Petroleum Releases. RR-614. January 2014.

ARCADIS

Tables

Table 1 – PCE Concentration Trend Analysis Results

Monitoring Well	Location Relative to PCE Plume	Quantitative or Qualitative Analysis	Trend Direction	R² Value	p-value
MW-14	Margin	Quantitative	Decreasing	0.01	0.59
MW-2S	Within	Quantitative	Decreasing	0.58	5 x 10 ⁻⁸
MW-2D	Within	Quantitative	Decreasing	0.85	3 x 10 ⁻⁶
MW-5S	Within	Quantitative	Decreasing	0.54	4 x 10 ⁻⁶
MW-5D	Within	Quantitative	Decreasing	0.45	1 x 10 ⁻⁸
MW-5D2	Within	Quantitative	Decreasing	0.01	0.61
MW-5D3	Within	Qualitative	Decreasing	--	--
MW-22S	Within	Qualitative	Decreasing	--	--
MW-22D	Within	Qualitative	Decreasing	--	--
MW-16	Margin	Quantitative	Decreasing	0.06	0.26
MW-23S	Within	Qualitative	Decreasing	--	--
MW-23D	Within	Qualitative	Stable	--	--
MW-11S	Within	Qualitative	Decreasing	--	--
MW-4S	Margin	Quantitative	Increasing	0.08	0.14
MW-4D	Margin	Quantitative	Decreasing	0.23	0.01
MW-4D2	Margin	Quantitative	Decreasing	0.31	0.003
MW-24	Margin	Qualitative	Decreasing	--	--
MW-17	Within	Qualitative	Decreasing	--	--
MW-6S	Within	Quantitative	Decreasing	0.24	0.003
MW-6D	Within	Quantitative	Stable	0.01	0.65
MW-25D	Margin	Qualitative	Stable	--	--
MW-25D2	Margin	Qualitative	Stable	--	--

Notes:

See Appendix A for data and trend lines.

“Within” = the monitoring well is located within the PCE plume.

“Margin” = the monitoring well is located at the margin of the PCE plume.

Table 2 – Fate and Transport Model Parameters

Parameter	Range of Values Evaluated	Final Parameter Value
Fracture Avg. Lin. Groundwater Velocity (ft/day) ¹	3 - 96	23.5
Fracture Dispersivity (ft)	--	1.0
Fracture Hydraulic Aperture (microns) ¹	93 - 544	270
Fracture Spacing (ft) ¹	0.74 – 9.2	2.6
Matrix Tortuosity (-) ²	--	0.10
PCE Diffusion Coefficient in Water ³ (ft ² /d)	--	8.79x10 ⁻⁴
Fracture Retardation Factor (-)	--	1.0
Matrix Retardation Factor (-) ¹	1.3 – 2.4	1.4
PCE Half-Life (days) ²	--	1,775
Bedrock Matrix Porosity (%) ¹	17 – 29	25
Bedrock Matrix Fraction Organic Carbon (foc) (%) ¹	0.01 – 0.07	0.019
Bedrock Matrix Bulk Density (g/cm ³) ¹	2.16 – 2.37	2.26
PCE Partition Coefficient (cm ³ /g) ⁴	--	238
PCE Source Concentration (µg/L) ¹	--	7,900

Notes:

¹Calculated or based on site investigation data.

²Estimated during calibration.

³Diffusion coefficient in water from EPA Soil Screening Guidance.

⁴Partition Coefficient from EPA Technical Factsheet on PCE.

ft – feet

ft²/d – square feet per day

g/cm³ – grams per cubic centimeter

µg/L – micrograms per liter

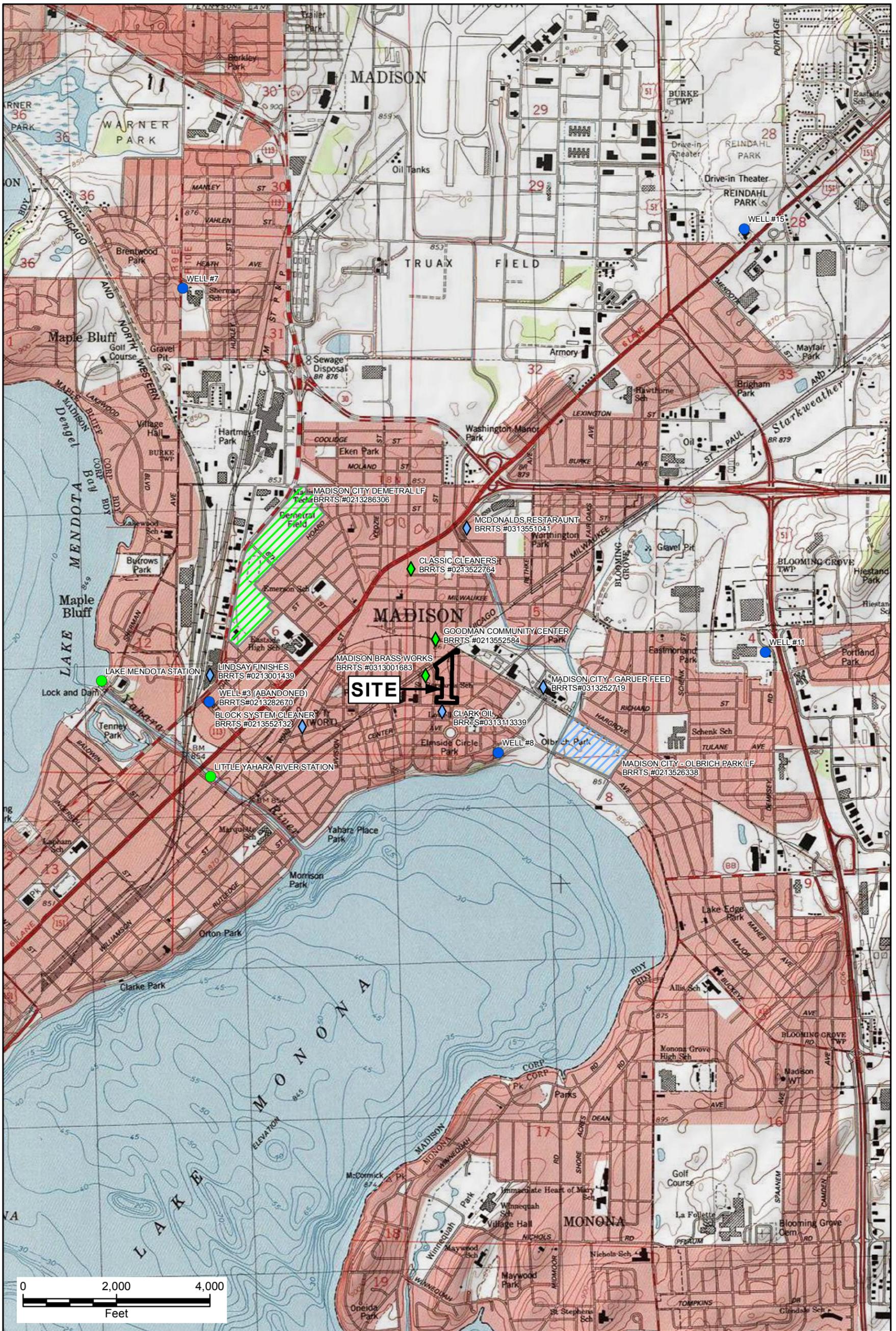
Table 3 - Calibration Targets

Observation Name	Number of Observations	Average PCE Concentration (µg/L)
MP-13	4	7,233.33
MW-19D	5	2,175.00
MW-19D2	5	1,225.00
MW-20D	5	657.50
MW-20D2	5	620.00
MW-03D2	11	1,137.50
MW-03D	9	577.50
MW-21D	5	1,225.00
MW-21D2	5	2,700.00
MW-03S	8	364.50
MW-18S	5	1,947.50
MW-05D2	3	646.67
MW-05S	7	200.00
MW-05D	6	1,566.67
MW-22D	2	485.00
MW-22S	2	170.00
MW-23S	2	435.00
MW-23D	2	93.00
MW-24	1	3.00
MW-17	2	1,045.00
MW-06D	9	23.50
MW-25D	1	0.76
MW-25D2	1	0.17

Notes:

Average PCE concentrations calculated with site analytical data from 1/14/2013 through 5/6/2013.
 µg/L – micrograms per liter.

Figures



CITY: MPLS DIV/GROUP: IMDV DB: MG LD: CK MADISON-KIPP
 G:\GIS\Projects\MadisonKipp\Map\2014-04\Fig1_Site_Location_Map_20140411.mxd

- LEGEND**
- OPEN SITE (ONGOING CLEANUP)
 - OPEN SITE - SITE BOUNDARIES
 - CLOSED SITE (COMPLETED CLEANUP)
 - CLOSED SITE - SITE BOUNDARIES
 - GAUGING STATION
 - MUNICIPAL WATER SUPPLY WELL
 - PROJECT BOUNDARY

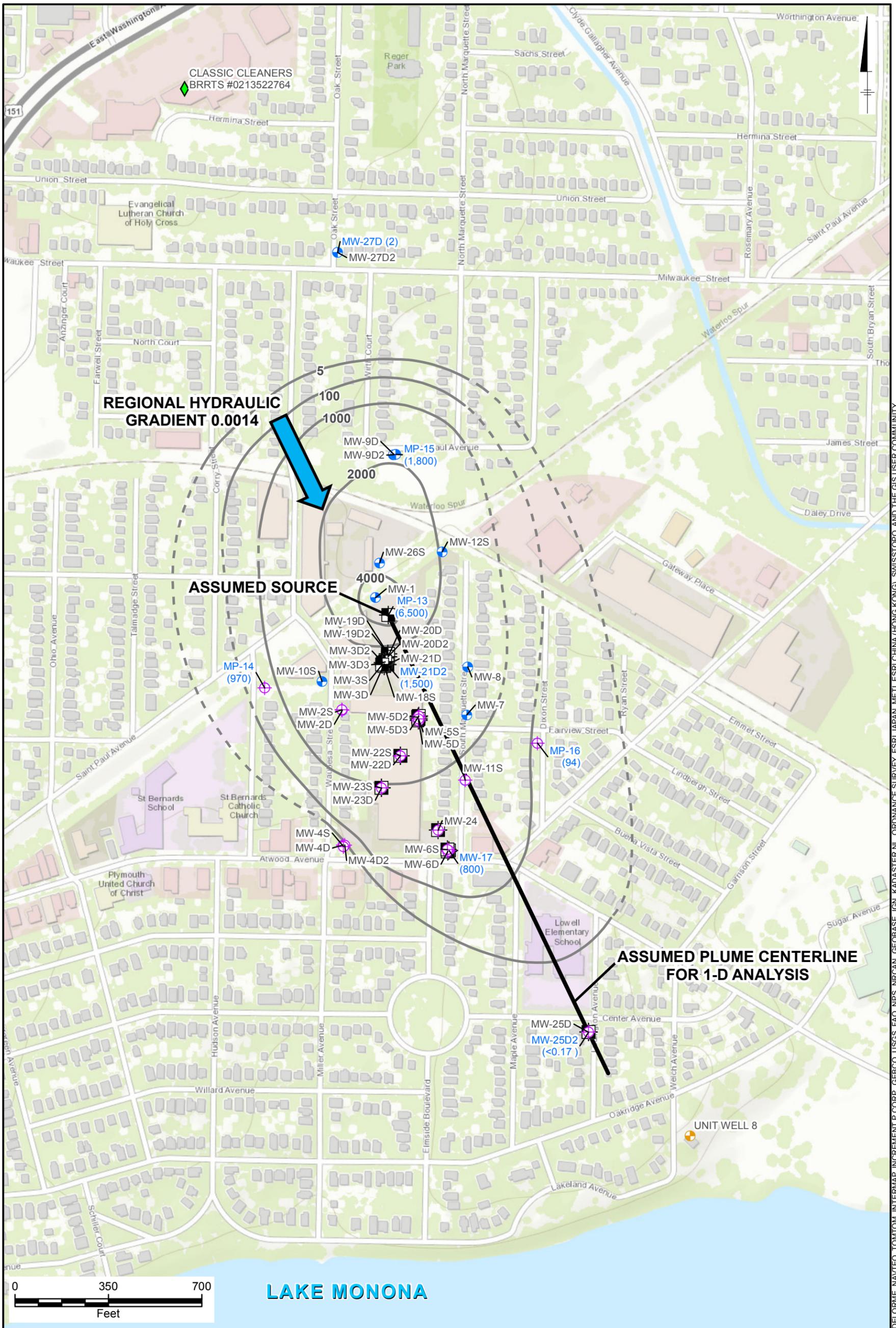


NOTE:
 TOPO BASE MAP OBTAINED FROM
 ESRI ONLINE MAPPING, USING
 ARCMAP 10, ACCESSED 4/15/2014
 USGS 15' QUADRANGLE, MADISON
 EAST, WISCONSIN, 1983.

