

**GEO-SPATIAL MAPPING OF IRON (Fe) AND MANGANESE (Mn)
PRESENT IN GROUNDWATER OF CLARK, PHILIPPINES**

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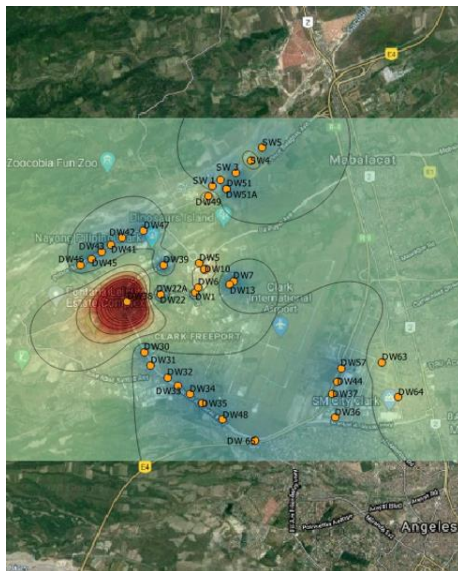
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Graphical abstract



Abstract

The study covers a comprehensive analysis of Fe and Mn to characterize their distribution and occurrence within the Clark Freeport Zone. 3-year groundwater samples taken from 39 wells/boreholes scattered throughout the study area. Fe was most frequently detected with concentrations near the limits of Philippine National Standards for Drinking Water (PNSDW). 0.42% of the 958 studied samples for Fe had concentration greater than the 1mg/L limit. As for Mn, none of the 909 samples for Mn had concentration greater than the PNSDW. Of those wells that have shown presence higher than the minimum detection level (MDL), 5 have been installed with individual filtration system (DMI-65) to capture Fe and Mn. No correlation has been found between the two parameters. As for seasonality, there is an obvious spike in Fe for all wells during the months of July, September, and October. Mn on the other hand manifested a spike in July for the shallow wells. The QGIS3 software was also used to develop a spatial map and report the distribution presence. From the generated maps, Fe and Mn gradually increase in concentration going north to northeastern directions of CFZ. The produced map can be key in raising awareness of the public and fellow water concessionaires with regards to the possible extent of underground Fe and Mn presence. Information generated here will be valuable as resources, and engineering controls can be applied to give priority to the low probability affected areas.

Keywords: Groundwater, Iron, Manganese, PNSDW, QGIS, Spatial mapping

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1.0 INTRODUCTION

Over the last decade, Clark Freeport Zone (CFZ) has faced an increase in water demand due to the upsurge of infrastructure projects. This was further amplified by the “Build, build, build” cry of the Duterte Administration. It has led to increased urbanization which in turn triggered a rapid growth in its working population. For now, the sole source of freshwater for the area is a groundwater bore field. In some of these wells, concentrations of Fe and/or Mn pose problems as their concentrations are either close or beyond the limits of the Philippine National Standards for Drinking Water (PNSDW) [1].

Therefore, better characterization of the distribution and occurrence of dissolved iron (Fe) and manganese (Mn) is needed to help assess future sustainability and the implications for drinking water and other water uses.

A characteristic of Fe and Mn that sets them apart from other potential groundwater elements is that they naturally occur in soils, rocks, and minerals [2]. In aquifers, groundwater contamination start when water dissolves the minerals (including Fe and Mn). Groundwater with high iron and/or manganese will initially look colorless but will develop orange brown (Fe) or black (Mn) stains when exposed to oxygen [3]. From the domestic consumer’s standpoint, Fe and Mn are

objectionable since they destroy brightness and impart undesirable color to laundered goods and appreciably impair the taste.

Levels of dissolved Fe and Mn in groundwater may vary seasonally for a given area. This is usually associated with water redox conditions, where oxygenated water from the ground level enter the aquifer during the high recharge period [4,5].

The current manuscript focused on 39 working deepwells of Clark Water Corporation (CWC) scattered throughout the Freeport area. Its main objectives were to investigate concentrations of both Fe and Mn in groundwater of Clark, and to correlate their seasonal form of occurrence. Results also include spatial patterns of these elements and their transferability to unsampled areas.

