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TECHNICAL MEMORANDUM

Date: January 13, 2016

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Subject: Groundwater Manganese in Land Application Areas

Introduction

Morning Star operates a tomato processing plant in Williams, CA that produces bulk tomato paste. The plant operates seasonally, from July through October. Wastewater from the tomato processing operations is discharged to fields just north of the processing plant, and discharge is regulated by the Central Valley Regional Water Quality Control Board (Board) under Waste Discharge Requirements (WDRs) Order No. R5-2013-0144. The groundwater monitoring network consists of nine (9) groundwater monitoring wells. Five (5) groundwater monitoring wells (MW-5, MW-6, MW-7, MW-8, and MW-9) are associated with the land application area (LAA) and are used to monitor constituents, as specified in the Monitoring and Reporting Program (MRP) of the WDRs, for potential groundwater degradation due to land application of tomato processing wastewater. Monitoring wells MW-1, MW-2, MW-3, and MW-4 are located near the processing plant, and used to monitor impacts from the tomato processing area.

Regulatory Background

In the 2013 WDRs, monitoring wells MW-2, MW-3, MW-6, MW-7, MW-8, and MW-9 are considered compliance wells, in that they are used to assess impact of plant operations on groundwater quality. Monitoring wells MW-1, MW-5 and MW-9 are upgradient of plant processing operations and MW-4 is upgradient of the site's Settling Pond, and thus are considered background wells. Manganese compliance in MW-2, MW-3, MW-6, and MW-9 is determined using the secondary maximum contaminant level (MCL_{SEC}) of 0.05 mg/L, specified in Section 64449 of Title 22 (Division 4, Chapter 15, Article 16). Manganese compliance in wells MW-7 and MW-8 is determined based on current groundwater quality. In Morning Star's Groundwater Limitations Compliance Assessment Plan (Reinhard 2014), manganese compliance in MW-7 and MW-8 is to be determined using a Tarone-Ware two-sample test with 95% confidence interval, in which the current year's data from a given well (MW-7 or MW-8) is compared to an historical dataset from that same well. The historical dataset is based on the groundwater concentrations that existed prior to the adoption of the WDRs on December 5, 2013. This test determines if there is a statistically significant difference between manganese data from a well's current year to the same well's previous years.

Morning Star received a Tentative Cease and Desist Order (CDO) No. R5-2016-XXXX, dated November 20, 2015, which showed instances when monitoring wells MW-7, MW-8, and MW-9 were out of compliance with their respective manganese limitations, specified in the CDO as "about 0.175 mg/L",

"about 0.65 mg/L", and 0.05 mg/L, respectively. The CDO (paragraph 67) alleges biochemical oxygen demand (BOD) overloading to the LAA as the cause of manganese in the groundwater.

Groundwater Chemistry for Manganese Mobilization

Iron and manganese are trace metals, found commonly in minerals, oxides, and hydroxides. Free iron and manganese are typically solubilized into water under acidic (pH <8) and anaerobic conditions (reducing environment) to form Fe^{2+} and Mn^{2+} (see Appendix A for Eh-pH stability diagrams). Iron and manganese, in these forms, will persist until they reach aerobic environments, in which they will precipitate out of solution, and typically complex onto soil surfaces.

Monitoring data from MW-7, MW-8, and MW-9 suggest a pH range of 7-8.5 in the groundwater. At this pH range, and under anaerobic conditions, manganese will mobilize within an oxidation-reduction potential (ORP) range of 0-0.3 V (Inglett et al. 2005). At the pH ranges found in the groundwater at the Morning Star site, manganese has a higher potential to solubilize than iron.

Manganese Behavior in Groundwater Wells

A time-series plot of manganese in MW-7 is shown in **Figure 1**. Manganese ranges from non-detect to 2.20 mg/L, with 43% of values being reported as non-detect, less than the reporting limit (RL), or less than the method detection limit (MDL). Between 2006 and 2011, manganese was consistently under the MCL_{SEC}; however, manganese concentrations exhibit an increasing trend beginning in August 2013; samples collected in 2015 continued this trend.

