Notes from Final_OWP-CWP_HydroCSM_AnnotatedBib.doc

Monitoring of dioxins/furans, PCBs, metals, perchlorate and haloacetic acids (HAA) in 19 surface water samples collected from PRIs 5-7 during winter 2014 and Spring 2015 found the following surface water quality characteristics:

- Chemical detections were generally highest in the CWP.
- Detections were higher in the northwest CWP samples than southeast CWP samples.
- Detections were markedly lower in the OWP, Star Pond overflow ditch, and the SVDD.
- Dioxins/furans were consistently detected in surface samples from PRI 1,4,5,6, and 8 but rarely detected in PRI 7 or 14.
- Octachlorodibenzofuran (OCDF) was detected at the highest concentrations of any dioxin/furan congeners.
- PCBs were detected in all surface water samples, with decachlorobiphenyl being the dominant homolog in PRI 1,4,5,6 and 8, and monochlorobiphenyls and dichlorobiphenyls being the dominant homolog groups in PRI 7.
- The highest chlorinated VOC detections within the ponds were typically associated with samples collected near the Main Ditch discharge point in the SE CWP, Star Pond overflow ditch, and OWP sample adjacent to NW CWP.
- Haloacetic acids (HAAs) were detected in nearly all surface water samples.
- Metals measured in SE CWP and SVDD were markedly lower (several orders of magnitude) relative to detections in other CWP samples except Ca, Co, and Mn.

Monitoring of 63 wells/piezometers in Nov 2015, which followed monitoring of 30 piezometers earlier in January-March, 2015, found the following hydraulic properties:

- The shallow aquifer appears to be hydraulically connected to the CWP (well and surface water levels were similar).
- An upward vertical gradient is prevalent in the shallow aquifer with a range of 0.05 ft/ft (downward) to -0.45 ft/ft (upward).
- The CWP likely contains a mixture of wastewater and groundwater.
- Laterally, the shallow aquifer generally flows towards the GSL.
- The lateral hydraulic gradients ranged from 0.0005 to 0.003 ft /ft, far smaller than the vertical gradients.
- Groundwater mounding was observed below the ditches and CWP. Downward vertical gradients were observed in areas where mounding was apparent.
- The Main Ditch appears to seep into the shallow aquifer.
- The hydraulic conductivity of the oolitic sand ranged from 4.9E-3 to 1.1E-2 cm/s, which is 20 to 50 times greater than the hydraulic conductivity of the silty sand, which ranged from 2.5E-4 to 2.7E-4 cm/s .

Collection of groundwater 20 samples from PRIs 5-7 during winter 2014 and spring 2015 found the following groundwater quality characteristics:

- The southeast portion of the CWP (PRI 5) mainly had major ion signatures (Stiff diagrams) similar to those of US Magnesium wastewater in Main Ditch, and the Stiff diagram for a well screened over a deeper interval (deeper groundwater) had an appreciably different Stiff profile relative to shallower wells.
- The northwest portion of the CWP (PRI 6) had major ion signatures representative of US Magnesium process wastewater.
- Concentrations of dioxins/furans were generally orders of magnitude lower relative to surface water, with OCDF being detected at the highest concentrations.
- PCBs were relatively low in groundwater (maximum detection of 0.038 μg/L).
- In general, groundwater tends to have higher proportions of lesser chlorinated homolog groups (monochlorobiphenyl and dichlorobiphenyl) than surface water.
- Concentrations of metals were markedly lower in groundwater than surface waters except Co, Mg, Mn, K, and Na.
- Hexachlorobenzene (HCB), the only SVOC routinely detected in CWP surface water samples, was not detected in any groundwater samples.
- Numerous VOCs were reported in groundwater samples with concentrations higher than those in surface water, but within the same order of magnitude.
- Trichloroethene (TCE) was detected in groundwater samples from 14 of the 17 wells at a maximum concentration of 26 μg/L (the MCL for TCE in drinking water is 5 μg/L). TCE was not detected in the majority of surface water samples (only in 3 out of 19 surface water samples collected from PRIs 5-7 had TCE detections). **WPJ notes that this raises the possibility of a legacy spill of dense non-aqueous phase chlorinated solvent (DNAPL)**.
- Total dissolved solids (TDS) was higher in groundwater than surface water, but within the same order of magnitude, consistent with USGS classification of briny water.
- HAAs were detected in 50% of groundwater samples, with highest concentrations observed along the downgradient edge of the northwest portion of the CWP.

The above observations identified the following potential tracers of plant wastewater transport into groundwater:

- Mn, since detections exceeded 10,000 μg/L near the downgradient edge of the CWP, the western edge of the OWP, the outflow ditch, the and Star Pond.
- Ni since wastewater from ditches, CWPs, and/or the gypsum pile appears to contribute to Ni concentrations in groundwater.
- Bromoform and Chloroform (VOCs) since concentrations of these VOCs are higher in groundwater than surface water and occurred near wastewater discharges from the Main Ditch into the CWP. Their concentrations decrease with increased residence time in the CWP, indicating possible volatilization from the CWP.
- Perchlorate, since many concentrations were below the quantitation limit, but above the detection limit. Concentrations were higher in upgradient (of the CWP) wells than in downgradient wells. Wastewater in the CWP had higher perchlorate concentrations than groundwater, therefore the CWP appears to contribute perchlorate to groundwater.