MADISON-KIPP CORPORATION
 201 WAUBESA STREET
 MADISON, WISCONSIN
 2014 FATE AND TRANSPORT MODEL

SITE LOCATION MAP

FIGURE
1



CITY: MPLS DIV/GROUP: IMDV DB: MG LD: TS MADISON-KIPP
 G:\GIS\Projects\MadisonKipp\Map2014-04\Fig2_FTM_UWF_POE_20140415.mxd

LEGEND

- ◆ CLOSED SITE (COMPLETED CLEANUP)
- MUNICIPAL UNIT WELL 8
- MONITORING WELL
- (6,500) TETRACHLOROETHENE CONCENTRATIONS ARE REPORTED IN MICROGRAMS PER LITER (µg/L).
- TETRACHLOROETHENE ISOCONCENTRATION CONTOUR (DASHED WHERE INFERRED)
- ⊕ WELLS FOR EVALUATION OF PLUME STABILITY
- ⊠ WELLS FOR FATE AND TRANSPORT MODEL

THE UPPER WONEVOC FORMATION IS INTERPRETTED TO BE FROM APPROXIMATELY 87 - 139 FEET BELOW LAND SURFACE OR 767 - 690 FEET ABOVE MEAN SEA LEVEL

MADISON-KIPP CORPORATION
 201 WAUBESA STREET
 MADISON, WISCONSIN

**2014 FATE AND TRANSPORT MODEL
 UPPER WONEVOC FORMATION
 TETRACHLOROETHENE
 ISOCONCENTRATION MAP, OCTOBER 2013**



SERVICE LAYER CREDITS: SOURCES: ESRI, DELORME, NAVTEQ, TOMTOM, INTERMAP, INCREMENT P CORP., GEBCO, USGS, FAO, NPS, NRCAN, GEBCO, IGN, KADASTER NL, ORDNANCE SURVEY, ESRI, JAPAN, METI, ESRI CHINA (HONG KONG), SWISS TOPO, AND THE GIS USER COMMUNITY

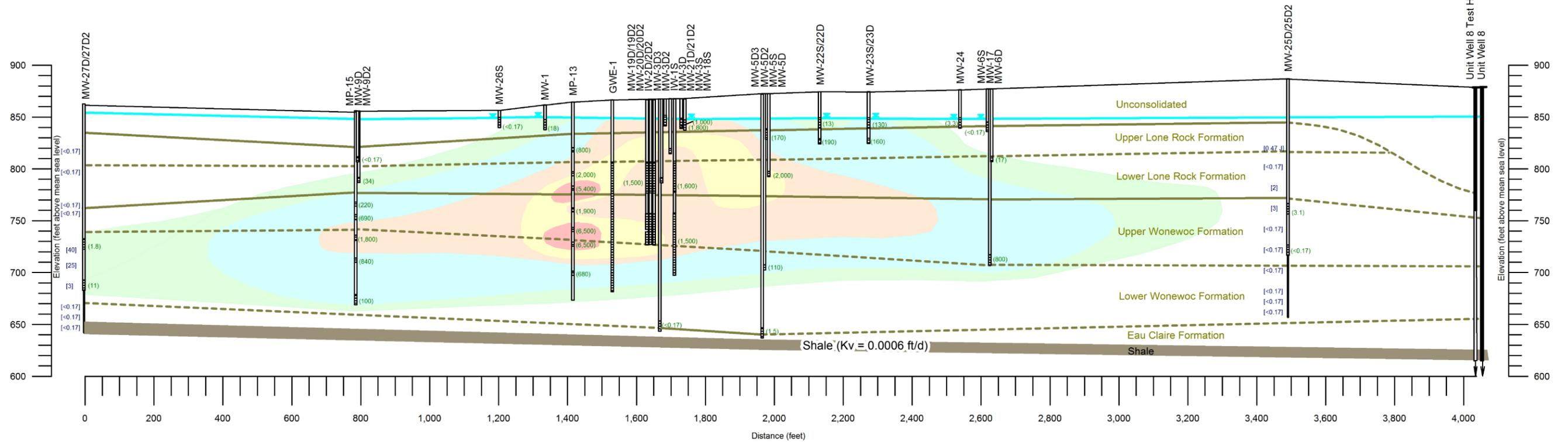
Lake Mendota

Regional Hydraulic Gradient 0.0014

Lake Monona

A North

A' South



Tetrachloroethene Isoconcentration Contour (ug/L)



LEGEND

- Well Screen or Multipoint Sample Interval
- Water Table
- (18) Tetrachloroethene Concentration in Micrograms per Liter (ug/L)
- (<0.17) Tetrachloroethene concentration from vertical aquifer profiling
- Geologic Contact (dashed where inferred)

NOTE:

1. Vertical exaggeration = 3x
2. Unit Well 8 is cased from ground surface to 280 feet below grade, and an open bedrock borehole from 280 feet to 774 feet below grade. Casing is below the Eau Claire Shale aquitard. Test hole is cased from the ground surface to 107 feet below grade and an open bedrock borehole from 107 feet to 540 feet below grade.
3. Tetrachloroethene concentrations are from October 2013, except for MW-27D/27D2 which are from December 2013.

MADISON-KIPP CORPORATION
 201 WAUBESA STREET
 MADISON, WISCONSIN
 2014 FATE AND TRANSPORT MODEL

**TETRACHLOROETHENE ISOCONCENTRATION
 CROSS SECTIONAL VIEW A-A', OCTOBER 2013**



FIGURE
3

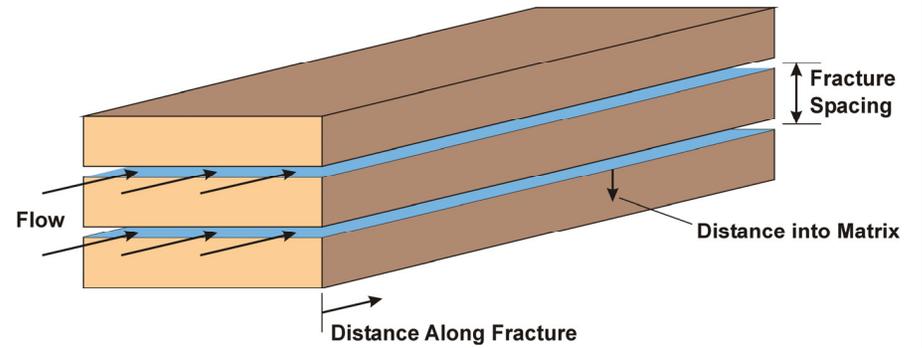
Reality: Wonewoc Formation

Bedrock Outcrop Near Site

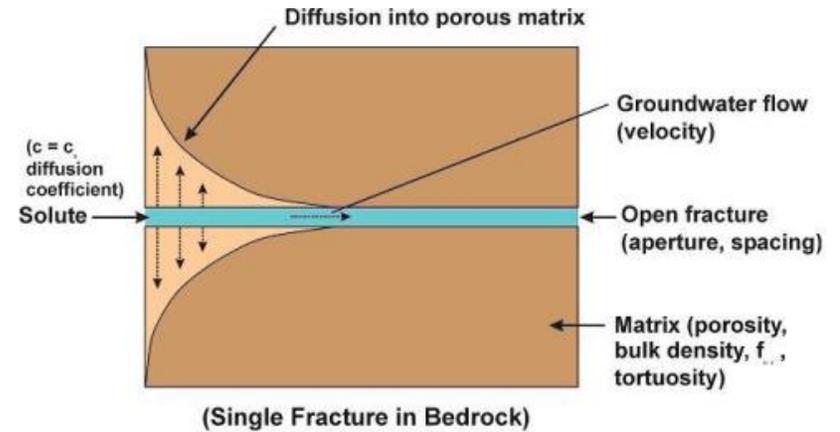


Mathematical Model Formulation

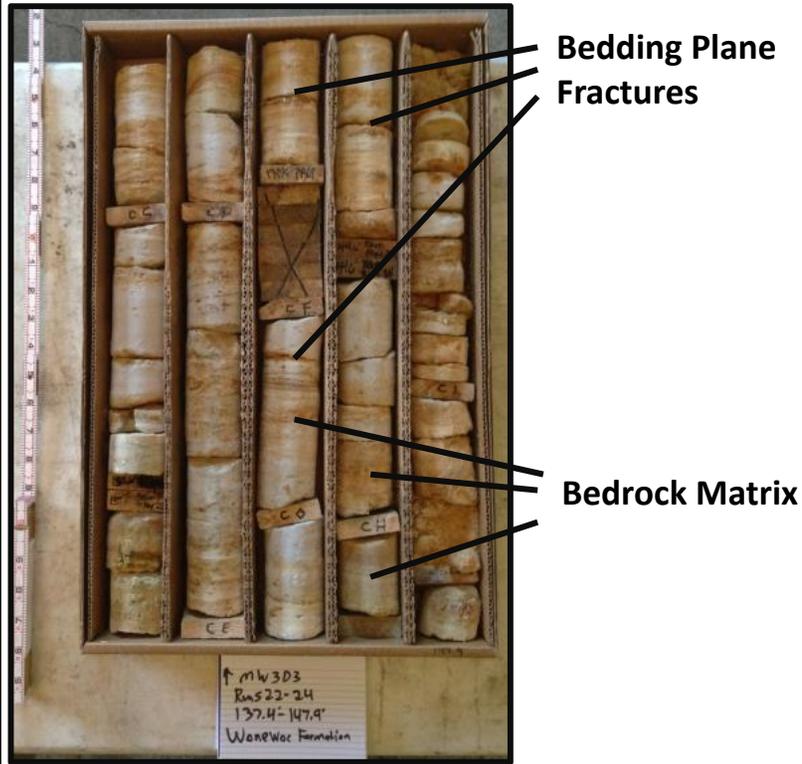
Parallel Plate Groundwater Flow



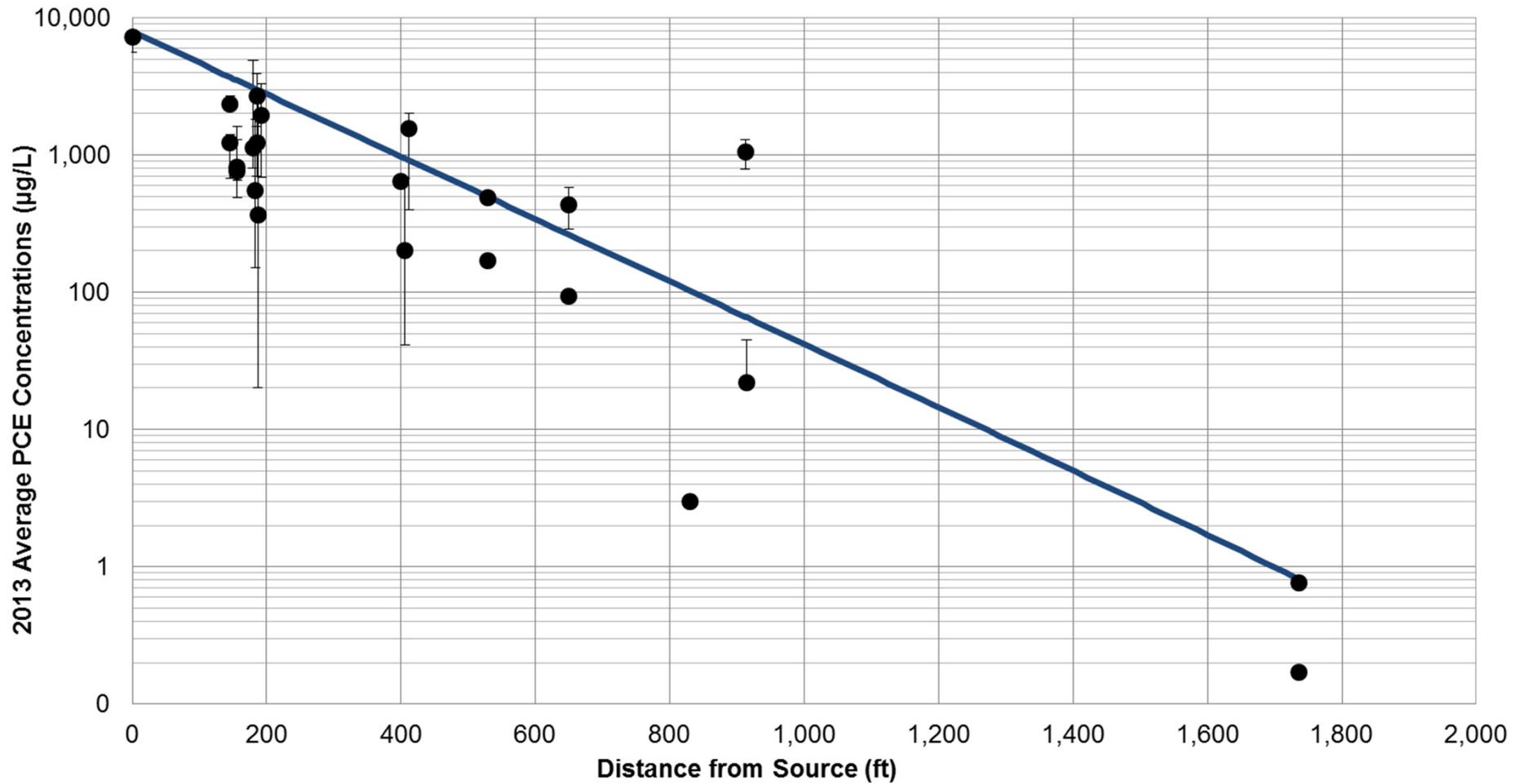
Matrix Diffusion



Rock Core from Site



MADISON-KIPP CORPORATION 201 WAUBESA STREET MADISON, WISCONSIN 2014 FATE AND TRANSPORT MODEL	
Conceptual Model for Fate and Transport Evaluation	
	FIGURE 4



Notes:

● Average of 2013 data and range of all data (µg/L)

— Simulated PCE concentrations (µg/L)