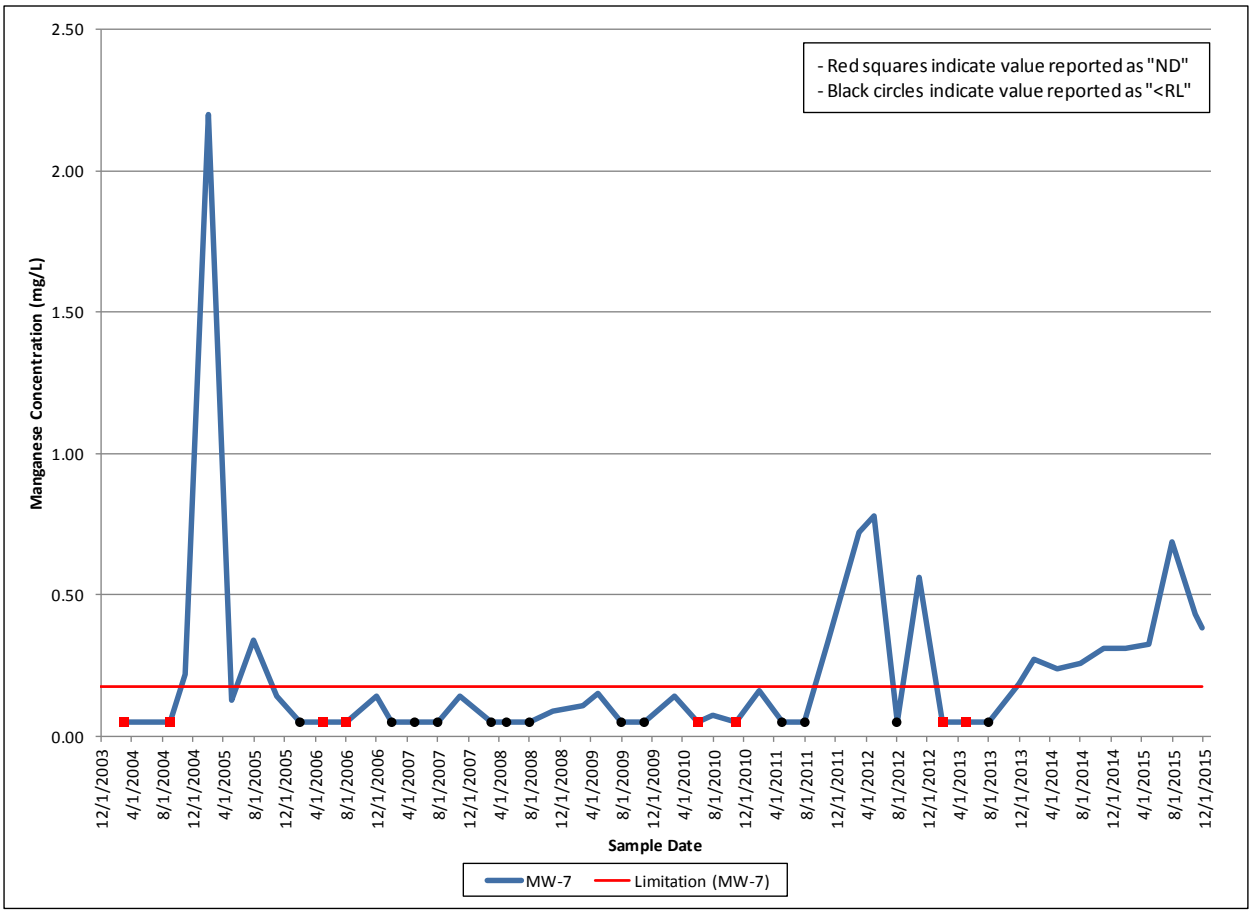

Figure 1. Time series for manganese concentrations in groundwater monitoring well MW-7. Non-detect or values less than the RL or MDL were reported as one-half of the RL or MDL, whichever was available.

A time-series plot of manganese in MW-8 is shown in **Figure 2**. Manganese ranges from non-detect to 1.98 mg/L, with 37% of values being reported as non-detect, less than the reporting limit (RL), or less than the method detection limit (MDL). Historically, manganese in MW-8 is highly variable between sampling dates, and a discernible trend in manganese is not evident. However, similar to MW-7, manganese concentrations began an increasing trend in August 2013, which continued through 2015.

