



Post Office Box 8043
Madison, WI 53708-8043

**Madison-Kipp
Corporation**

201 Waubesa Street
Madison, WI 53704-5728

September 15, 2015

Nicolas Bertolas
Waste Water Specialist - Bureau of Water Quality
Wisconsin Department of Natural Resources
South Central Region
3911 Fish Hatchery Rd.
Fitchburg, WI 53711

Subject: Discharge Monitoring Report - Groundwater Extraction and Treatment System (GETS)
Madison Kipp Corporation (MKC), 201 Waubesa Street, Madison, Wisconsin

Dear Mr. Bertolas,

This letter summarizes the activities completed from August 1 through August 31, 2015 as part of the Groundwater Extraction and Treatment System (GETS) at the Madison Kipp Corporation (MKC) site under the Wisconsin Pollution Discharge Elimination System (WPDES) Permit WI-0046566-6. A summary of operation and activities completed during August 2015 is presented below.

GETS Operation and Monitoring

The GETS system ran intermittently from August 1 through August 31, 2015. Compliance samples were collected on August 5, August 13 and August 21, 2015 per the WPDES permit. On August 9, 2015, the hydrogen peroxide tank that provides neutralization of sodium permanganate emptied and was not replaced for several hours. During this time, water with sodium permanganate was discharged. Once the issue was discovered, the hydrogen peroxide tank was immediately changed. On August 28, 2015, a pressure transducer was installed on the hydrogen peroxide feed line and programming of the system was modified to prevent the GETS from operating if hydrogen peroxide is not being dosed into the system. Between August 9 and August 28, the GETS was operated only during times when a staff member was available to monitor effective hydrogen peroxide dosing for permanganate neutralization.

Influent groundwater continue to fall in the 3.8 milligram per liter range, using the Ground Water Sample Preservation at In-Situ Chemical Oxidation Sites - Recommended Guidelines colormetric chart dated August 2012, Attachment B. With the exception of the period mentioned above, sodium permanganate has not been present in the system discharge water. Sodium permanganate neutralization is documented in Attachment C.



Post Office Box 8043
Madison, WI 53708-8043

**Madison-Kipp
Corporation**

201 Waubesa Street
Madison, WI 53704-5728

If you have any questions or need additional information, please contact myself at asatkoski@madison-kipp.com or (608) 242-5200.

Alina Satkoski

Environmental Engineer
Madison Kipp Corporation

Attachment A Discharge Monitoring Report Form

Attachment B Ground Water Sample Preservation at In-Situ Chemical Oxidation Sites -
Recommended Guidelines colorimetric chart dated August 2012

Attachment C Neutralization Photos

Copies:

Jennine Trask - ARCADIS (electronic)

Mike Schmoller - WDNR (electronic)

George Parrino - Madison Department of Health (electronic)

plan, or in general EPA documents such as the Resource Conservation and Recovery Act (RCRA) guidance document (U.S. EPA, 1992) or EPA SW-846 (U.S. EPA, 1982). Additional direction on ground water sampling techniques can be found in Yeskis and Zavala (2002).

2.1. Permanganate (MnO_4^-)

Data and information presented below are reported in terms of the permanganate anion (MnO_4^- ; 118.9 grams per mole (g/mol)). Permanganate is purchased either as sodium permanganate ($NaMnO_4$; 141.9 g/mol) or potassium permanganate ($KMnO_4$; 158.0 g/mol) and as a result conversion to the permanganate anion concentration is needed to determine sample preservation needs as per the *Issue Paper*. Specifically, the ratios 118.9/141.9 (g-mole/g-mole) and 118.9/158.0 (g-mole/g-mole) are used to convert $NaMnO_4$ and $KMnO_4$, respectively to MnO_4^- .

2.1.1. Analysis by Visual Observation

The characteristic pink or purple color of MnO_4^- in a 40 mL VOA vial can be used as a general guideline to

estimate the concentration by using the MnO_4^- colorimetric scale (Table 1). This method should be used with caution because ground water turbidity and colloidal manganese dioxide solids ($MnO_2(s)$) can affect sample color and result in deviations from the tabulated color scale. Field filtration can help minimize these interferences, but may not fully remove all color if sub-micron colloidal and/or dissolved constituents are present.

2.1.2. Spectrophotometric Analysis

The permanganate concentration can be determined using commercially available field test kits (SenSafe™, 2011; CHEMetrics, 2011). Additionally, an accurate measurement of the permanganate concentrations can be determined using a field spectrophotometer (maximum absorbance wavelength (λ) = 525 nanometers (nm) (A_{525})) and a calibration curve involving a linear correlation between MnO_4^- concentration and A_{525} (Figure 2, Table 1). Filtered samples (0.2-0.45 micron) may be required to eliminate background colloidal or suspended solid materials that can absorb light at 525 nm and interfere with permanganate measurement. Volatilization of

Table 1. Permanganate concentration, spectrophotometric absorbance at 525 nm, and required amount of ascorbic acid required to neutralize the oxidant in a 40 mL vial. The color scale represents actual photos of MnO_4^- vials and is included for conceptual guidance. Actual colors vary based on background lighting, and color printers. Additionally, photographs of low concentrations (i.e., clear solutions) do not accurately capture transparency.

[MnO₄⁻] (mg/L) (millimolar in parentheses)													
0	0.75	3.8	7.5	11.3	18.8	30.1	37.6	56.4	75.3	113	151	188	376
(0)	(0.01)	(0.03)	(0.06)	(0.09)	(0.16)	(0.25)	(0.32)	(0.47)	(0.63)	(0.95)	(1.27)	(1.58)	(3.16)
Absorbance⁽¹⁾, wavelength (λ) = 525 nm													
0	0.011	0.059	0.134	0.197	0.329	0.516	0.627	NL	NL	NL	NL	NL	NL
Ascorbic Acid Stock Solution (M)⁽²⁾													
-	0.015	0.015	0.15	0.15	0.15	0.15	0.15	1.5	1.5	1.5	1.5	1.5	1.5
Volume of Ascorbic Acid solution (μL)													
0	30	150	30	46	76	121	152	23	30	46	61	76	152
Mass of Ascorbic Acid (mg)													
0	0.08	0.4	0.79	1.21	2.1	3.32	4.17	6.1	7.9	12.2	16.1	20.1	40.2
(1) $[MnO_4^-]$ (mg/L) = $58.8 \times A_{525}$; A_{525} is the absorbance at 525 nm; non-linear above 38 mg/L MnO_4^- .													
(2) To minimize sample dilution, the ascorbic acid stock solution used was 0.015, 0.15, and 1.5 M.													

Attachment C
Neutralization Photos
August 2015 Discharge Monitoring Report
Madison Kipp Corporation



August 13, 2015



August 21, 2015



August 14, 2015



August 31, 2015