Coefficient of determination of 0.66

PCE observations are averages from 1/14/2013 to 5/6/2013

MADISON-KIPP CORPORATION
 201 WAUBESA STREET
 MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

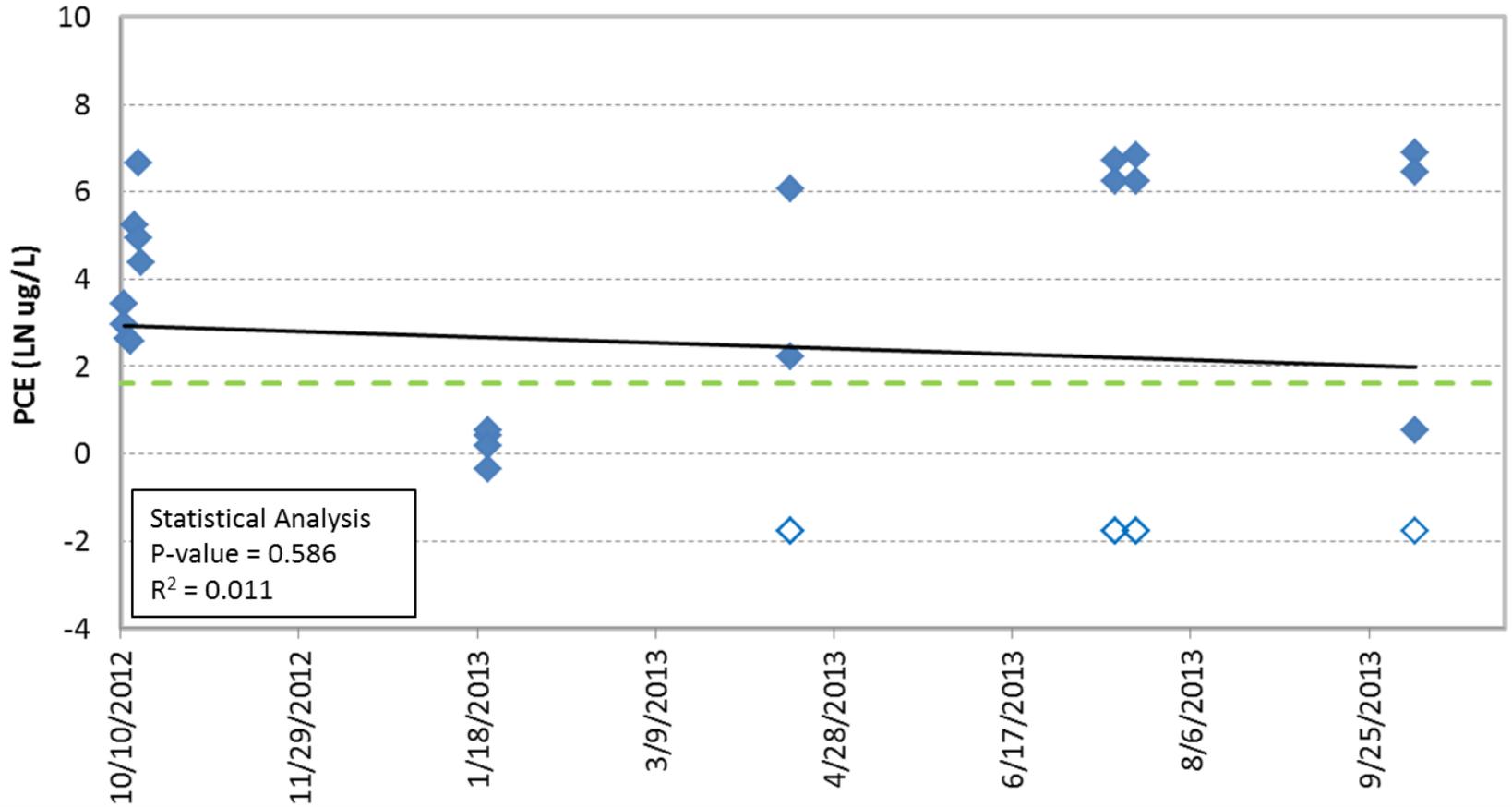
Calibrated Condition



APPENDIX A

Statistical Analysis of PCE Groundwater Analytical Data

MW-14



- Quantitative Trendline
- - - Qualitative Trendline
- ◆ PCE Detect (ug/L)
- ◇ PCE Non-detect (ug/L)
- MCL (5 ug/L)

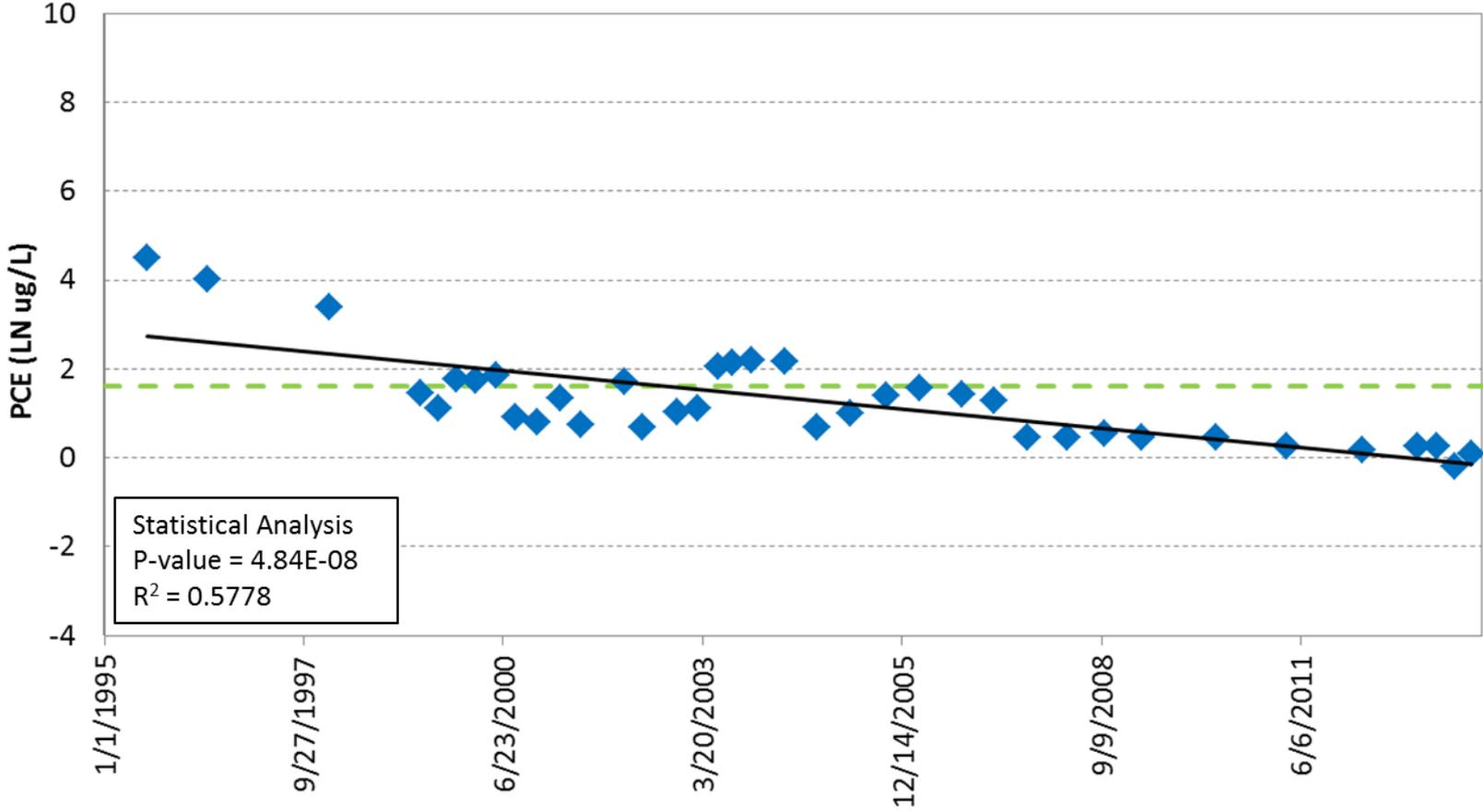
MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis



FIGURE
A-1

MW-2S

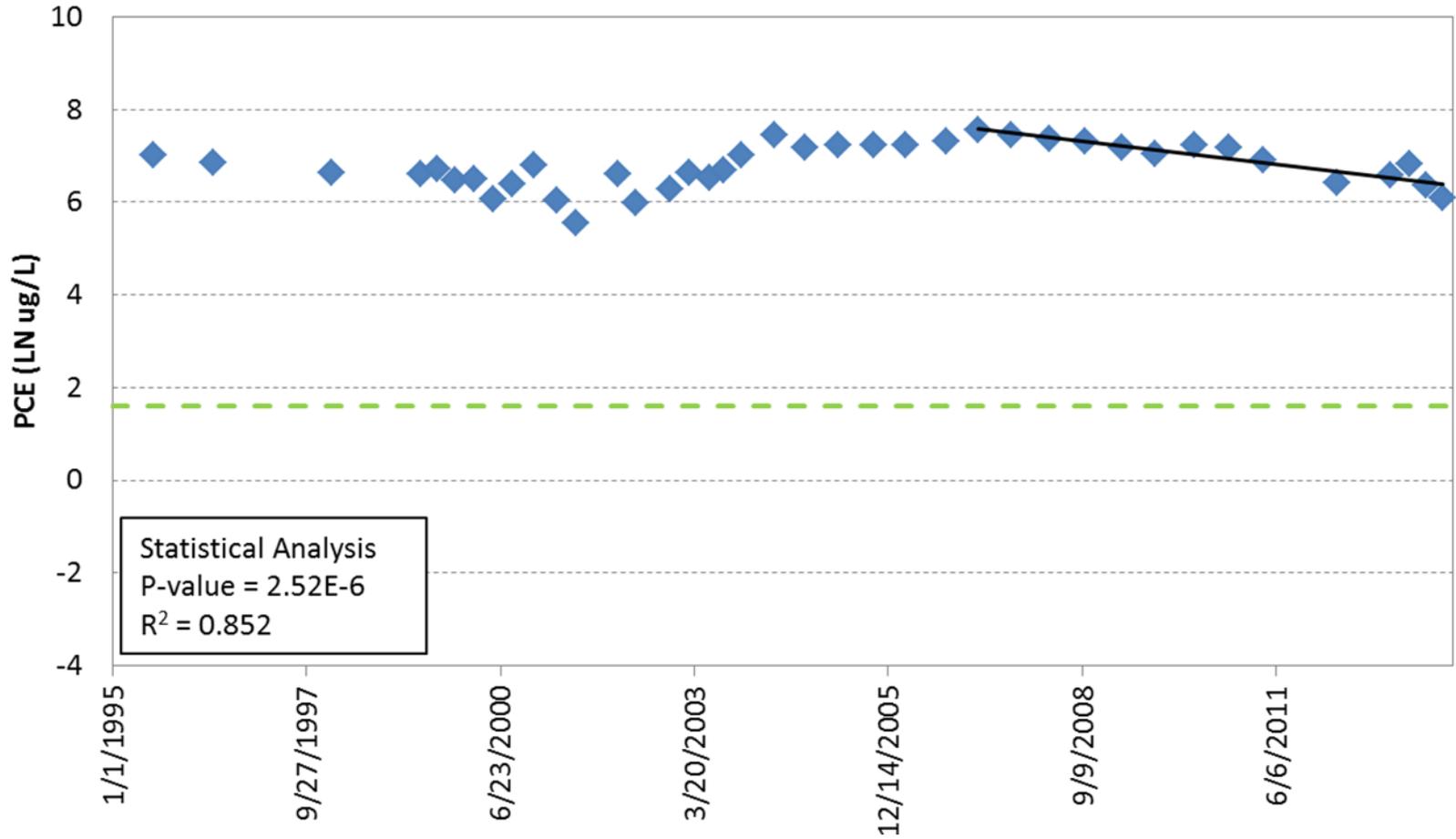


- Quantitative Trendline
- - - Qualitative Trendline
- ◆ PCE Detect (ug/L)
- ◇ PCE Non-detect (ug/L)
- - - MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis

MW-2D



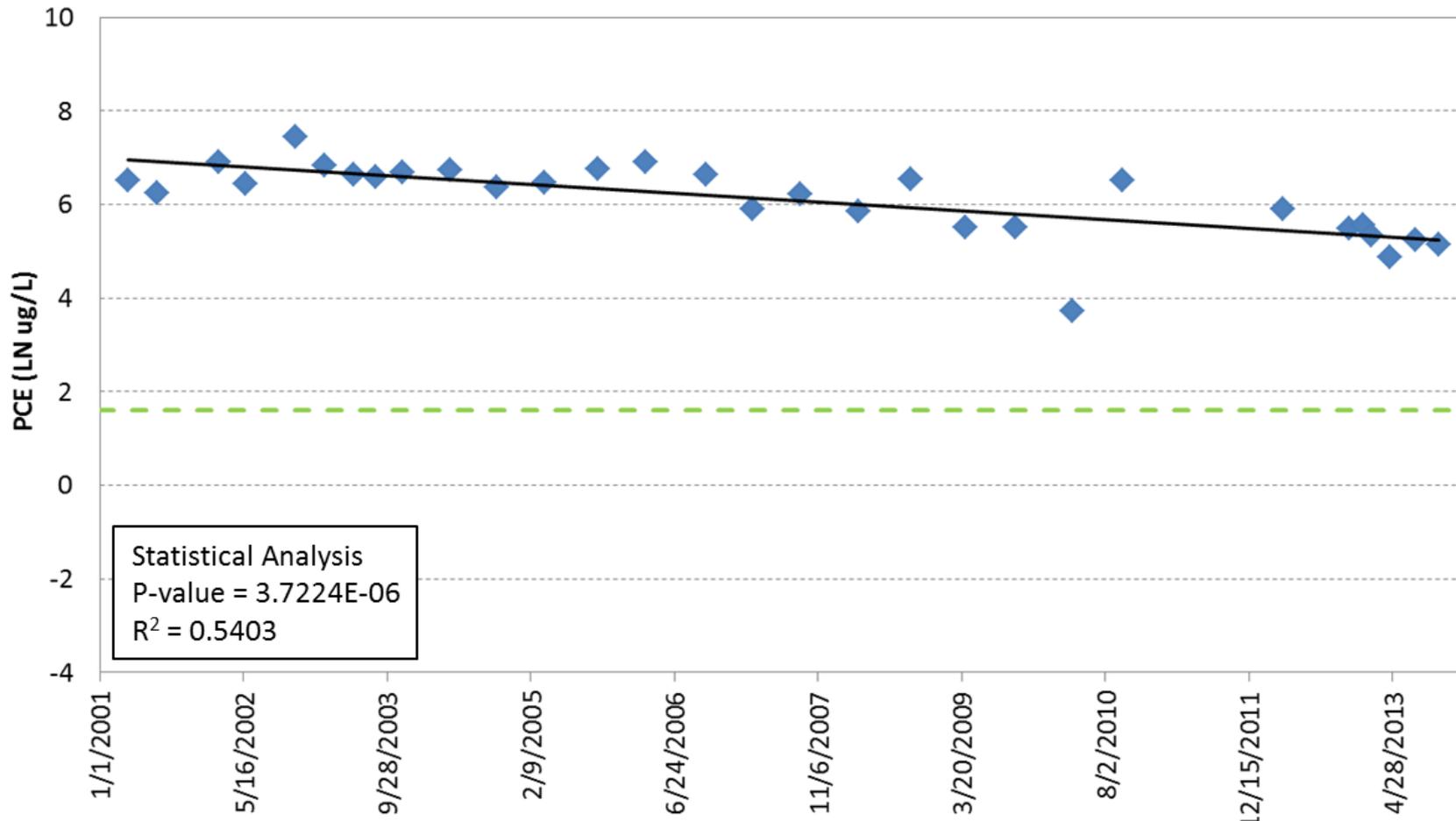
- Quantitative Trendline
- Qualitative Trendline
- PCE Detect (ug/L)
- PCE Non-detect (ug/L)
- MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis



MW-5S



- Quantitative Trendline
- Qualitative Trendline
- PCE Detect (ug/L)
- PCE Non-detect (ug/L)
- MCL (5 ug/L)

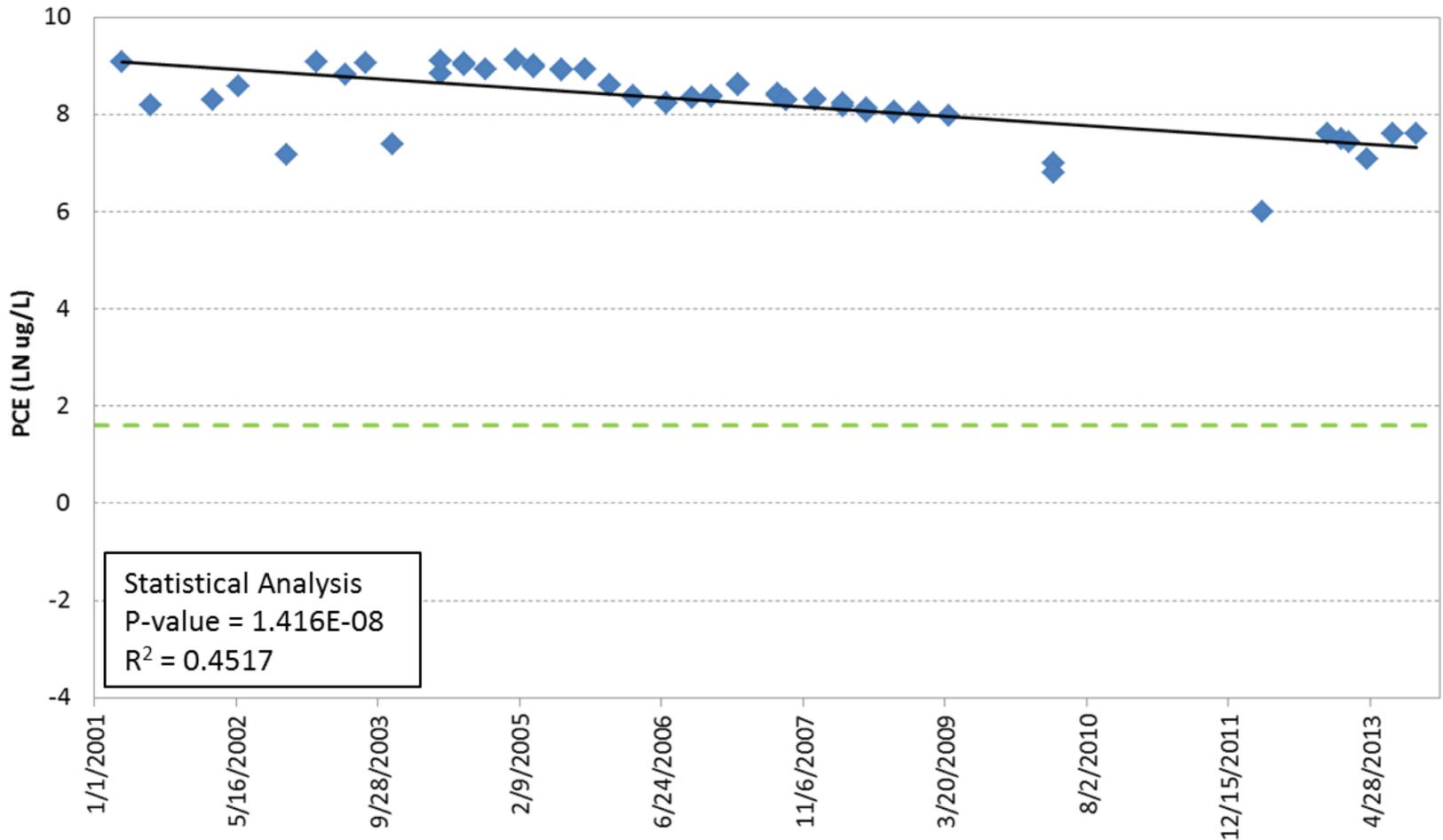
MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis



FIGURE
A-4

MW-5D



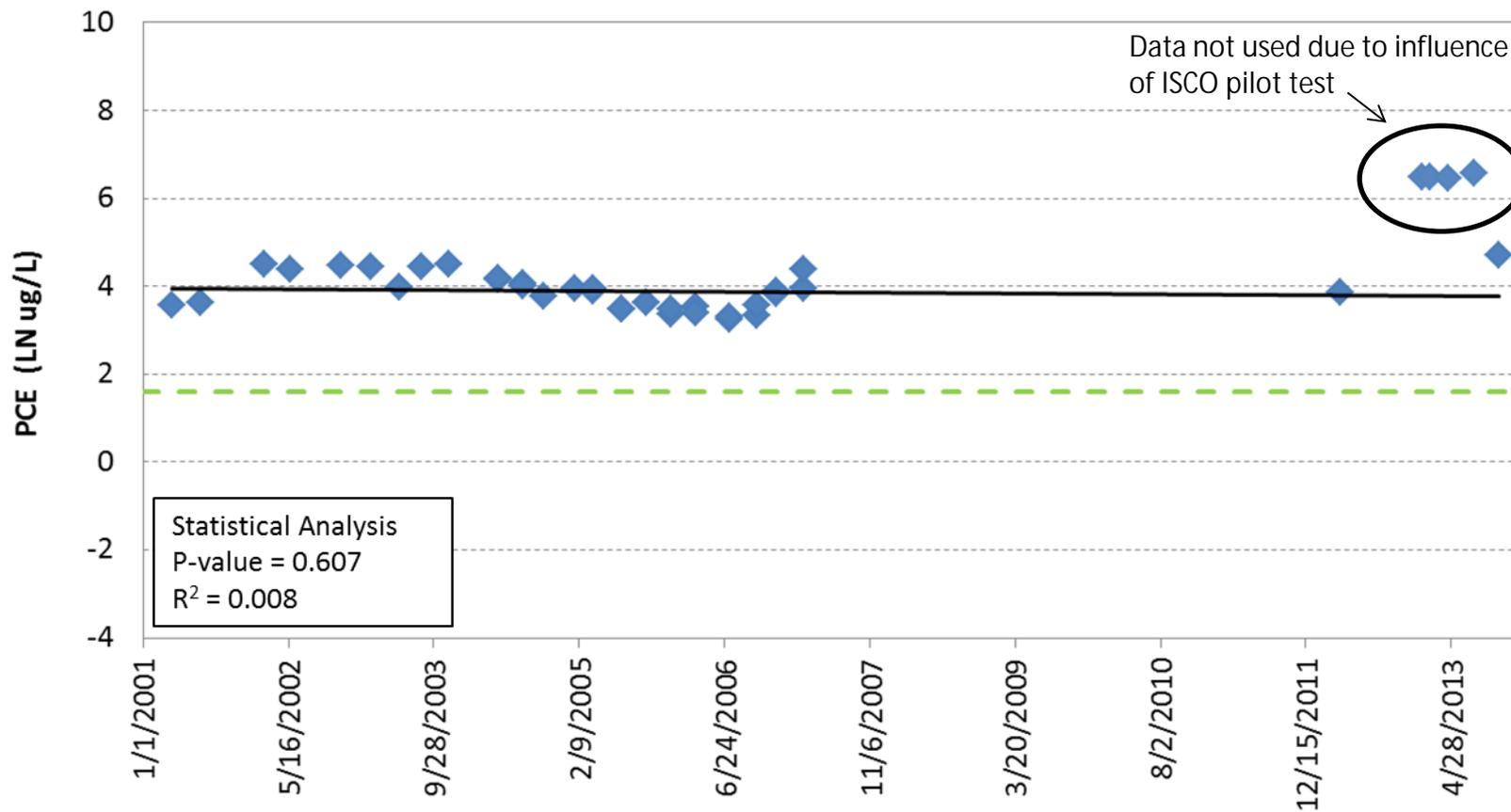
- Quantitative Trendline
- Qualitative Trendline
- PCE Detect (ug/L)
- PCE Non-detect (ug/L)
- MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis

FIGURE
A-5

MW-5D2

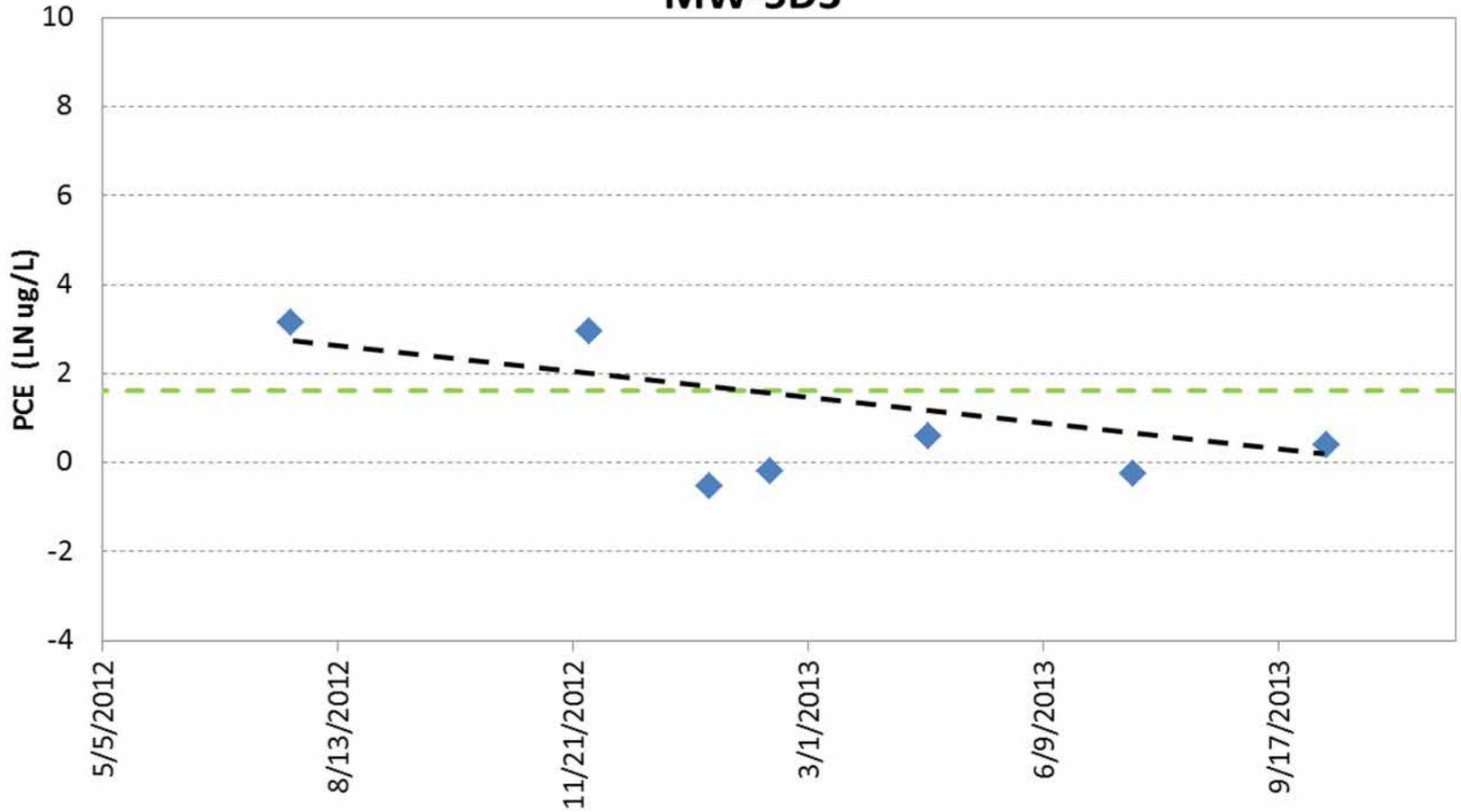


- Quantitative Trendline
- — Qualitative Trendline
- ◆ PCE Detect (ug/L)
- ◇ PCE Non-detect (ug/L)
- — MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis

MW-5D3



- Quantitative Trendline
- - - Qualitative Trendline
- ◆ PCE Detect (ug/L)
- ◇ PCE Non-detect (ug/L)
- - - MCL (5 ug/L)