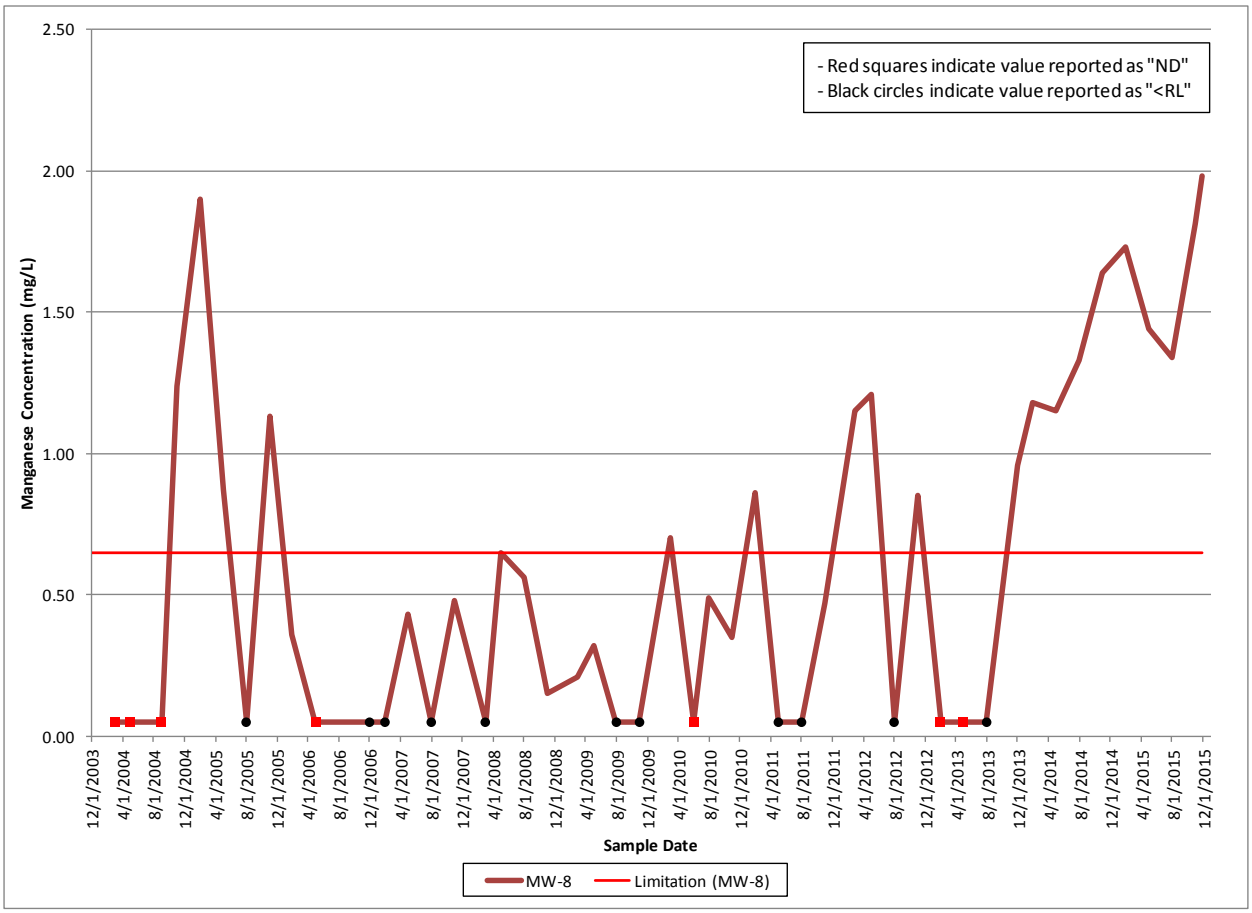

Figure 2. Time series for manganese concentrations in groundwater monitoring well MW-8. Non-detect or values less than the RL or MDL were reported as one-half of the RL or MDL, whichever was available.

A time-series plot of manganese in MW-9 is shown in **Figure 3**. Manganese ranges from non-detect to 0.91 mg/L, with 62% of values being reported as non-detect, less than the reporting limit (RL), or less than the method detection limit (MDL). Manganese in MW-9 has typically been at or near the MCL_{SEC} of 0.05 mg/L; however, similar to MW-7 and MW-8, manganese began an increasing trend in August 2013, which continued through 2015.