Geographical Information Systems (GIS) mapping technologies have created a better outlook of the contaminants present in groundwater sources [6]. To date, there is limited publicly available research in development of geospatial maps and distribution of Fe and Mn in Clark. The aims of the study were to tabulate Fe and Mn levels within the study area and create a spatial map based on the recorded groundwater quality data. The research aims:

- To collect 3-year internal sampling results for Fe and Mn contamination for CWC wells
- To plot coordinates of CWC wells and to tabulate gathered results and input findings into a GIS program
- To generate geospatial maps over the 3-year period to show seasonality and report the distribution of Fe and Mn within the study area.

The geo-spatial map generated in this study offers an overall insight into the groundwater quality of the CFZ. The generated map shall raise the public's awareness with the problem of underground contamination [7,8]. Spatial mapping can also aide administrators and planners as controls can be applied to give development priority to low contaminated areas. The paper may also serve as a guide for nearby concessionaires/water suppliers in search for an optimal location for their upcoming water sources.

This study is limited to the information provided (either visual or auditory) by CWC's Laboratory Services. The data used were collected during the last 3 years (January 2019 to June 2021) from a combination of shallow and deep wells sampled by a 3rd party laboratory employed by CWC. The researcher chose to select the first sample taken during the month as there were multiple sampling events for each well. All samples were of raw water quality which means it haven't undergone any form of treatment. Only data for Fe and Mn was extracted while other parameters were excluded.

2.0 METHODOLOGY

The study was conducted at CFZ using the data gathered from CWC wells. As a prelude, the existing groundwater production well network has been developed progressively since 1948. Older shallow wells were installed near the northern edge of the main historically developed area of Clark Air Base (represented by red dots). These wells were drilled prior to 1995 and records indicate that these wells are relatively shallow, with median depth to the base of the screen being

approximately 60 m only. These are the DW's 1, 6, 7, 10,13, 22 and DW 22A (constructed by CWC) [9]. The yellow dots represent the DW 30 series of wells. These wells are screened to about 100 meter and deeper and supply water to the Bicentennial Hill Tanks. On the other hand, 40 Series wells represented by blue dots and numbered 41, 42, 43, 45, 46, 47, 49, (40-series) 51, 51A, SW1, SW2, SW3, SW4, SW5 (SW-Series). Finally, the IE5 wells (DW65,36,66,37,44,57,63 and 64) are direct pumping wells represented by the green dots. Both 30, 40 and IE5 series of wells have depths of more than 100 meters.

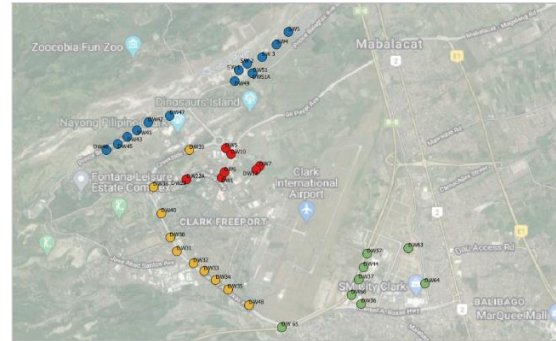


Figure 1: CFZ location of wells

A simple input-process-output model (Figure 2) was used in the study. It anchors on the gathered data and processing in the free and opensource QGIS software [10].

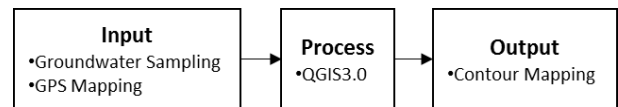


Figure 2: Paradigm of the study

Sampling results were collected from 39 deepwell locations: a combination of shallow wells (ranging for to 60mtrs) and deep wells (>60 to 200mtrs deep) [11]. These samples were collected and tested by CRL Environmental Corporation (CRL). CRL is a third party laboratory accredited by the Department of Environment and Natural Resources – Environmental Management Bureau (DENR-EMB) and Department of Health (DOH) [12,13,14,15,16,17,18].

Distribution of groundwater contaminants is primarily controlled by geochemical heterogeneity [19]. To estimate the contamination exposure within a given area, spatial interpolation techniques were used to provide a representaiton of their geogenic distribution [20,21,22]. Variations of Fe and Mn present in the groundwater of Clark were drawn using QGIS3. The spatial interpolation built within QGIS was utilized to measure the variability of the water quality dataset.

Interpolation that cover data such as mineral content, population etc. usually utilize the Inverse Distance Weighted (IDW) method due to its simplicity [23,24,25]. The IDW method presumes that each point away from the source has impact that decreases with distance. It gives more bearing points nearest, and less bearing to those farther from the sampled area.