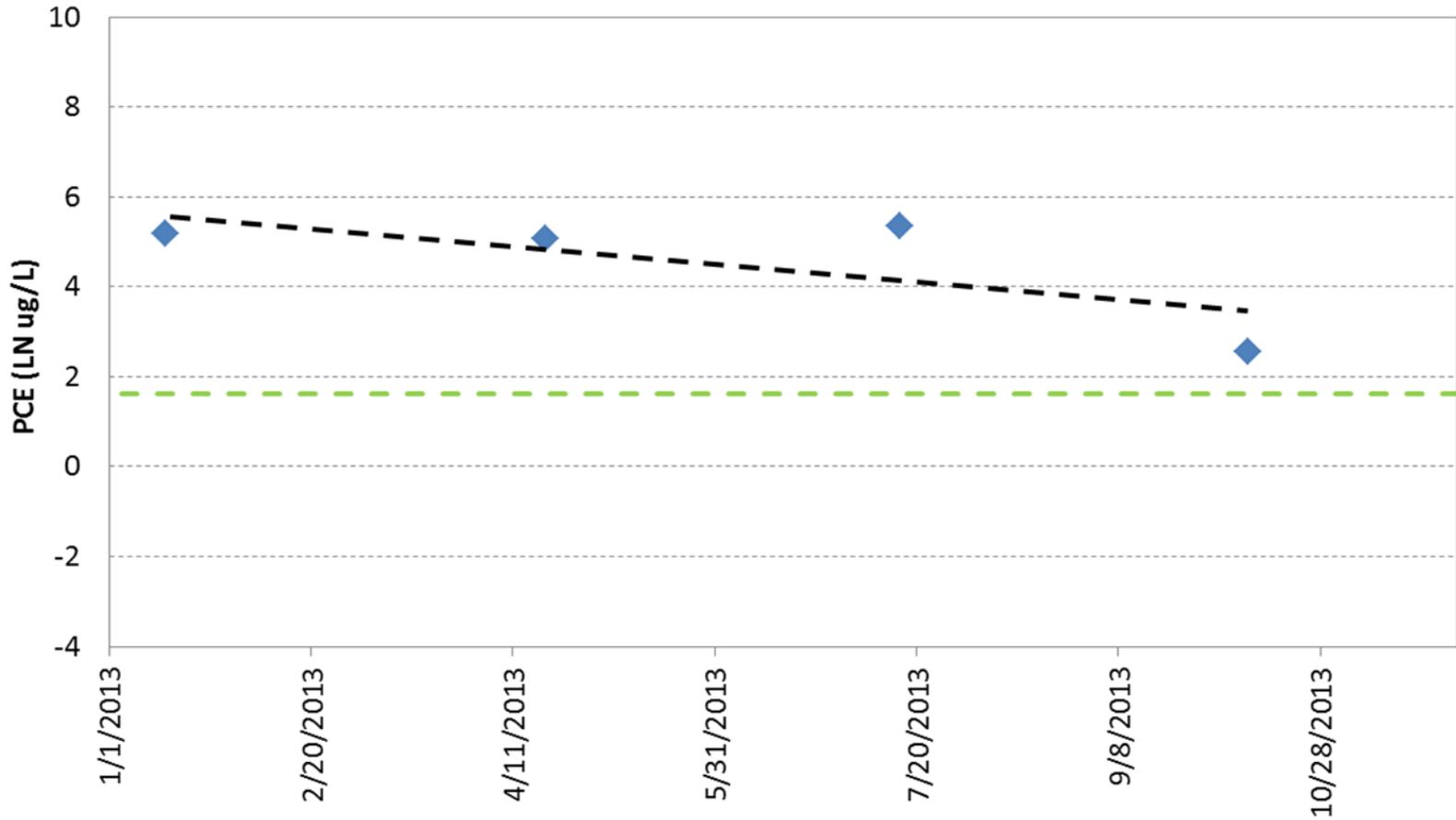
MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis



FIGURE
A-7

MW-22S



- Quantitative Trendline
- - - Qualitative Trendline
- ◆ PCE Detect (ug/L)
- ◇ PCE Non-detect (ug/L)
- - - MCL (5 ug/L)

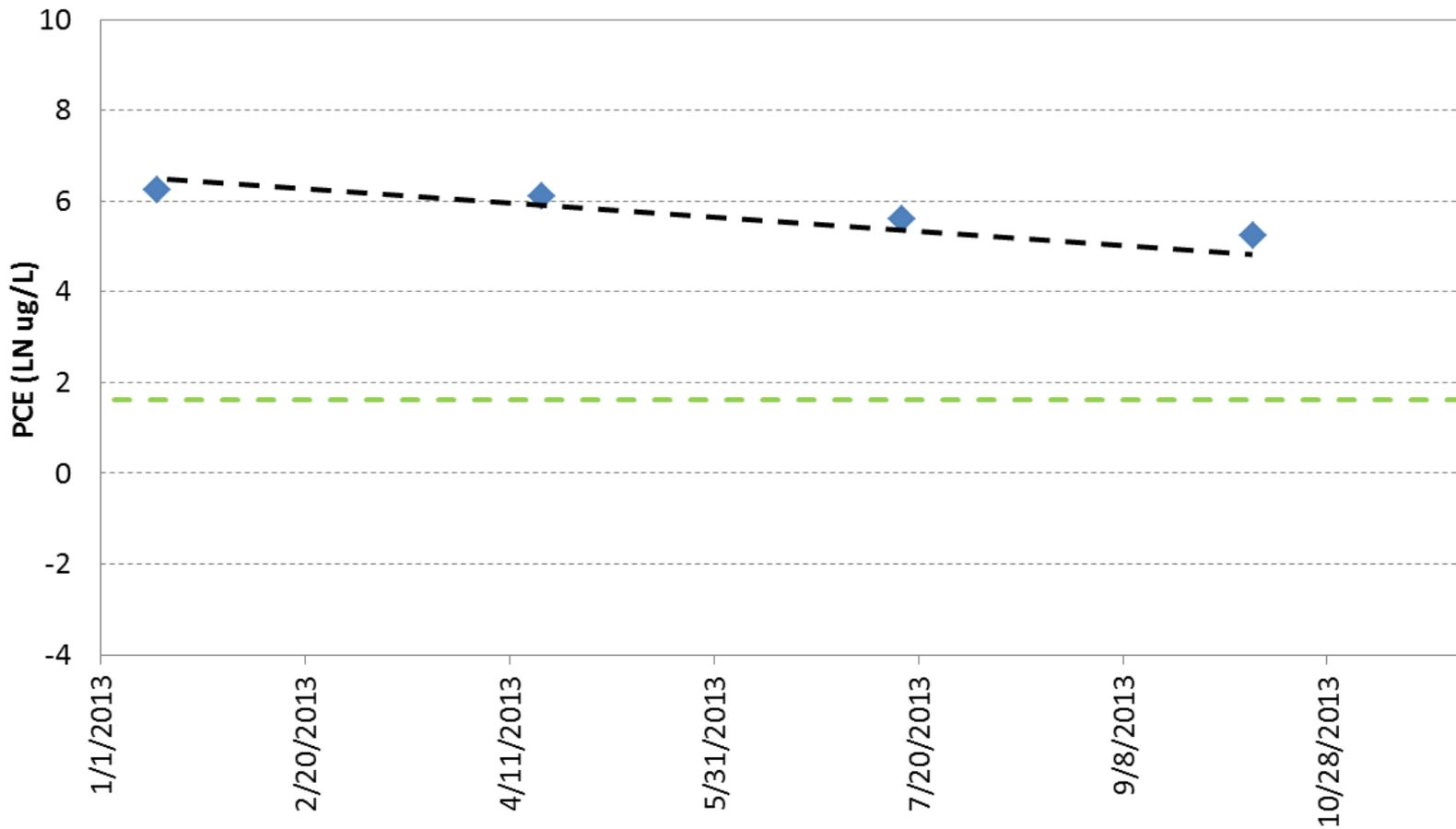
MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis



FIGURE
A-8

MW-22D

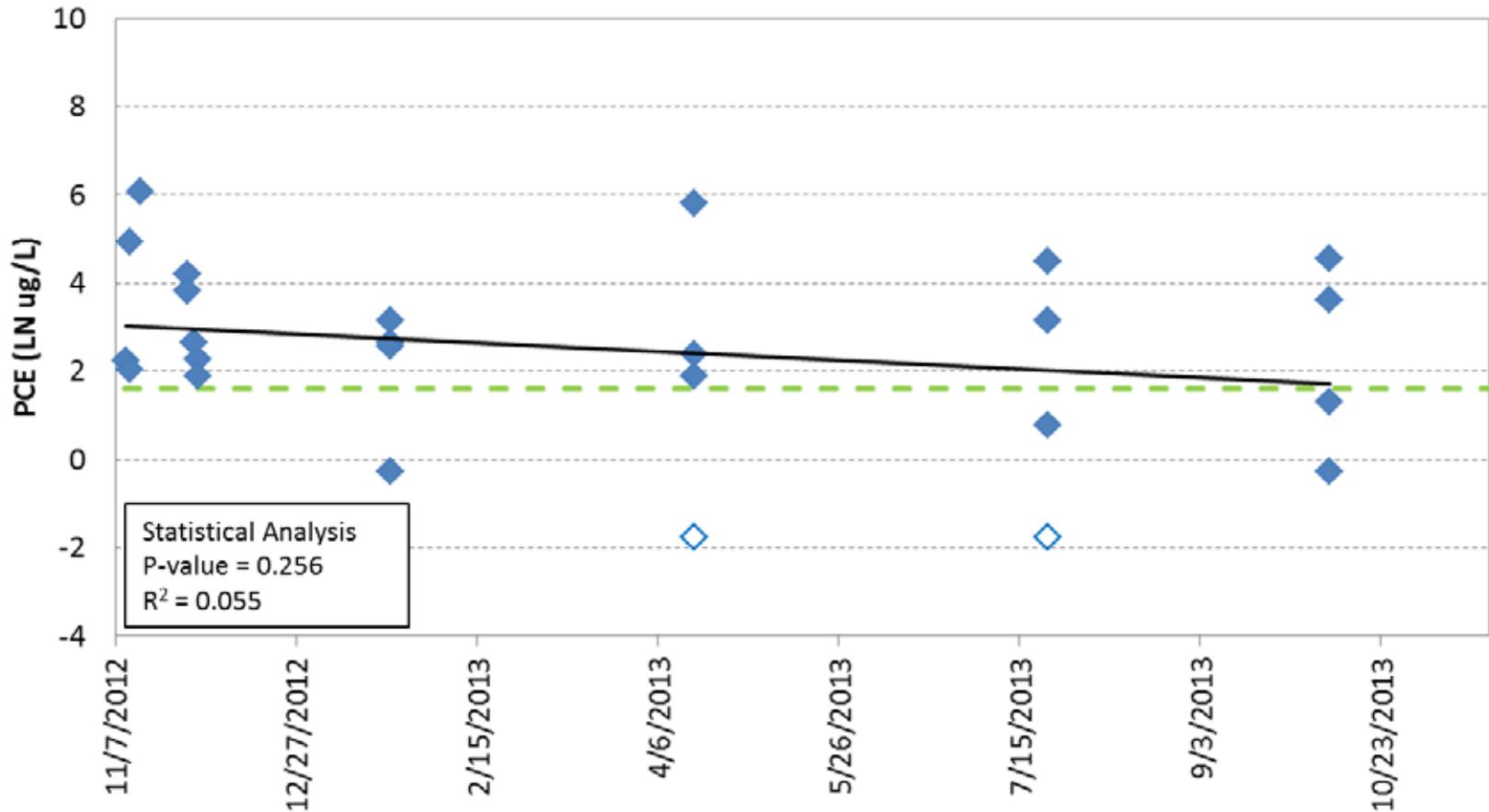


- Quantitative Trendline
- Qualitative Trendline
- PCE Detect (ug/L)
- PCE Non-detect (ug/L)
- MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis

MW-16



- Quantitative Trendline
- - - Qualitative Trendline
- ◆ PCE Detect (ug/L)
- ◇ PCE Non-detect (ug/L)
- - - MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