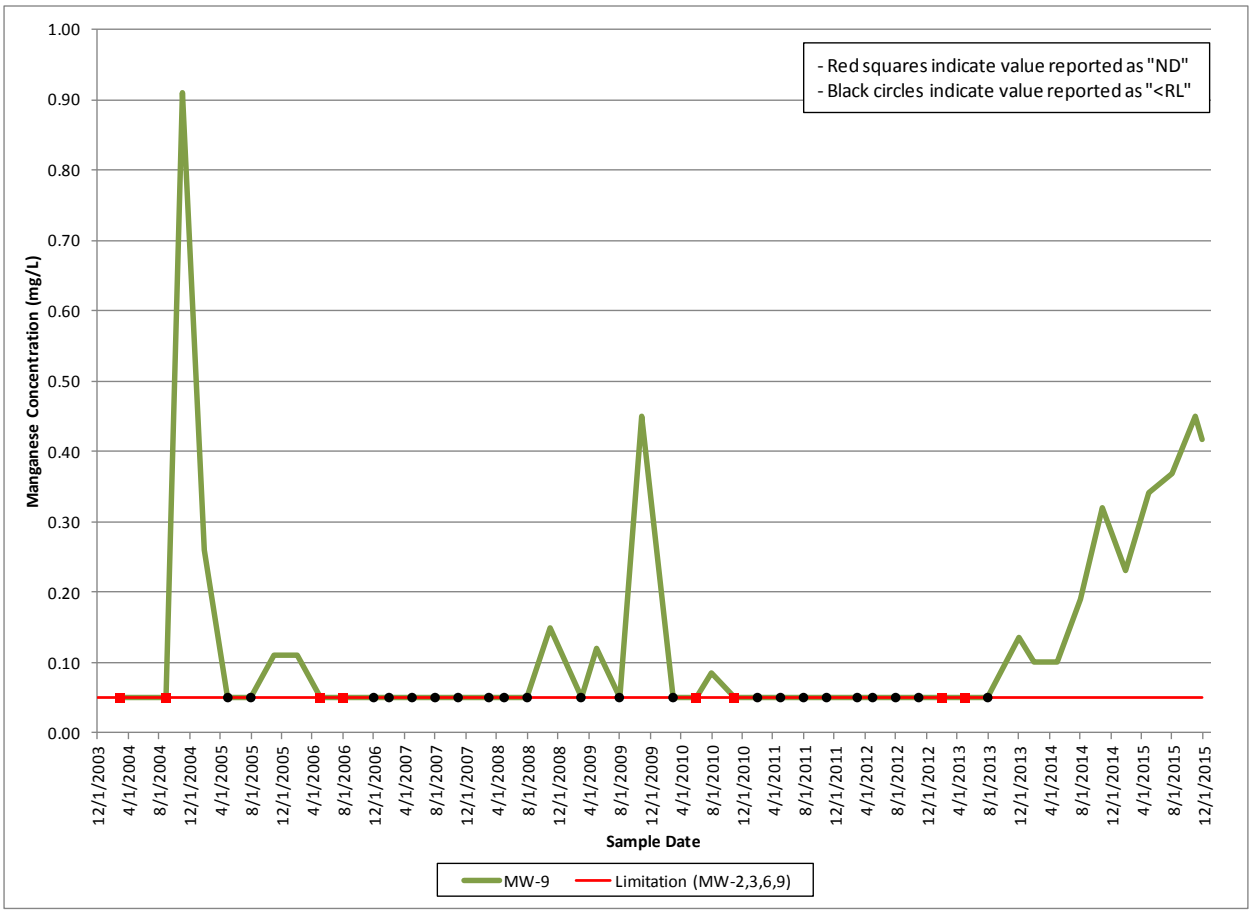

Figure 3. Time series for manganese concentrations in groundwater monitoring well MW-9. Non-detect or values less than the RL or MDL were reported as one-half of the RL or MDL, whichever was available.

Manganese Limitations for MW-7 and MW-8

Manganese limitations for MW-7 and MW-8 were specified in the CDO as "about 0.175 mg/L" and "about 0.65 mg/L", respectively. These limitations, as presented in the CDO, uses the Sanitas groundwater program, which used an historical mean of data prior to the issuance of the 2013 WDRs, without a confidence interval. While these limitations may be appropriate, alternative manganese limitations for MW-7 and MW-8 were computed in a similar manner to the Board's approach; however, a 95% confidence interval was applied to an historical mean of the manganese data from samples collected prior to issuance of the 2013 WDRs. Data values that were reported as non-detect, less than the reporting limit (RL), or less than the method detection limit (MDL) were included in the statistical at ½ of the MDL or RL. These limitations, and accompanying manganese exceedances in MW-7 and MW-8 are shown in **Table 1**; both limitations are different than those specified by the Board in the CDO, with the limitation for MW-7 being greater and the limitation for MW-8 less.

Table 1. Manganese exceedances for MW-7 and MW-8 for samples collected after the issuance of 2013 WDRs.

Monitoring Well	Sample Date	Manganese Concentration (mg/L)	Revised Limitation (mg/L)[1]
MW-7	2/17/2014	0.27	0.2
	5/12/2014	0.24	0.2
	8/25/2014	0.26	0.2
	11/13/2014	0.31	0.2
	2/19/2015	0.31	0.2
	5/18/2015	0.33	0.2
	8/24/2015	0.69	0.2
	11/12/2015	0.43	0.2
	12/3/2015	0.383	0.2
MW-8	2/17/2014	1.18	0.56
	5/12/2014	1.15	0.56
	8/25/2014	1.33	0.56
	11/13/2014	1.64	0.56
	2/19/2015	1.73	0.56
	5/18/2015	1.44	0.56
	8/24/2015	1.34	0.56
	11/12/2015	1.81	0.56
	12/3/2015	1.98	0.56

[1] Limitations for wells MW-7 and MW-8 were developed by summing the upper 95% confidence interval and the historical mean from each well, both calculated using data up to, and including, December 2013. Previous limitations, as stated in the CDO, were "about 0.175 mg/L" and "about 0.65 mg/L" for wells MW-7 and MW-8.

Manganese Limitation for MW-9

Manganese compliance in monitoring well MW-9 is assessed using the MCL_{SEC} of 0.05 mg/L. MW-9 is adjacent and downgradient to field MS1 (owned and operated by Gobel), on which rice was grown in 2014. However, as the Gobel field (MS-1) is now out of service as a LAA, MW-9 is likely upgradient or cross-gradient. Investigations of the manganese behavior in MW-9 revealed a similar pattern to those seen in MW-7 and MW-8, most notably the increasing trend beginning in August 2013. MW-9 appears to be influenced by similar factors as MW-7 and MW-8, and thus, it is suggested that manganese compliance in MW-9 be determined using current groundwater quality, as it is in MW-7 and MW-8. As such, an alternative limitation for MW-9 was developed in a similar manner to those developed for MW-7 and MW-8, using an historical mean of data collected prior to issuance of the 2013 WDRs, with a 95% confidence interval. Data values that were reported as non-detect, less than the reporting limit (RL), or less than the method detection limit (MDL) were included in the statistical at ½ of the MDL or RL. The limitation developed, and ensuing exceedances are shown in **Table 2**.

Table 2. Manganese exceedances for MW-9 for samples collected after the issuance of 2013 WDRs.

Monitoring Well	Sample Date	Manganese Concentration (mg/L)	Revised Limitation (mg/L)[1]
MW-9	8/25/2014	0.19	0.1
	11/13/2014	0.32	0.1
	2/19/2015	0.23	0.1
	5/18/2015	0.34	0.1
	8/24/2015	0.37	0.1
	11/12/2015	0.45	0.1
	12/3/2015	0.416	0.1

[1] The limitation for well MW-9 were developed by summing the upper 95% confidence interval and the historical mean from, both calculated using data up to, and including, December 2013. The previous limitation was the MCL_{SEC} of 0.05 mg/L.