The resultant output was used for the illustration of the magnitude and the distribution of the contaminant across the study area.

3.0 RESULTS AND DISCUSSION

3,183 raw water samples were collected from the 39 deepwells operated by CWC. Among these, only 2,131 samples (first sample taken for the month) were used for plotting in the GIS program.

The sample results ranged from mostly quantified concentrations to less than the laboratory reporting level (<LRL). For this manuscript, values reported as quantified concentrations were used unchanged and those values reported as below the reporting level were adjusted to the minimum detection level (MDL).

Numbers above were used to generate the geospatial distribution maps representing the overall Fe and Mn presence using an IDW approach. Similar months for each year were listed in the same row for better appreciation of seasonality. Renders were color coded in 20 intervals to show contaminant fluctuations between the wells. Non detection (0mg/L) will show up as blue renders and samples nearing maximum allowable limit (MAL) will return with an orange to red hue. Contour lines with 0.1mg/L intervals were also included in the rasters to show Fe variability to other locations. Figure 3 show the Fe generated rasters for January in years 2019, 2020 and 2021. The January average Fe concentration for all sites is 0.30mg/L.

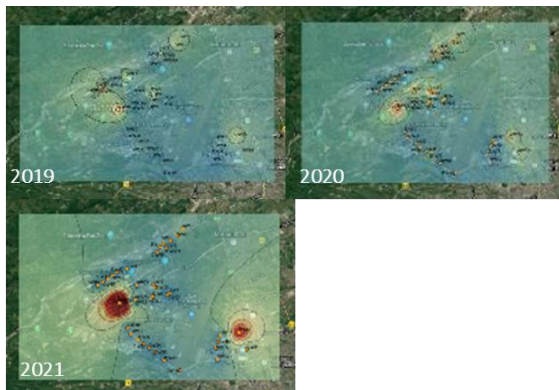


Figure 3: Fe raster for January 2019, 2020, and 2021

Meanwhile, Figure 4 show the generated rasters for February. The average Fe concentration for the month is also 0.30mg/L.

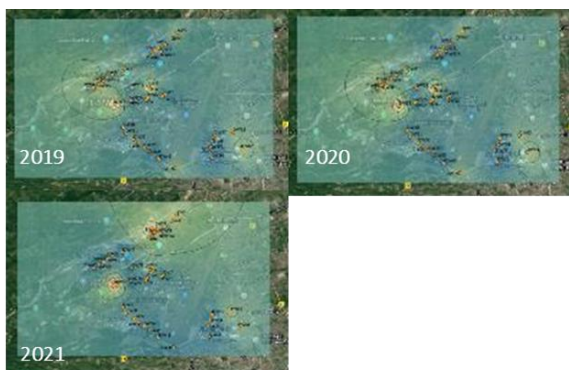


Figure 4: Fe raster for February 2019,2020, and 2021

Figure 5 show the generated rasters for March with an average of 0.26mg/L.

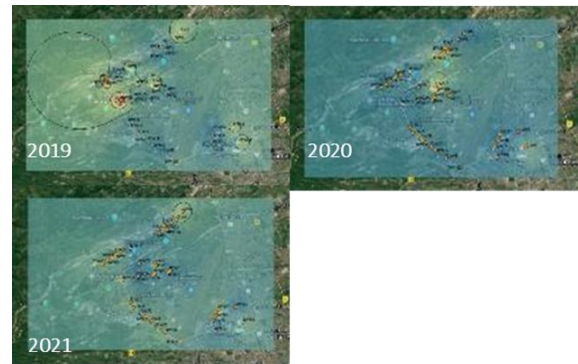


Figure 5: Fe raster for March 2019,2020, and 2021

For April, Fe averaged 0.24mg/L for all sites (refer to Figure 6 for the generated rasters for April).

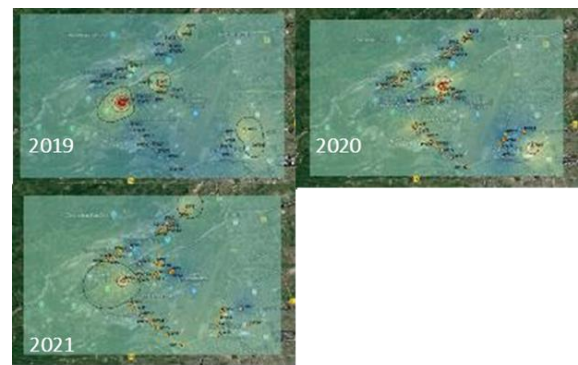


Figure 6: Fe raster for April 2019,2020, and 2021

Similar Fe concentration 0.24mg/L were recorded for the months of May (Figure 7).

