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Memo

To:	John Chapman, Daryl Hockley	**Date:**	March 25, 2010
cc:		**From:**	Christina James
Subject:	Suitability of Grum Pit Lake for Sludge Disposal	**Project #:**	1CY001.035

Options for the deposition of waste treatment plant (WTP) sludge into Grum pit lake are currently under consideration. Physio-chemical conditions at depth may dictate the suitability of the pit lake for storage of WTP sludge. Several possible mechanisms for contaminant release were evaluated based on results of the 2009 field studies. These mechanisms included:

- Degradation of stratification,
- Re-suspension of sediments, and,
- Reductive dissolution of ferric hydroxides.

This memo reviews each of these processes in the context of this project.

1 Available Data

Data used in this analysis was taken from the 2009 annual monitoring program. Water chemistry from discrete samples and continuous profiles of conductivity and temperature were considered acceptable for analysis.

The most recent profile of dissolved oxygen (DO) was taken in April 2009 using a YSI 6600 multimeter. DO measurements were taken continuously in the Grum pit lake while the multimeter descended through the water column at rate of approximately 6 m/s. Typically, a DO meter takes approximately 60 seconds to equilibrate in order to provide accurate measurements. The time stamp for DO measurements shows that the multimeter was not allowed to equilibrate at discrete depths. At the profile's maximum depth of 45 m, the DO sensor was likely reading concentration from ~ 6 m higher in the water column (*i.e.*, 40 m). Therefore, no accurate DO measurements are available for Grum pit lake below 40 m to the pit lake bottom at a depth of 65 m.

Redox potential was not measured as part of the pit lake profiling in summer 2009. Instead, discrete water samples were collected on September 9, 2009 and sent to Maxxam Analytics in Vancouver, BC for analysis on September 15, 2009. The redox potential of a water sample changes very quickly – on the order of minutes – and therefore the results produced by measurement days after the samples were collected are considered unreliable.

2 Potential Mechanisms of Contaminant Release

2.1 Degradation of Stratification

Thermal stratification is established annually in Grum pit lake, creating two layers. The upper layer has proven to be suitable for plankton blooms promoted by the annual fertilization program. The lower layer has higher concentrations of dissolved solids and, to date, little or no biological activity has been observed (through chlorophyll *a* measurement) in the lower layer.

If a stream of WTP sludge were allowed to flow into a pit-lake, it may have an important impact on the lake's stratification. The impact may differ depending on the form of the inflow. As either a waterfall or cascade down the pit wall, the stream could potentially plunge through the upper layer and mix with water from the lower layer before losing momentum. Sub-aqueous deposition of the sludge at a depth greater than the thermocline (~5 m in August 2009) may be possible without interfering with the stratification. However, the upward energy introduced by the inflow would need to be compared to the energy required to degrade the stratification to determine if this deposition strategy would cause stratification degradation. This would highly depend on the engineering of the inflow and the energy dissipated before entering the lake.

Degradation of the Grum pit lake stratification may affect the suitability of the pit lake's upper layer for plankton growth. In particular, temperature and DO concentrations would likely change in the upper layer if mixing between upper and lower layers were to occur. To determine the extent of the potential change of these characteristics, a simple mixing calculation was completed. Table 1 summarizes the temperature and DO concentrations of each the upper and lower layers, as well as the concentrations of these parameters under a hypothetical fully mixed scenario. Data for the upper and lower layers are based on temperature, DO and bathymetry data collected in 2009.

Under a fully mixed scenario, temperature in the photic zone (where plankton would be exposed to sufficient light to grow) could be reduced to < 10 °C in August, and would likely be cooler throughout the summer. Cooler temperature will likely not eliminate plankton grown entirely. Instead, the rate of growth or the duration of the growing season may simply be reduced. This depends on the type of plankton present in Grum pit lake, and their sensitively to temperature.

A similar argument can be made for DO. DO may be reduced from saturation (~10 mg/L) to approximately 8 mg/L. However, this does not create anoxic conditions and plankton would likely continue to grow.

A reduced rate of growth or length of growing season for plankton would likely result in a reduction of zinc load removed from the Grum pit lake.

Table 1 Temperature and Dissolved Oxygen for Grum Lake Upper and Lower Layers (2009) Compared to the Fully Mixed Scenario

Parameter	Upper Layer	Lower Layer	Fully Mixed
Approximate Volume	$1x10^6$ m3	$3x10^6$ m3	$4x10^6$ m3
Temperature	14 °C (August 2009)	6 °C (August 2009)	8 °C (estimated)
Dissolved Oxygen	10 mg/L (April 2009)	7.5 mg/L (April 2009)	8.1 mg/L (estimated)

2.2 Sediment Re-Suspension

Sub-aqueous deposition may provide sufficient energy along the pit lake bottom to re-suspend deposited sediments. If sediments were re-suspended, both sludge solids and porewater of potentially poor water quality could be mixed upward, releasing contaminants to the water column.