Potential Sources of Dissolved Manganese in Groundwater

The CDO identified BOD overloading to the LAA in 2015 as the primary reason for manganese concentration exceedances observed in monitoring wells MW-7, MW-8, and MW-9. While there may be merit in this observation, it is not necessarily supported by manganese sampling data before 2015. Specifically, this observation is not supported by the increases in manganese concentrations between 2013 and 2015, a time frame when BOD overloadings only occurred once on two fields in 2014. As such, alternatives regarding the source of dissolved manganese in the groundwater monitoring wells should be considered.

Drought Related Manganese Increases in Groundwater

Climate in California's Central Valley has been highly variable in recent years. Currently, California is in the fourth year of a severe drought. The drought has caused aquifers to diminish due to the reduction in groundwater recharge via snowpack and surface water infiltration. In such circumstances, it is expected to experience degradation of groundwater quality, as the volume rainwater that percolates for dilution and oxidation is significantly less. **Figure 4** shows a time series of manganese concentrations in monitoring wells MW-7, MW-8, and MW-9, and the Sacramento Valley water year types during the data period, as specified by California Department of Water Resources (DWR 2014). In the recent severe drought, groundwater manganese concentrations in each well have increased significantly, when compared to previous years.

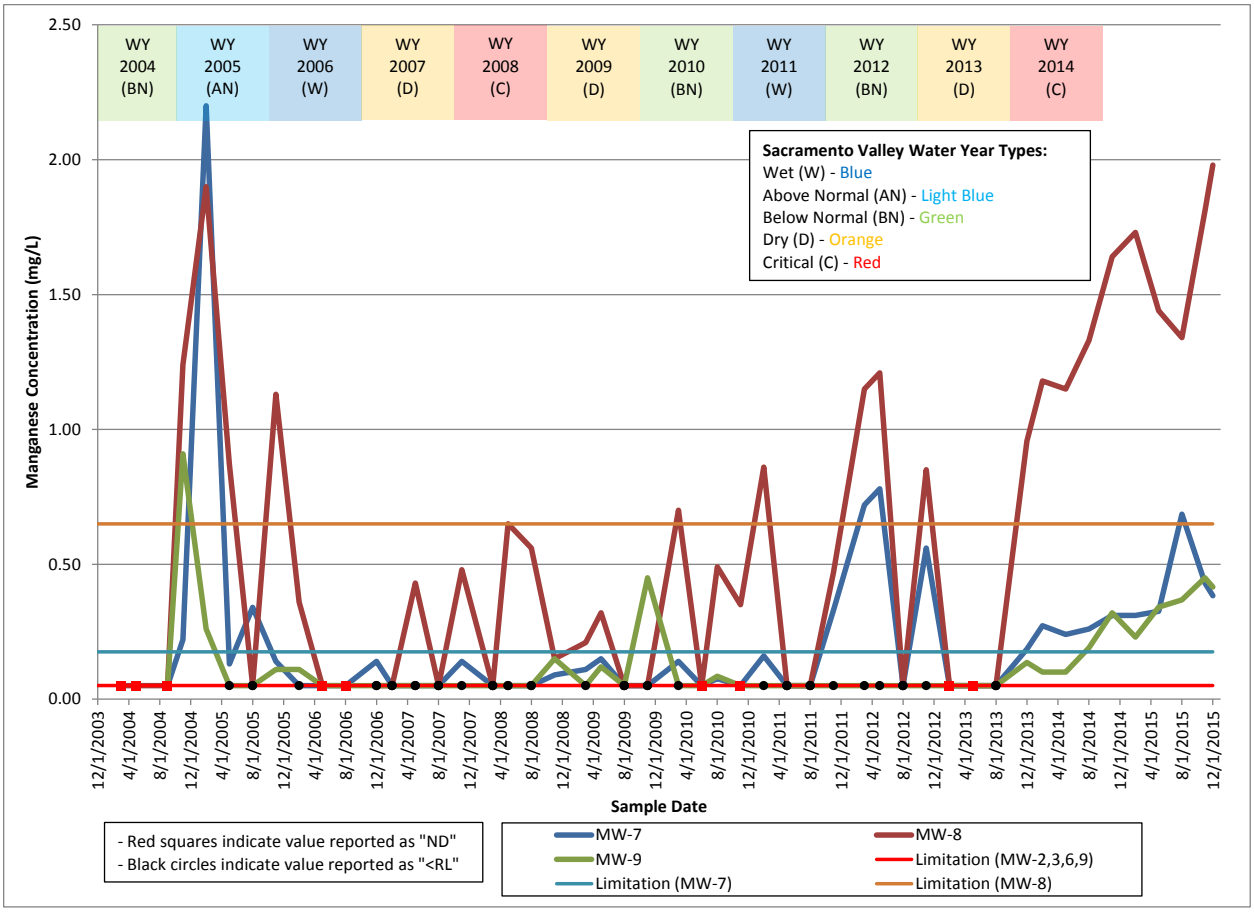

Figure 4. Manganese time series for MW-7, MW-8, and MW-9, and water year types.