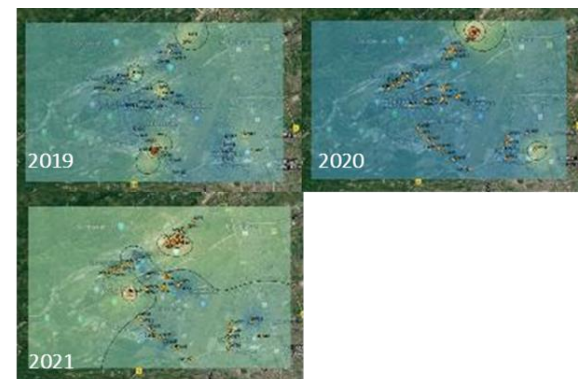


Figure 7: Fe raster for May 2019,2020, and 2021

Figure 8 show the generated Fe rasters for June with an average of 0.26mg/L. It is during this month that elevated values of Fe start to manifest.

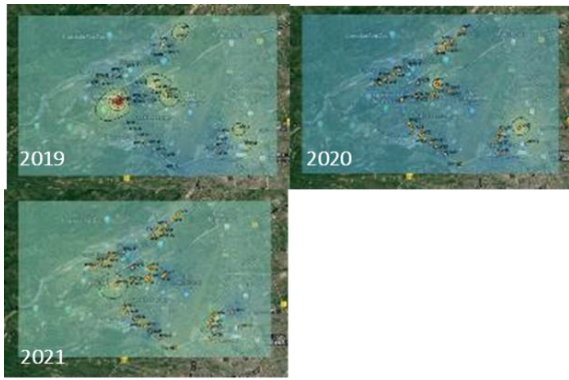


Figure 8: Fe raster for June 2019,2020, and 2021

The month of July registered the highest average Fe concentration of 0.40mg/L (refer to Figure 9). Majority of the wells with the exemption of DWs 1,5,6,13,31 and 65 registered an increase in Fe compared to their previous month’s reading.

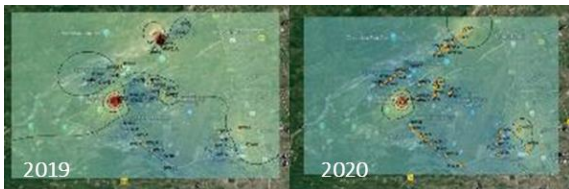


Figure 9: Fe raster for July 2019 and 2020

On the other hand, August average started to dip at 0.27mg/L. See Figure 10 for the generated rasters for August.

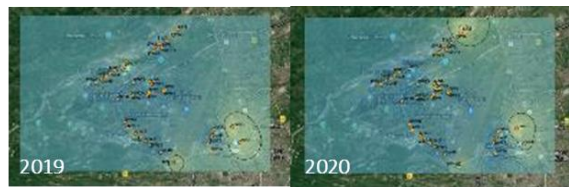


Figure 10: Fe raster for August 2019 and 2020

Figure 11 shows the Fe rasters for September. Fe averaged 0.35mg/L during this month. It is in this month in 2019 that the highest Fe concentration 2.21mg/L was recorded in DW39.



Figure 11: Fe raster for September 2019 and 2020

October Fe concentration averaged 0.38mg/L. Refer to Figure 12 for the generated rasters. In 2019, DW39 exhibited a lower Fe in comparison to the he previous month with an average of 1.19mg/L. October also triggers the decline of Fe detected in all wells.



Figure 12: Fe raster for October 2019and 2020

For November, Fe averaged 0.31mg/L for all sites (refer to Figure 13 for the generated rasters for the month.

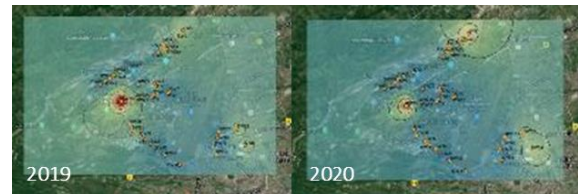


Figure 13: Fe raster for November 2019 and 2020

Fe averaged 0.28mg/L for December throughout the sites. Increased Fe values converge near the central wells (DW 39 and DW38). Refer to Figure 14 for the generated rasters.