However, as described in Section 2.1, the design of the inflow could dissipate the inflow's energy and significantly reduce or eliminate sediment re-suspension.

2.3 Reductive Dissolution

2.3.1 Current Chemistry

The sludge from the Faro WTP is composed of gypsum, ferric hydroxides and zinc hydroxides. During the process of precipitation, other metals will adsorb to the surfaces of ferric and zinc hydroxides.

Reducing conditions may be created at depth in Grum pit lake through oxygen consumption of decomposing plankton. If reductive conditions were present in Grum pit lake, iron (III) present in the ferric hydroxides could be expected to reduce to iron (II) (Figure 1). The solubility of iron (II) is much higher than iron (III) and, under reducing conditions, iron and any other metals adsorbed to the ferric hydroxide surface could be remobilized in the water column. Zinc hydroxides are not sensitive to reducing conditions – zinc hydroxides will generally remain stable provided pH remains stable (Figure 1).

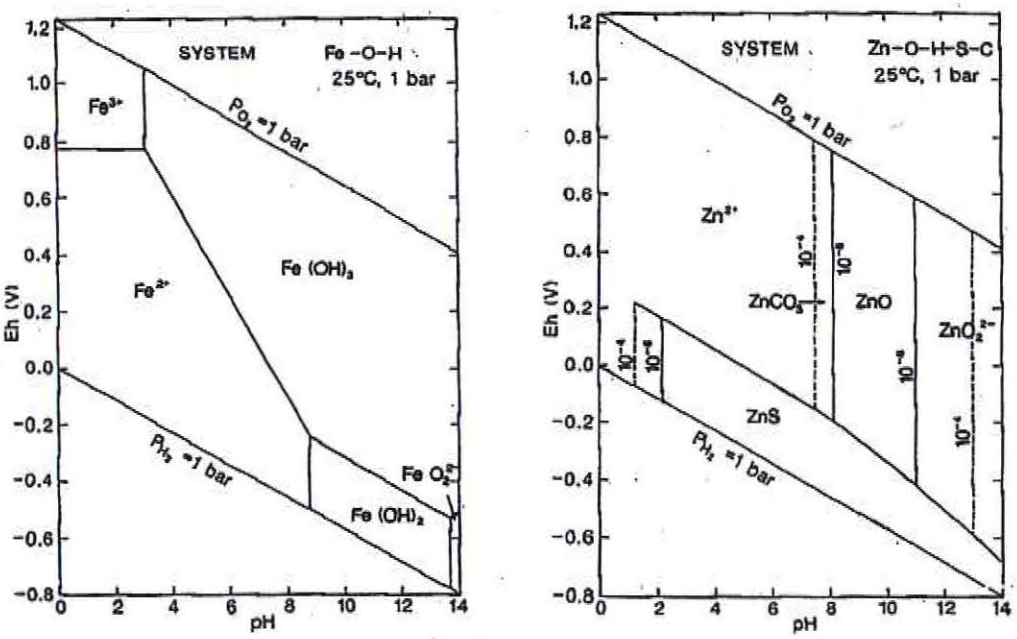

Figure 1 Phase Diagrams for Iron and Zinc

No direct measurements of the redox conditions are available for water at depth in Grum pit lake. Between the thermocline at 5m and approximately 40 m, DO concentrations ranged between 7.5 and 8 mg/L in April 2009. These measurements indicate that DO concentrations were below saturation, but not depleted, suggesting that reducing conditions were not present.

As an indication of whether reducing conditions could be present, current concentrations of dissolved iron at depth in Grum pit lake were examined (Figure 2). Dissolved iron concentrations are available in Grum pit lake to a depth of 50m, at a greater depth than available DO measurements.

Dissolved iron concentrations were generally elevated at the pit lake surface, decreasing in the mid-depth range and then increasing slightly at 50 m in August and September 2009. The increase of dissolved iron concentrations at depth may be an indication of a slight decrease in redox. However, the increase in iron concentration was not present in July, indicating that decreased redox conditions could be a seasonal effect. Also, if highly reducing conditions were present, iron concentrations would be expected to be higher.