Figure 5 shows the groundwater elevations for MW-7, MW-8, and MW-9 for water years dating back to 2004. It is evident that groundwater elevations in each well have decreased since 2013, to levels at or near the record minimum. This indicates that aquifer volumes have decreased at the Morning Star site during the same time period in which these wells began experiencing significant increases in manganese groundwater concentrations. Therefore, it is possible that, due to the drought, manganese concentrations in groundwater have increased due to less available groundwater volume for dilution. Figure 5 also shows that there has been no evidence of increased net seepage from the cooling pond in terms of any effects on shallow groundwater elevations in the LAA.

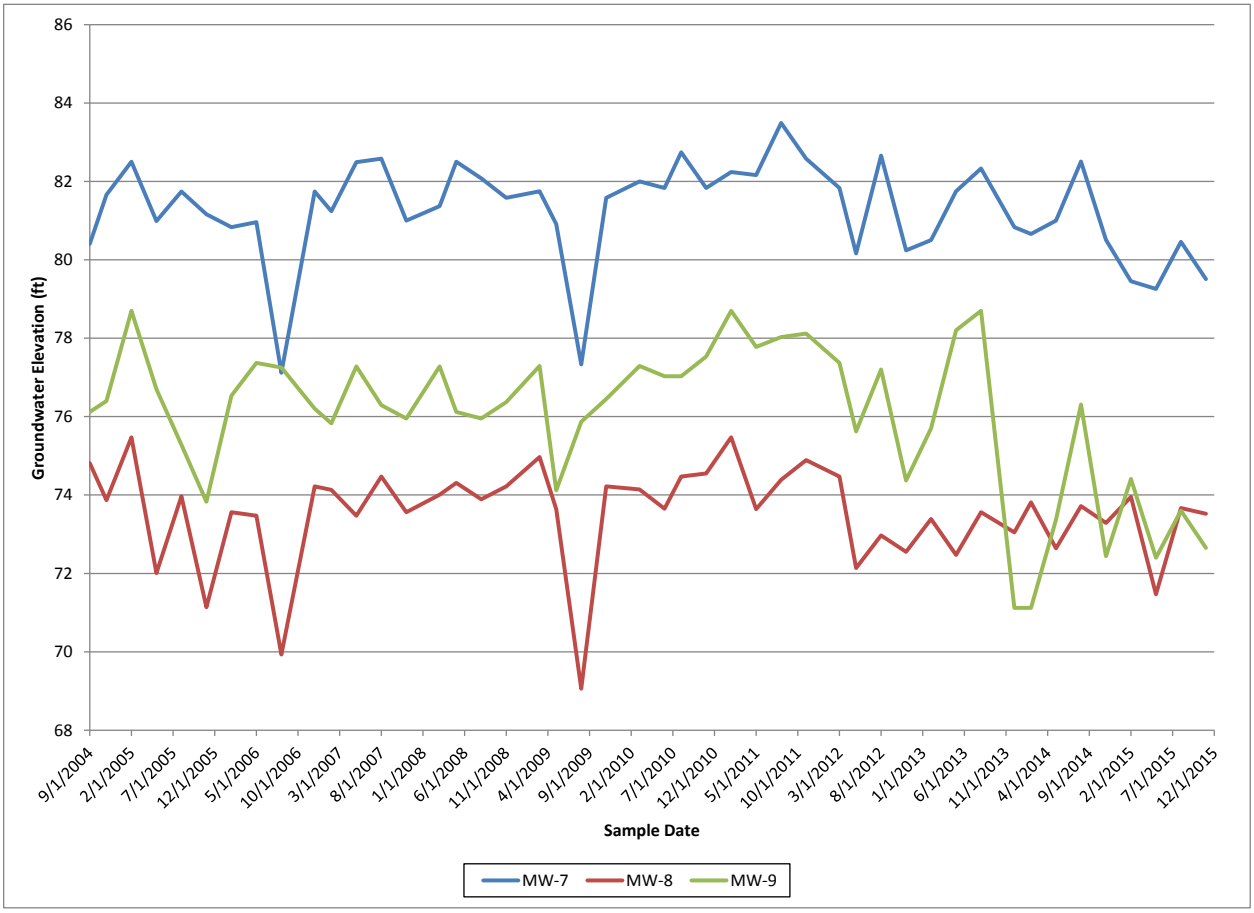

Figure 5. Groundwater elevations in wells MW-7, MW-8, and MW-9.

Manganese in Central Valley Aquifers

The California Rice Commission retained CH2MHILL and Plantierra to prepare the *Rice-Specific Groundwater Assessment Report* on behalf of the Central Valley Regional Water Quality Control Board (CH2MHILL 2013). Manganese was among the many constituents included in this report. The report found that "*A USGS analysis of the redox conditions of the shallow groundwater under the rice fields indicated that almost all of the wells reported anoxic or reducing conditions in the groundwater…"* The report also stated that manganese is a naturally occurring trace element and is not applied in rice farming. Manganese concentrations in shallow groundwater beneath rice fields were found well above the MCL_{SEC} and values as high as 1.1 mg/L were observed.