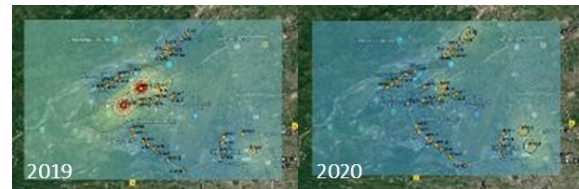


Figure 14: Fe raster for December 2019 and 2020

Data for Fe concentration in the water samples ranged between 0.10 to 2.21mg/L with an average concentration of 0.7mg/L. Most wells which recorded higher limit values were situated in the central (old wells and a few 30 series wells) and southeastern zone (IE5 wells) of the study area. This was also observed along the northeastern portion of CFZ (Sacobia Series Wells) where Sacobia river traverses. The area with the most extreme value (2.21mg/L) is located in DW38.

Figure 15 show the Mn generated rasters for January in years 2019, 2020 and 2021. The January average is 0.10mg/L.

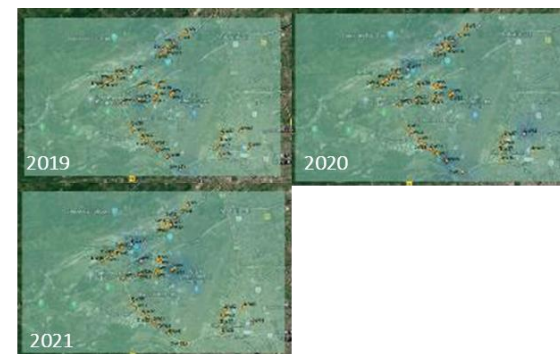


Figure 15: Mn raster for January 2019, 2020, and 2021

A slight increase in Mn concentration is observed for February with a Mn average of 0.11mg/L. Figure 16 show the Mn generated rasters for the month.

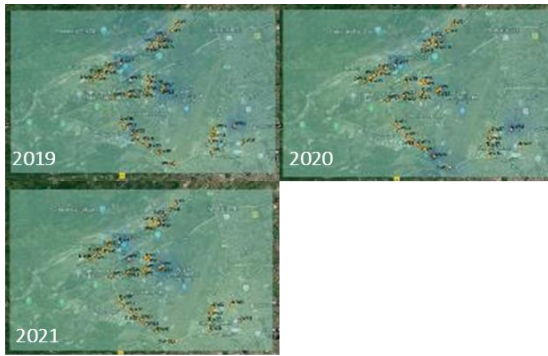


Figure 16: Mn raster for February 2019, 2020, and 2021

Likewise, a slight increase in Mn concentration was observed for March. Figure 17 show the generated rasters with an average of 0.12mg/L.

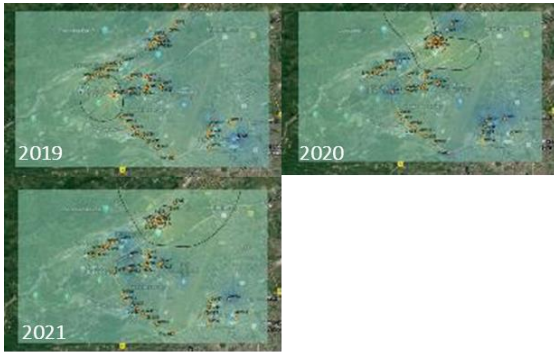


Figure 17: Mn raster for March 2019, 2020, and 2021

Figure 18 show the generated Mn rasters for April with an average of 0.10mg/L.

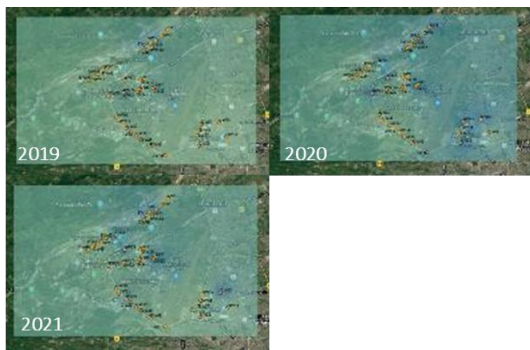


Figure 18: Mn raster for April 2019, 2020, and 2021

Similarly, May Mn averaged at 0.10mg/L see Figure 19 for the Mn rasters.