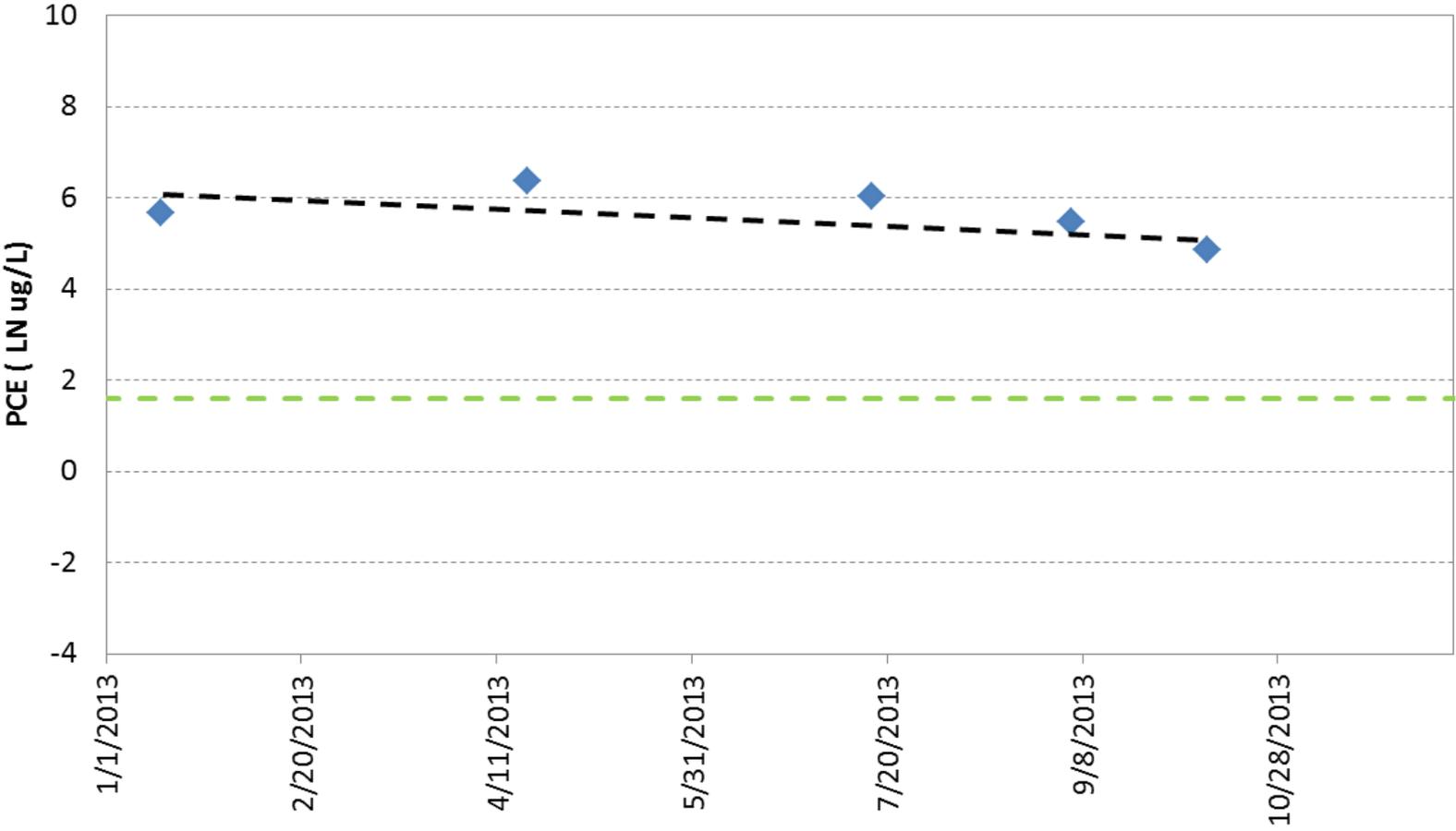
PCE Concentration Trend Analysis



FIGURE

A-10

MW-23S

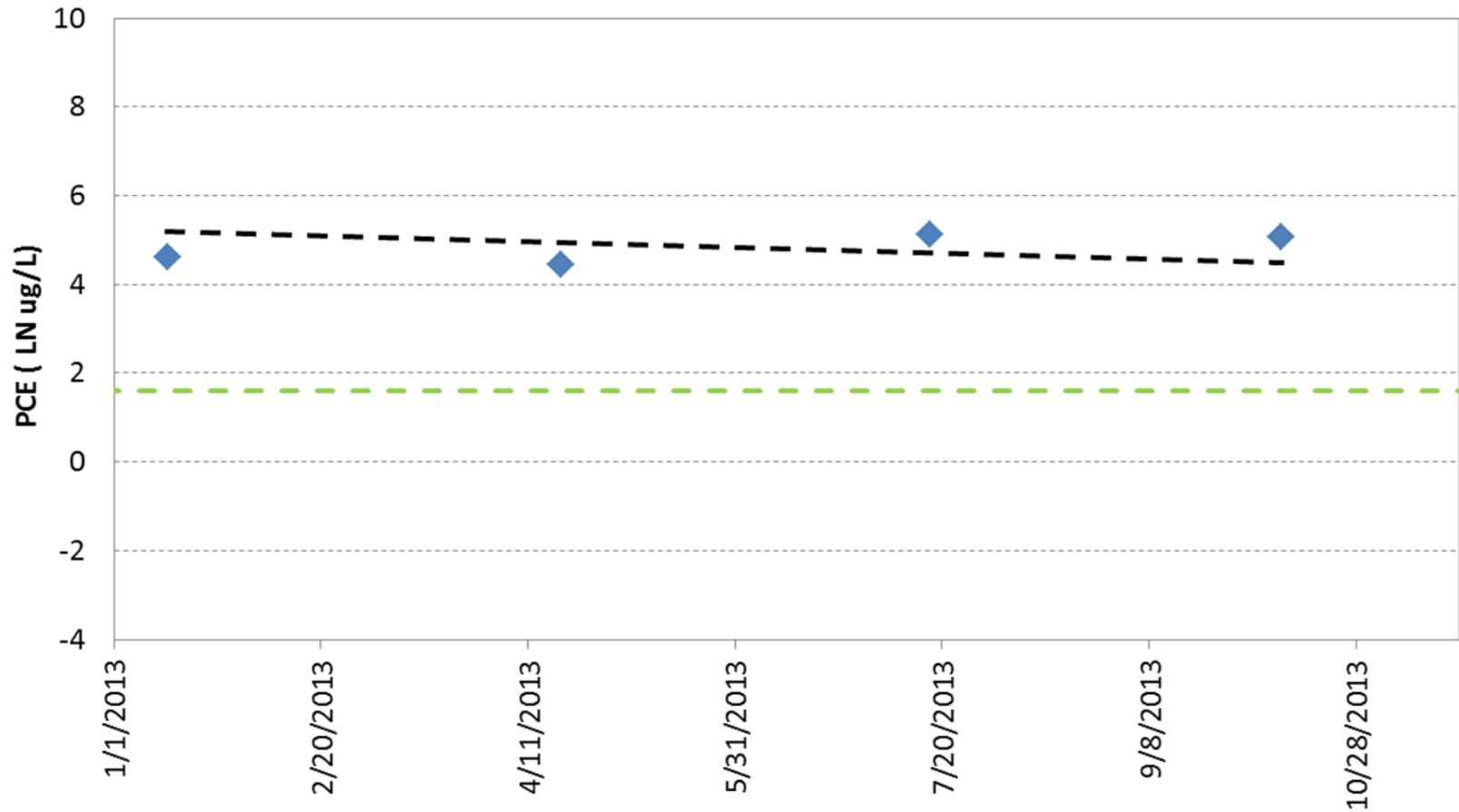


- Quantitative Trendline
- Qualitative Trendline
- PCE Detect (ug/L)
- PCE Non-detect (ug/L)
- MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis

MW-23D



- Quantitative Trendline
- - - Qualitative Trendline
- ◆ PCE Detect (ug/L)
- ◇ PCE Non-detect (ug/L)
- - - MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

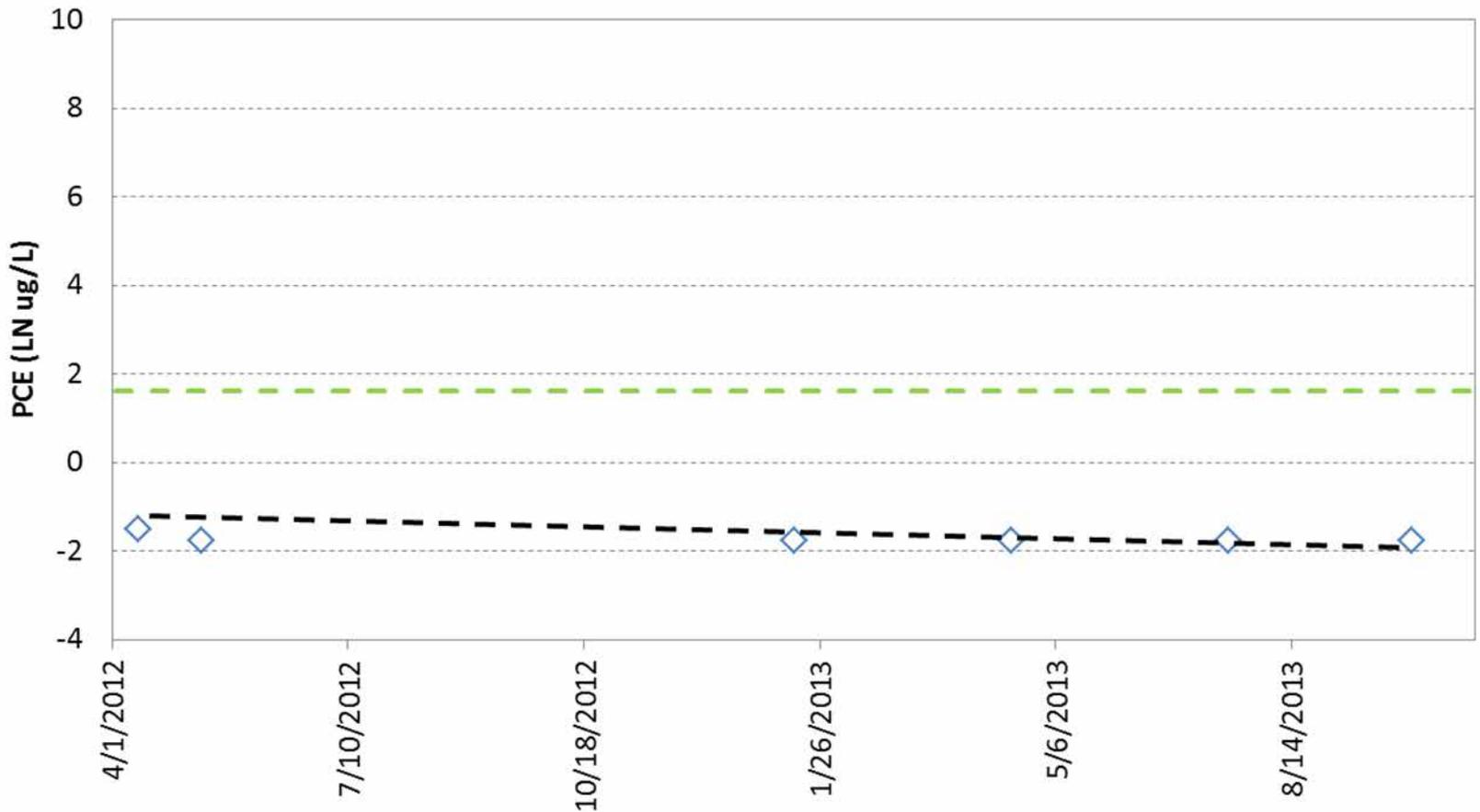
PCE Concentration Trend Analysis



FIGURE

A-12

MW-11S

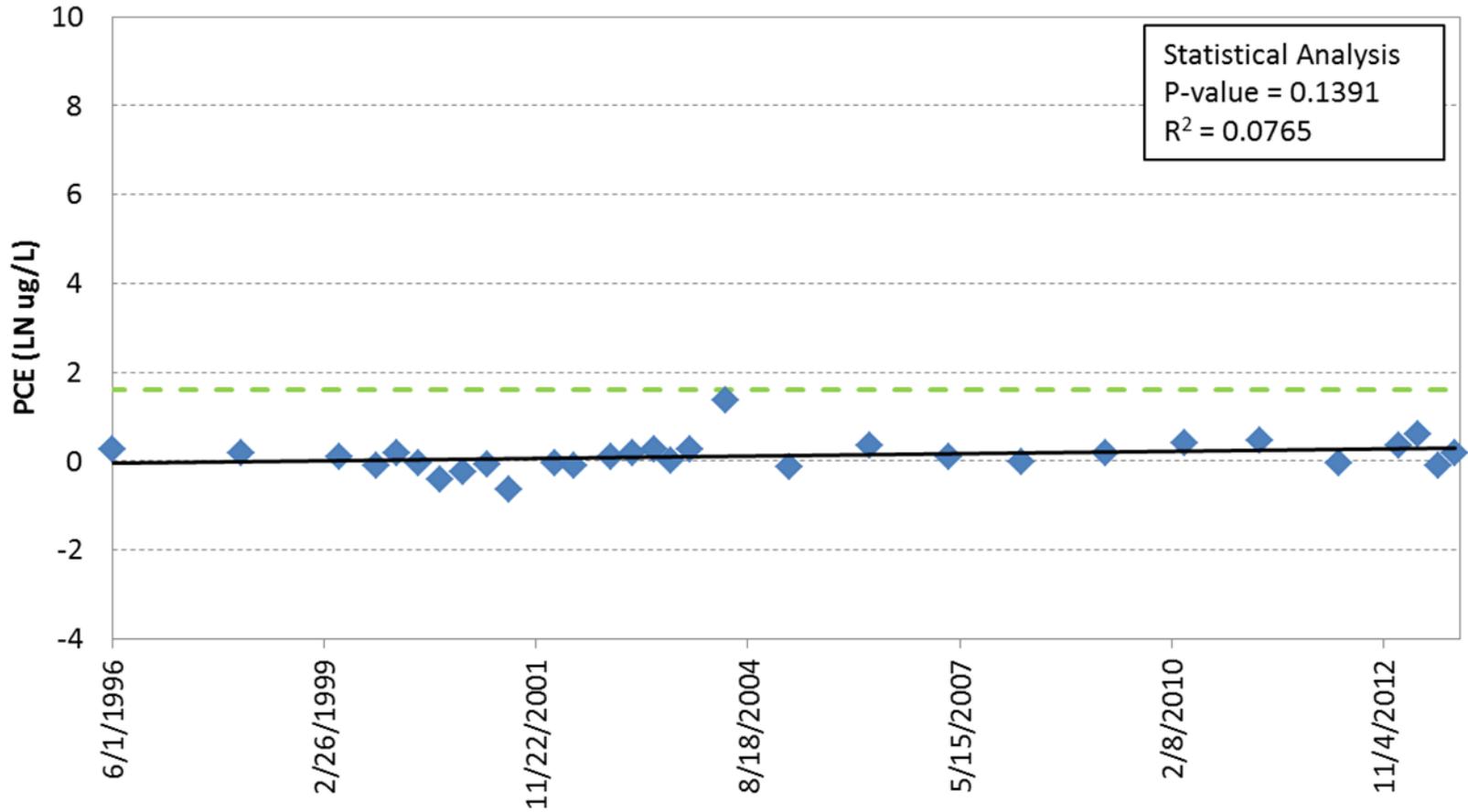


- Quantitative Trendline
- - - Qualitative Trendline
- ◆ PCE Detect (ug/L)
- ◇ PCE Non-detect (ug/L)
- - - MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis

MW-4S



- Quantitative Trendline
- - - Qualitative Trendline
- ◆ PCE Detect (ug/L)
- ◇ PCE Non-detect (ug/L)
- - - MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