It is clear that even rice farming has the potential to cause elevated levels of manganese in shallow groundwater. Rice is a common crop in the area surrounding the Morning Star site (see Appendix B). In addition, rice was farmed on field MS1 in 2014, which may have impacted manganese concentrations seen in MW-9. Elevated levels of manganese in shallow groundwater are not necessarily attributable to BOD loading on the LAAs and may be consistent with other findings of elevated manganese concentrations is Central Valley shallow groundwater.

Conclusions

Manganese concentrations in groundwater monitoring wells MW-7, MW-8, and MW-9 have increased most notably since August 2013. The source of observed increases in manganese concentrations in these groundwater wells is complex and could be attributed to causes unrelated to the LAAs. The CDO attributes elevated levels of manganese in the groundwater to BOD overloading in the LAAs; however, recent BOD overloading occurred primarily in 2015 (only 17 irrigation cycles out of 100 and the average loading approximately 50 lb/acre/day), while increased levels of manganese concentrations in groundwater was observed in each well beginning in 2013.

Evidence of drought related manganese concentration increases exists, in which aquifer volume has been significantly diminished, leaving less groundwater volume available for dilution of manganese that solubilizes into the groundwater. Groundwater elevations have decreased in recent years which contribute to the diminished aquifer volume.

In addition, research for the Central Valley Water Board has identified anoxic or reducing conditions in the groundwater below rice fields and the manganese concentrations can be elevated associated to the rice farming. Rice farming is ubiquitous in and around Morning Star's site. Increased levels of manganese are likely influenced by the rice farming activities near Morning Star.

The increased levels of manganese concentrations in groundwater monitoring wells MW-7, MW-8, and MW-9 is impacted by factors other than BOD loading. In order to return to compliance with the 2013 WDRs, it is appropriate to return to compliance with the BOD loading limitation for the LAAs, through which manganese mobilization from the discharge will be minimized. However, the manganese trends in groundwater suggest other factors, such as drought and nearby rice farming, will continue to influence manganese concentrations at the Morning Star site. It is further recommended that MW-9 compliance be determined similarly to MW-7 and MW-8.

References

CH2MHILL, Plantierra, July 2013. *Rice-Specific Groundwater Assessment Report.* Prepared for the Central Valley Regional Water Quality Control Board. On behalf of the California Rice Commission.

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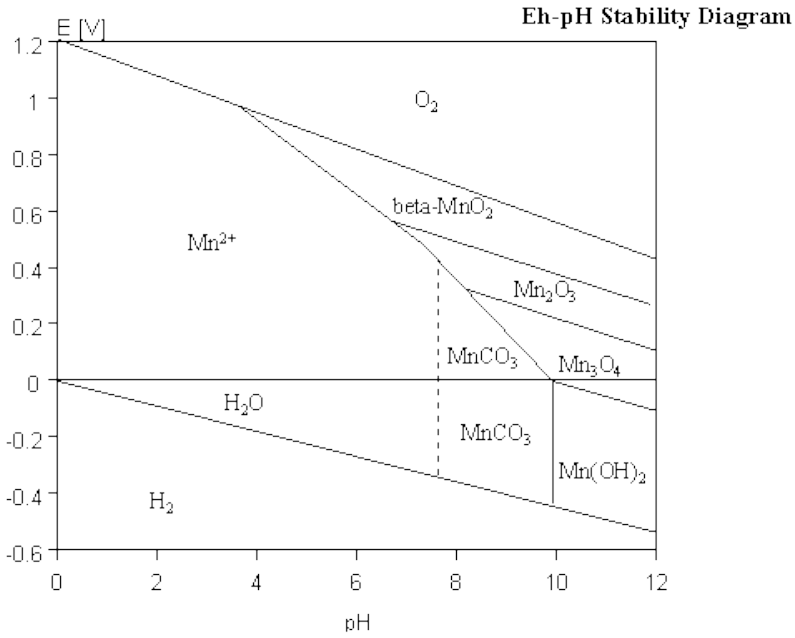
Inglett, P.W., Reddy, K.R., Corstanje, R. 2005. *Anaerobic Soils*. In Encyclopedia of Soils in the Environment. D. Hillel (ed). Academic Press. Pp. 71-78.

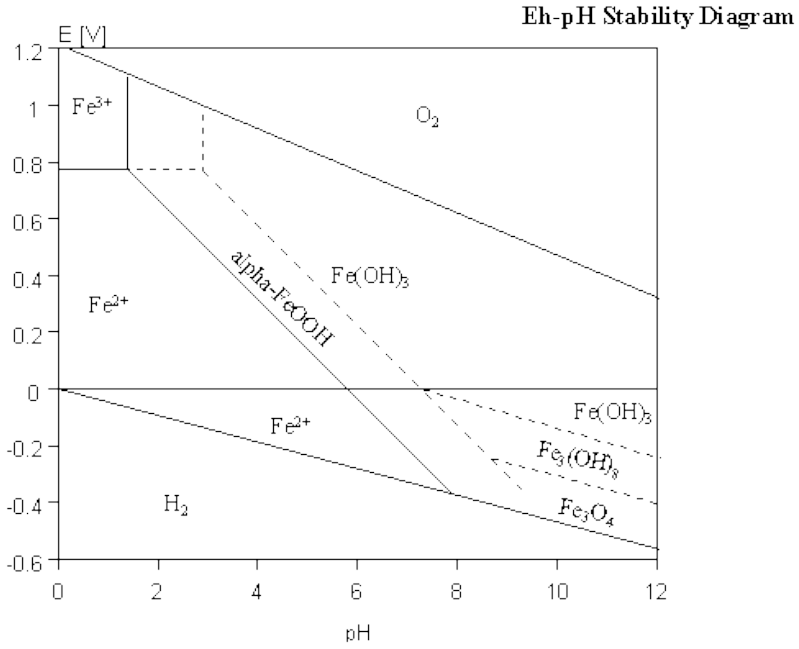
Reinhard, H.A., 2014. *Groundwater Limitations Compliance Assessment Plan*. Prepared for Morning Star Packing Company, L.P.