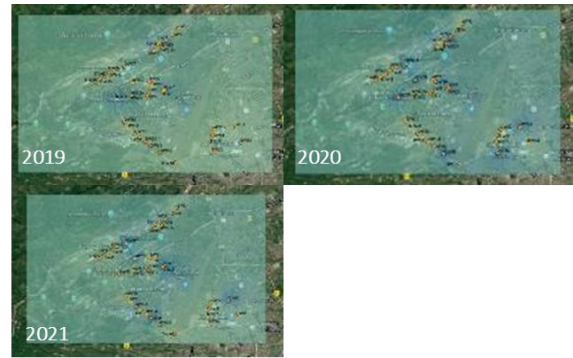


Figure 19: Mn raster for May 2019, 2020, and 2021

Figure 20 show the generated Mn rasters for June with an average of 0.11mg/L.

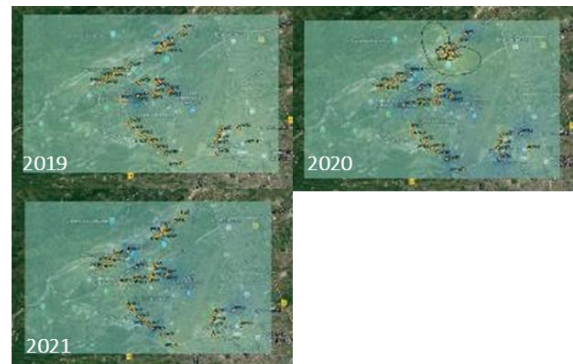


Figure 20: Mn raster for June 2019, 2020, and 2021

Figure 21 show the generated Mn rasters for July. The average concentration for all the wells is 0.25mg/L albeit there was no recorded sampling for year 2019.



Figure 21: Mn raster for July 2019, and 2020

August Mn average started to drop to 0.10mg/L. See Figure 22 for the generated Mn rasters for August 2019 and 2020.

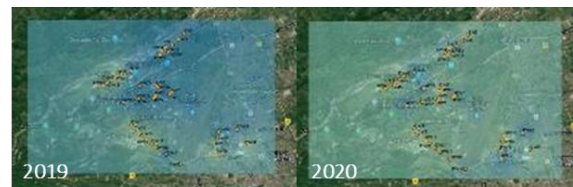


Figure 22: Mn raster for August 2019, and 2020

Figure 23 show the Mn raster for the months of September with an average concentration of 0.12mg/L.

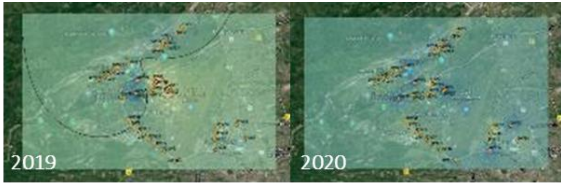


Figure 23: Mn raster for September 2019, and 2020

October Mn values averaged at 0.11mg/L. The developed rasters for the month are show in Figure 24.

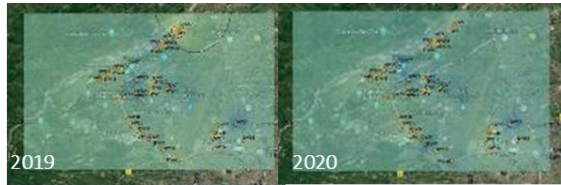


Figure 24: Mn raster for October 2019, and 2020

For November, Mn averaged 0.10mg/L for all sites. Refer to Figure 25 for the generated rasters for the month.

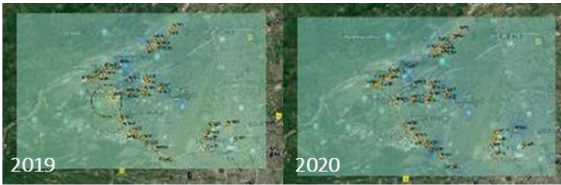


Figure 25: Mn raster for November 2019, and 2020

An average of 0.10mg/L is also recorded for all sites in December. See Figure 26 for the developed raster for Year 2019 and 2020.