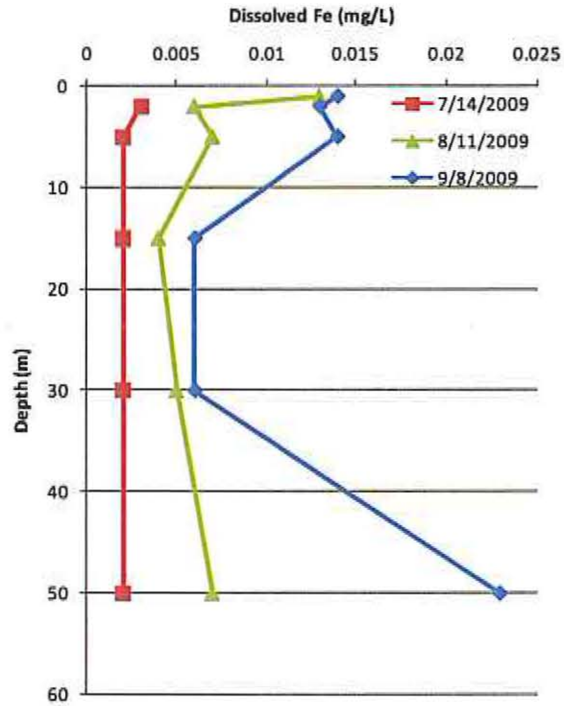

Figure 2 Dissolved Iron with Depth, Grum Lake, 2009

If through deposition, WTP sludge were to interact with water at depth with reducing conditions, reductive dissolution of ferric hydroxides could release iron and other metals to the water column.

Given the neutral pH and generally oxic conditions of the bulk of water in Grum pit, Fe (II) associated with WTP sludge in the pit lake bottom would likely be oxidized back to Fe (III) and re-precipitate if it were mixed upwards in the water column. Based on the conditions observed in 2009, this cycle would like occur relatively close to the bottom of the pit lake, confining mobile metals at depth.

2.3.2 Future Chemistry

If, over time, an accumulation of decomposing plankton on the pit lake floor were to result in an increase in oxygen demand, more of the Grum lake water column could become seasonally reducing. Should this occur, Fe (II) associated with WTP sludge may not mix with oxygenated waters of neutral pH and therefore not oxidize to Fe (III). Instead, Fe (II) and associated metals may remain in solution, contaminating Grum pit lake waters.

In 2009, the Grum pit lake turned over, providing complete mixing of the water column. Provided annual turnover continues, oxic conditions will likely be sustained in the bulk of Grum pit lake water in the long term. Under these conditions, Fe (II) and associated metals would likely remain confined at depth, isolated from surface water and the surrounding environment.

The dominance of one of these processes (development of reducing conditions at depth vs. turnover of the water column) would dictate the chemical environment in which WTP sludge would be deposited.

3 Conclusions

Sludge deposition could have physical effects on the functioning of the Grum pit treatment system. The deposition energy could impair stratification and affect the length of the growth season for plankton in Grum pit lake, thereby reducing the amount of zinc removed from surface waters. Energy introduced into the pit lake (and therefore the extent of stratification degradation) could be minimized through sub-aqueous deposition and an energy dissipating design for the discharge.

Similarly, the physical remobilization of bottom sediments by sludge deposition could be minimized through careful design of the deposition system.

Ferric hydroxide components of the sludge will dissolve in a reducing environment, mobilizing iron and any additional metals that were adsorbed to the hydroxide surface. Dissolved iron concentrations measured at depth in Grum pit lake indicate the presence of slightly reducing conditions, but the data are not definitive.

Future accumulation of plankton residues may generate stronger reducing conditions. Even in that case, there are plausible mechanisms that could prevent degradation of the pit lake surface water, but these would need to be examined more fully before they could be relied upon.

4 Recommendations

To further determine the presence of reducing conditions in Grum pit lake, *in-situ* DO and redox potential profiles should be collected during the 2010 field program. Profiles should be taken to the maximum depth of the Grum pit lake (~65 m) to characterize the conditions in which WTP sludge would be deposited. It is important that the response time of each sensor be considered when the measurements are taken. If the instrument is not allowed to equilibrate, the measurements will not be accurate.

Sediment samples could be used to assess the development of reducing conditions in the pit lake sediments. The presence of hydrogen sulphide in the sediment porewater would indicate reducing conditions have developed. Samples could be collected using an open-barrelled gravity corer. Samples would need to be sealed at the surface and handled in an anoxic environment to prevent oxidation of the sediments prior to analysis.

Iron speciation may give the most robust measure of whether reducing conditions are present at depth in Grum pit. At the low concentrations of iron present in the pit lake, a field program for iron speciation would be difficult. The possibility of a laboratory based iron speciation program could be investigated to definitively determine the redox conditions of Grum pit lake water.