- Trichloroacetic Acid (TCAA) since the detected concentrations in the CWP were higher than those in groundwater, indicating that the CWP contributes TCAA to groundwater. Detected concentrations in upgradient wells were lower than detected concentrations in wells downgradient of the CWP.
- TDS since TDS data suggests the presence of a TDS plume in groundwater originating at the Star Pond.

Notes from the US Magnesium GWDP Hydrogeologic Report December 15, 2017, archived as 1 – Hydrogeologic Report.

> In section 3.2.1.5 (pages 15-16) the report states:
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> Organic constituents have been detected at varying concentrations in groundwater at the site including dioxins/furans, polychlorinated biphenyls (PCBs), semi-volatile organic compounds (SVOCs) and volatile organic compounds (VOCs) (ERM, 2016). During the 2017 field investigation, the only Upper Aquifer Zone wells sampled and analyzed for organics were MW-22A and PZ-13. These data are summarized in detail in a preliminary report which also includes an evaluation of organic water chemistry for the wells screened in the Lower Aquifer Zone (ERM, 2017).
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> Dioxins/furans have been detected at groundwater and surface water sampling locations throughout the site from the plant area (monitoring well MW-4A) to the western edge of the OWP (piezometer PZ-6). Dioxin/furans were not detected in PZ-13 and MW-22A during the July 2017 sampling event (ERM, 2017).
>
> PCBs were routinely detected at low concentrations in groundwater samples in the CWP/OWP areas. With the exception of monochlorobiphenyls, concentrations of PCB were generally one or more orders of magnitude lower than surface water measurements (ERM, 2016). PCBs were detected in low concentrations in PZ-13 and MW-22A during the July 2017 sampling event (ERM, 2017).
>
> SVOCs were detected at groundwater sampling locations at the site, notably bis(2-ethylhexyl)phthalate, 2-methylnaphthalene, and naphthalene were detected in more than half of groundwater samples collected and analyzed during the 2014/2015 sampling events. VOCs detected in groundwater include bromoform, chloroform, acetone, 2-butanone, bromodichloromethane and dibromochloromethane. In general, concentrations of SVOCs and VOCs were higher and more prevalent in groundwater samples than in surface water samples; however, they were not as widespread as the dioxin/furans described above, with no VOC detection in PZ-6, located in the northwest corner of the OWP (ERM, 2016). SVOCs were generally not detected or were reported at trace concentrations (an estimated value between the laboratory reporting limit and the method detection limit) in samples collected during the July 2017 sampling effort with the exception of acetophenone which was detected in MW-22A (ERM, 2017).
>
> Groundwater samples were collected during June/July, August, September and November 2017 at three new wells screened in the Lower Aquifer Zone (MW-21, MW-22B and MW-23) (Figure 3-1a). The first round of sampling at these wells included sampling for inorganic constituents in

> June 2017 and organic constituents in July 2017, which was performed and analyzed by ERM as part of the Remedial Investigation (RI) Phase IA Study (ERM, 2017). Water quality in the Lower Aquifer Zone is notably different than impacted groundwater in the Upper Shallow Aquifer Zone which suggests the Lower Aquifer Zone is not hydraulically connected to the impacted waters of the overlying Upper Aquifer Zone.
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Notes from the US Magnesium Groundwater Discharge Permit Application Interim Compliance Monitoring Plan (2018) archived as GroundwaterDischargePermit2018-Appendix B.pdf

> Organic wastewater constituents (bromodichloromethane, bromoform, chloroform, dibromochloromethane, trichloroacetic acid) were selected as tracers of wastewater on the basis of their:
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> - Relatively high solubility in water (>1,000 mg/L) and relatively low octanol/water partition coefficients (log $K_{ow}$) (<4), which values indicate that they are likely to remain in solution and not sorb to the aquifer matrix during subsurface migration (Table 4-1 of cited report).
> - Distinct concentrations in wastewater versus unimpacted groundwater, as shown in Figure 3 of cited report (Figure 14). These organic parameters have not been detected in downgradient surface water and groundwater locations (PRI-7-001, MW-10, PZ-6), and they have not been detected in wells completed below the deeper silty clay unit (MW-21, MW-22B, MW-23, MW-9, and MW-10); however, they have been detected in the evaporation pond waters and some shallow groundwater monitoring wells (i.e., PRI7-007, PRI5-002, PZ-8, PZ-12).
> - Laboratory analyses of these proposed organic wastewater tracers are not affected by site water matrix (high TDS, low pH). (Analyses of major ions and metals analyses are affected by high TDS and low pH).