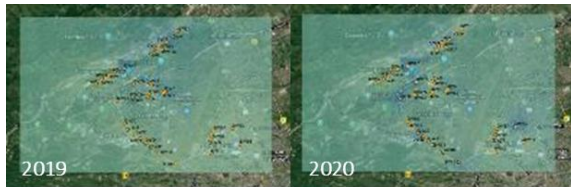


Figure 26: Mn raster for December 2019, and 2020

Mn presence follow a similar trend with Fe albeit at lower concentrations. Concentrations from the data provided by Laboratory services lie between 0.10 to 0.90mg/L with an average of 0.11mg/L. The highest value for Mn was recorded at DW51a (0.90mg/L, drilled 1.8kms from Sacobia river). Mn concentration gradually increased around the north, northeastern portions of the Freeport. Figure 27 represents a cross plot of Fe vs. Mn. It indicates no correlation ($r = 0.066$) between iron and manganese in all groundwater samples.

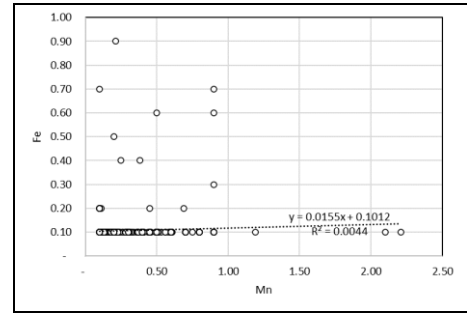


Figure 27: Fe vs Mn cross plot

For seasonality, there was an obvious spike in Fe for all wells on the months of July, September, and October. Mn on the other hand manifested a spike in July for the Old shallow wells. The increase can be associated to the water redox conditions during the wet season.

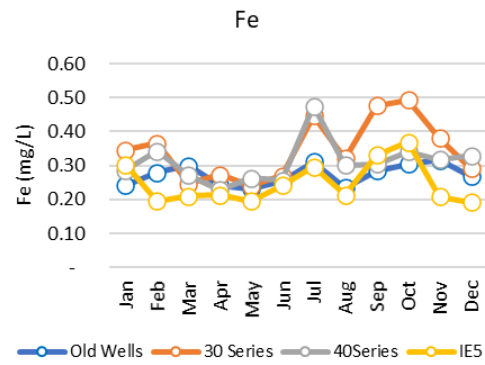


Figure 28: Fe Seasonality

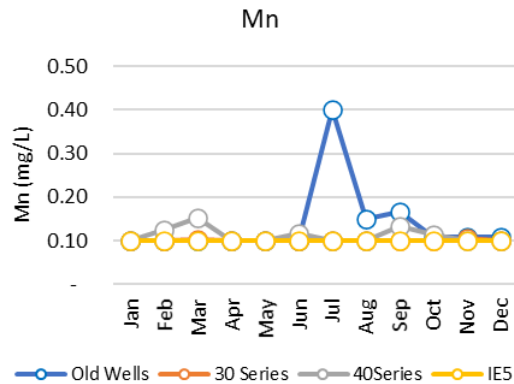


Figure 29: Mn Seasonality

4.0 CONCLUSION

Groundwater still functions as the primary water source for CFZ and neighboring areas [25]. Majority of water samples passed the PNSDW threshold levels, however, major industrial companies in Clark can only tolerate around 0.5ppm of Fe [26]. Fe was most frequently detected with concentrations close or above the PSDNW threshold limits. Only 4 or 0.42% of the 958 studied samples for Fe had concentration greater than 1ppm.

As for Mn, none of the 909 samples for Mn had concentration greater than 0.4ppm. No correlation has been found between the two parameters.

Of those wells that showed presence higher than the MDL, 5 have been installed with individual filtration systems (DMI-65, a catalytic water filtration media designed for the removal of Fe and Mn in water) [27] to capture Fe and Mn present. CWC's Lab Services also invested its own Fe and Mn testing capability to ensure quick response in case of spikes in either level. Moreover, CWC's Fe and Mn testing has a turnaround time (TAT) of 3 days which is significantly faster as compared to the TAT of 7 days for a 3rd party laboratory [28].

Generated maps showed that Fe and Mn gradually increase in concentration going north to northeastern directions. It is recommended that planned water sources located in the south southwestern portion of CFZ be prioritized instead of the northern portions to minimize probability of Fe and Mn presence in raw water. This can considerably lessen the capital and operational expense in building and maintaining additional water treatment facilities. As for seasonality and overall profiling, it is recommended to have regular Fe and Mn sampling even for backup wells that are turned off during sampling.

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