Appendix A

Eh-pH Stability Diagram for Manganese and Iron



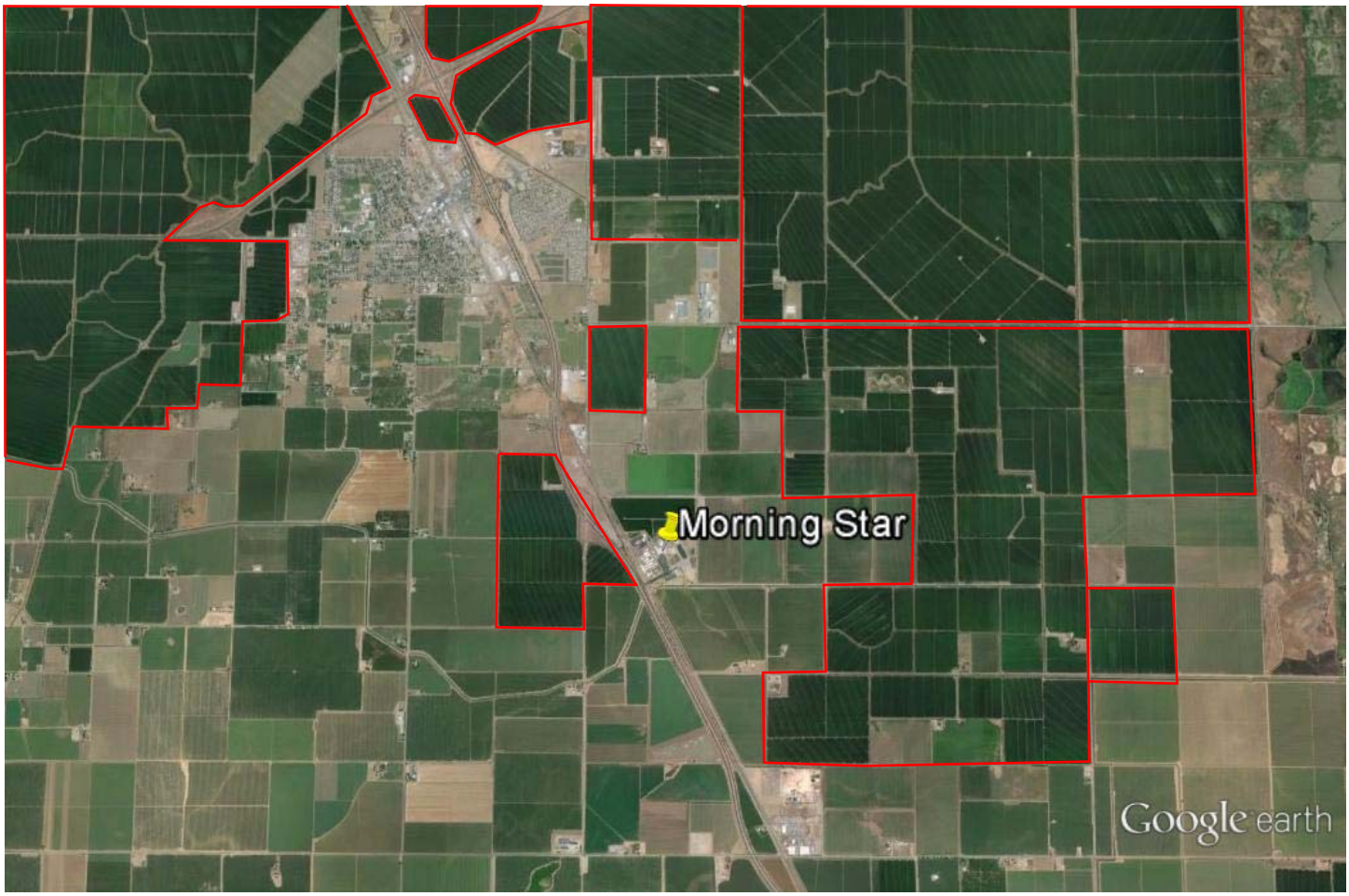
Manganese



Iron

Appendix B

Map of Morning Star site and Surrounding Rice Fields



Google earth

miles 3
km 6

Rice fields are outlined in red.

Imagery Date: 7/10/2013