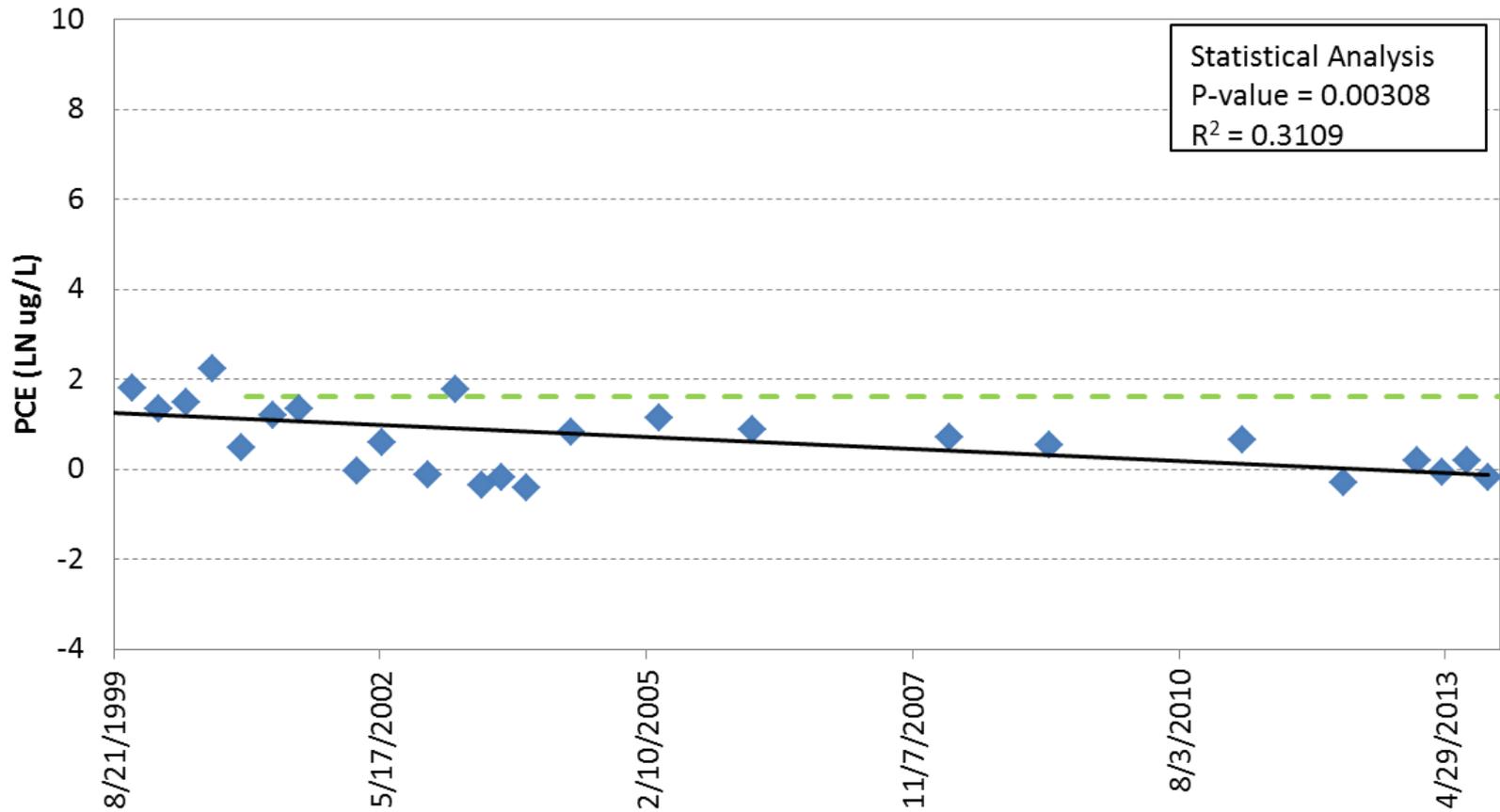
PCE Concentration Trend Analysis



FIGURE

A-14

MW-4D2



- Quantitative Trendline
- Qualitative Trendline
- PCE Detect (ug/L)
- PCE Non-detect (ug/L)
- MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

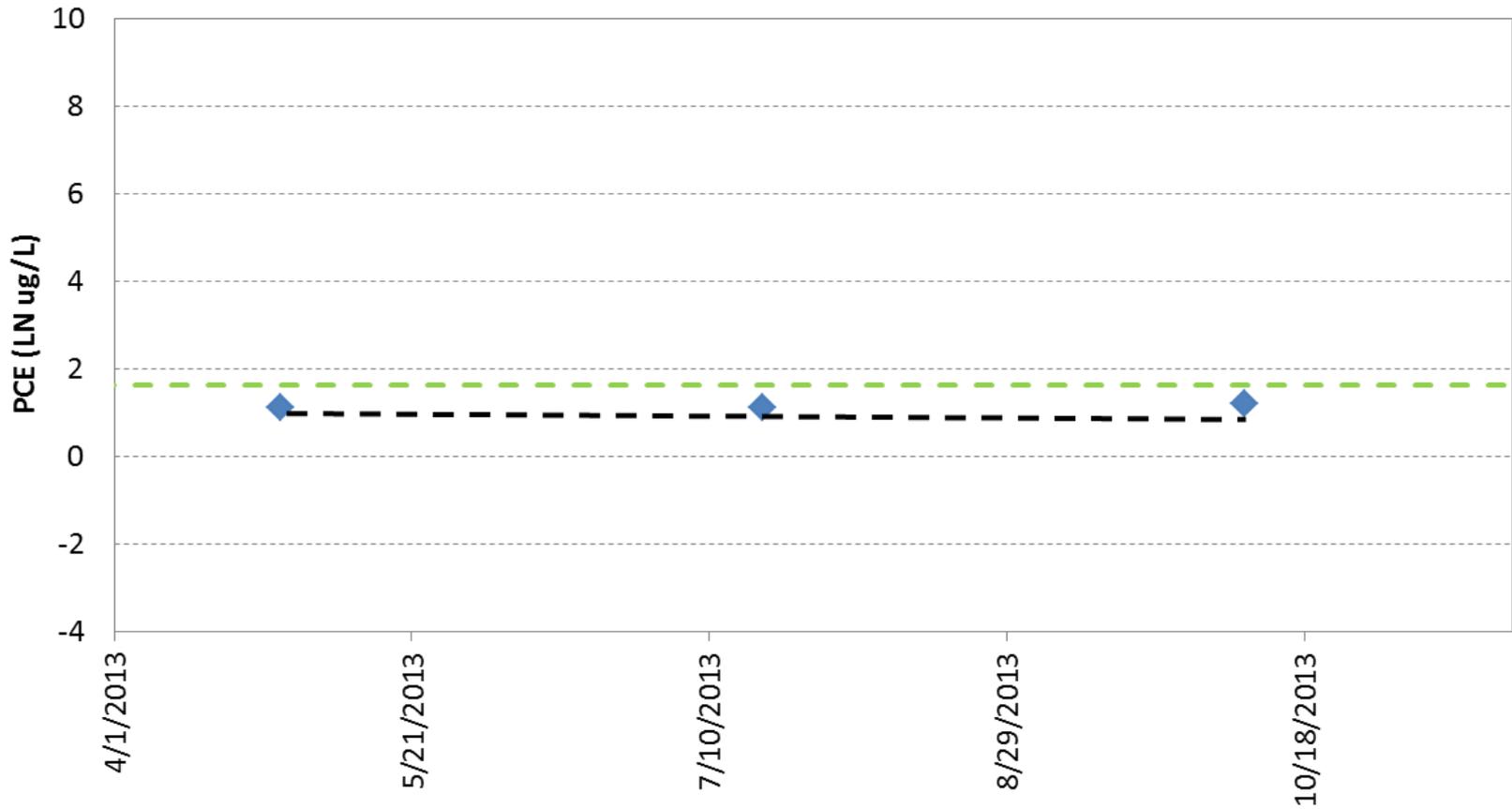
PCE Concentration Trend Analysis



FIGURE

A-16

MW-24

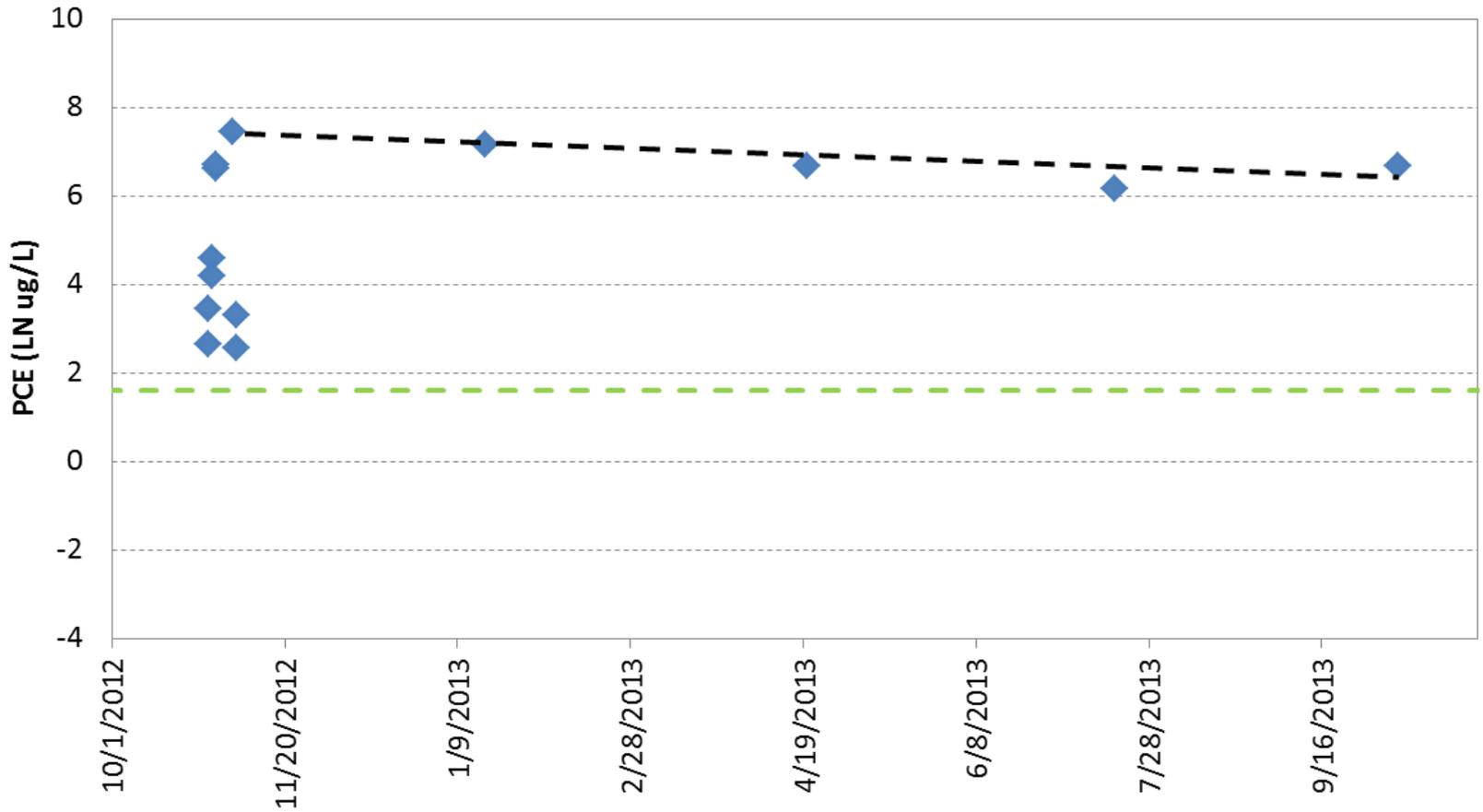


- Quantitative Trendline
- - - Qualitative Trendline
- ◆ PCE Detect (ug/L)
- ◇ PCE Non-detect (ug/L)
- - - MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis

MW-17



- Quantitative Trendline
- - - Qualitative Trendline
- ◆ PCE Detect (ug/L)
- ◇ PCE Non-detect (ug/L)
- - - MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis

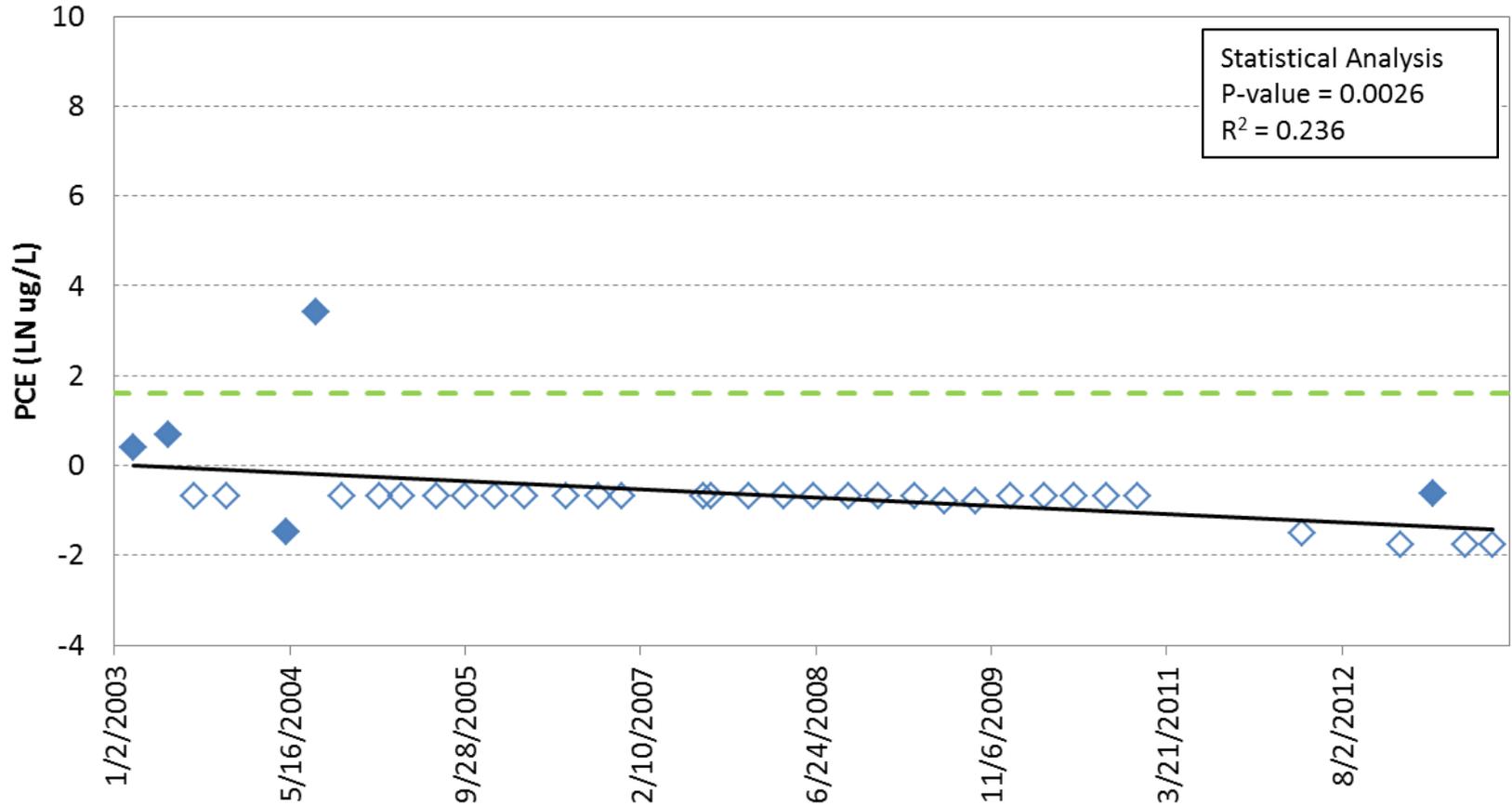


FIGURE

A-18

MW-6S

Statistical Analysis
P-value = 0.0026
R² = 0.236

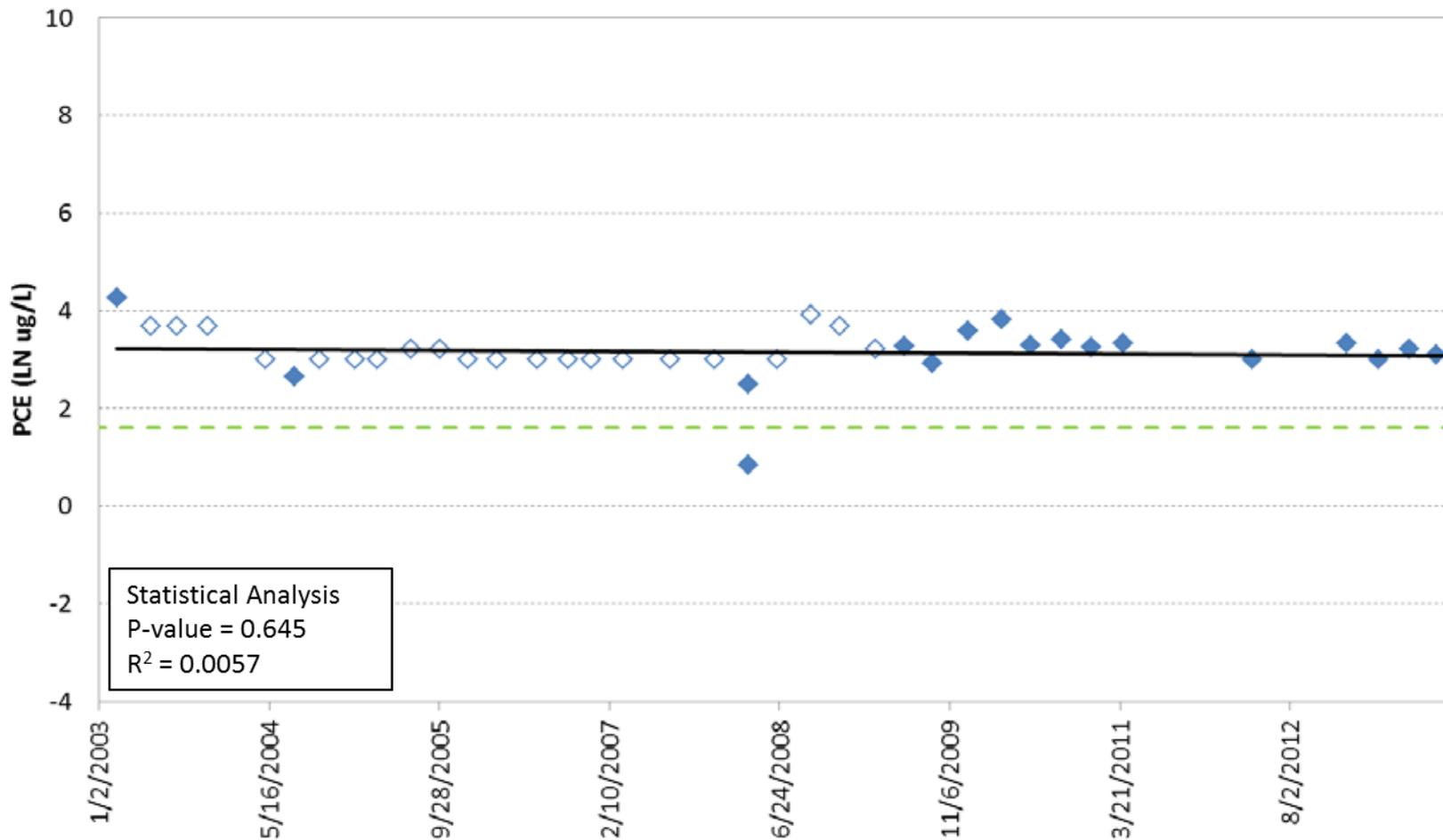


- Quantitative Trendline
- Qualitative Trendline
- PCE Detect (ug/L)
- PCE Non-detect (ug/L)
- MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis

MW-6D

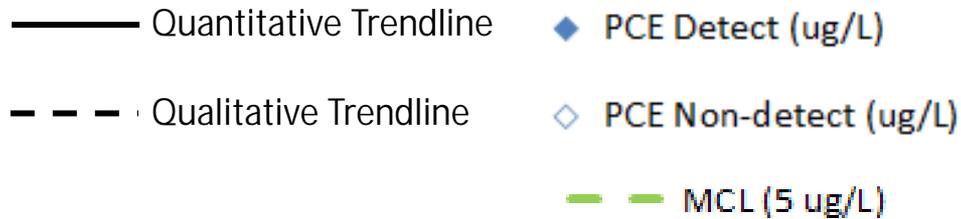
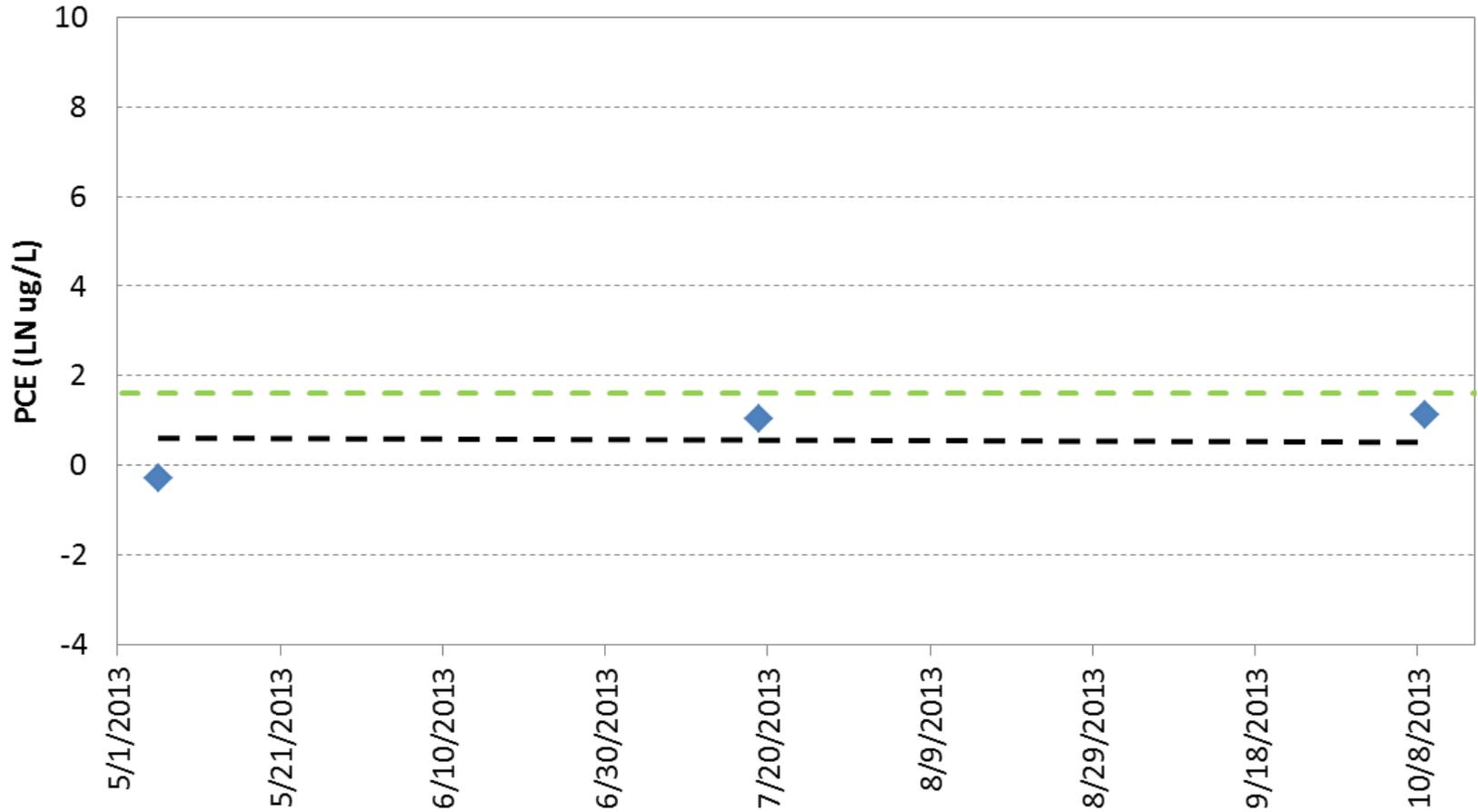


- Quantitative Trendline
- - - Qualitative Trendline
- ◆ PCE Detect (ug/L)
- ◇ PCE Non-detect (ug/L)
- - - MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis

MW-25D



MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

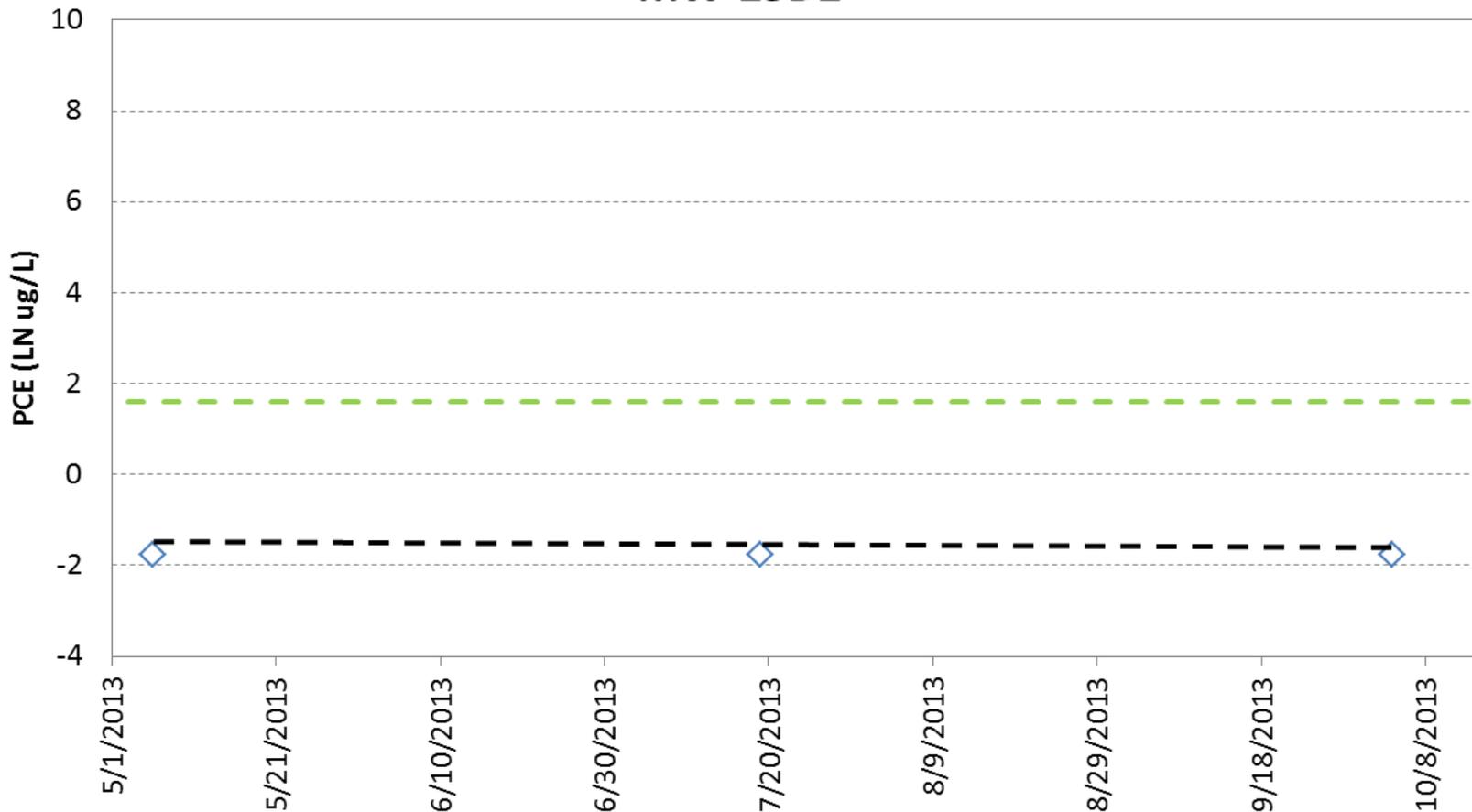
PCE Concentration Trend Analysis



FIGURE

A-21

MW-25D2



- Quantitative Trendline
- Qualitative Trendline
- PCE Detect (ug/L)
- PCE Non-detect (ug/L)
- MCL (5 ug/L)

MADISON-KIPP CORPORATION
201 WAUBESA STREET
MADISON, WISCONSIN
2014 FATE AND TRANSPORT MODEL

PCE Concentration Trend Analysis