January 5, 2018

MPCA Conclusions and Recommendations
Related to Poly Met Mining, Inc.'s NorthMet Project "Cross-Media Analysis to Assess Potential Effects on Water Quality from Project-Related Deposition of Sulfur and Metal Air Emissions"
Ann Foss

The Minnesota Pollution Control Agency (MPCA) has reviewed Poly Met Mining, Inc.'s (PolyMet) NorthMet Project (Project) "Cross-media Analysis to Assess Potential Effects on Water Quality from Project-Related Deposition of Sulfur and Metal Air Emissions" (Cross-media Analysis). This memorandum summarizes MPCA conclusions and recommendations. Technical staff conclusions and recommendations are attached.

BACKGROUND
The MPCA is in the process of evaluating a 401 certification request, an air permit application and a wastewater National Pollutant Discharge Elimination System/State Disposal System (NPDES/SDS) permit application submitted by PolyMet for its Project.

The MPCA requested that PolyMet conduct a Cross-media Analysis for the NorthMet Project. The Cross-media Analysis evaluates the potential for air deposition of sulfide mineral dust from Project fugitive dust sources and stack air emissions (gas and aerosol sulfur species and fine particulate) to contribute sulfur and metals to waterbodies. In addition, the Cross-media Analysis evaluates the potential for sulfur deposition to result in changes in methylmercury concentrations in downstream waters and changes in fish mercury concentrations. This Cross-media Analysis will provide information relevant to MPCA's permitting/certification decisions for the Project.

OBJECTIVES
The overall objectives for the Cross-media Analysis include:

1) Estimating potential sulfur deposition from Project fugitive and stack air emission sources to the area surrounding the Project to assess potential changes in methylmercury concentrations in downstream waters and potential effects on fish mercury concentrations.
2) Estimating potential release of individual metals as a result of air deposition of dust from these same Project sources to the area surrounding the Project to assess potential changes in water quality to wetlands and other waterbodies.
3) Estimating the potential cumulative consequences of these air-related effects when added to the other effects of the Project water quality-related releases to downstream waters.

Technical staff reviewed the methods, assumptions and results in the Cross-media analysis. Technical staff drafted memos summarizing their conclusion (Attachments 1-4). This memorandum is based on those technical memos and discussions with MPCA staff. Technical staff have reviewed this memorandum and agree it accurately reflects their views. Outside counsel for the MPCA also retained two consulting firms. One consulting firm reviewed the geochemical portions of the report and conducted a QA/QC evaluation of the GoldSim modeling. The other reviewed the air modeling protocol and the air modeling. Both consultants reviewed the Cross-media Analysis, this memorandum, and attachments to this memorandum. The consultants support the MPCA technical conclusions and recommendations.

MPCA CONCLUSIONS

Wetland of Interest. The Wetland of Interest (WOI), a small wetland at the Mine Site, located near the proposed Rail Transfer Hopper was estimated to receive the highest sulfide mineral dust deposition per unit area. Additional reasons are provided in Attachment 4. Using the WOI throughout the Analysis was a protective assumption. It is reasonable to assume that other waterbodies, including wetlands, would receive less atmospheric loading per unit area from the Project air emissions and thus be less affected.

Air modeling. The MPCA concludes that the data developed from the air quality modeling files is consistent with the MPCA-approved modeling protocol and is suitable for use in the hydrological and geochemical analysis. See Attachment 1 for more detail.

Geochemistry. As Attachment 2 describes in detail, MPCA technical staff would have used different calculations in conducting the geochemical portion of the Cross-media Analysis. As stated in Attachment 2:

> Despite the issues discussed above, the "Cross-Media Analysis" chalcopyrite reaction rate calculation appears to over-predict the release of copper and sulfate from chalcopyrite. The lack of peer-reviewed science that is directly applicable to the natural chemical system applicable in the Cross-Media Analysis requires some assumptions to be made to reasonably estimate the potential loading of metal and sulfur to surface water from air-deposited sulfide particulate.
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> Collectively, the MPCA and the Cross-media Analysis use the best available data, methods, and execution of those methods to reasonably estimate the potential effects from the deposition of sulfide mineral particulate for the NorthMet project.

Mercury and methylmercury. As attachment 3 describes in detail: MPCA staff used a different method of determining whether a change was measurable and used the human health-based water quality standard of 0.2 mg/kg total mercury in edible fish tissue rather than fish consumption advisories. The MPCA staff conclusion states: "I have concluded the Cross-Media Analysis developed a reasonable and protective scenario showing no measurable changes of mercury in water or fish from project-related deposition of sulfur."

Metals. As Attachment 4 describes in detail: "MPCA staff concludes that the Analysis methods for determining the increment of potential change (including evaluation of existing concentrations, removal rates, and water yield) as applied to the concentration of copper, cobalt and arsenic in the WOI rely on the best available data and are reasonable." The estimated concentrations "would remain in compliance with the applicable Class 2D Water Quality Standards." Additionally, MPCA staff concludes that the report is reasonable in finding that the estimated project concentrations of arsenic and cobalt in the WOI are also below the applicable drinking water standard in Colby Lake (where a more stringent standard applies), even without consideration of the mixing/dilution of the WOI outflow with downstream waters. MPCA staff reviewed the supplemental memorandum submitted by PolyMet's consultant (Barr Engineering Memorandum: "Estimated Potential Concentrations of Arsenic, Copper and Cobalt in the St. Louis River at Forbes, November 29, 2017") and concludes that the Project would not result in any measurable changes to water quality downstream of the Project in the St. Louis River at Forbes.

Overall Conclusion. MPCA staff review concludes there will be no measurable changes of mercury in water or fish nor exceedances of copper, cobalt and arsenic Class 2D water quality standards from project related air emissions. This is the best estimate of potential effects that we can reach using the best available data and MPCA's best professional judgement, but there is sufficient uncertainty, as detailed in the attachments, that MPCA will require monitoring to confirm the expected outcomes. MPCA will also ensure the Agency's ability to mitigate effects (see Recommendations

below). As noted in Section 4.5.2 of the Cross-media Analysis, potential mitigation options are available for metals (including mercury) if needed. MPCA staff reviewed this section of the Analysis and concluded that these are feasible and practical options.

SUMMARY OF RESULTS

Metals

MPCA concludes that the estimated project concentrations in the wetland of interest (WOI) (i.e., background concentration + calculated incremental increase) for copper, cobalt and arsenic remain below the applicable Class 2D Water Quality Standards.

Below is a summary of the Analysis results related to copper, cobalt and arsenic. This table summarizes Table 6-3 in the Cross-media Analysis. As the table demonstrates, the estimated total concentrations in the wetland of interest (WOI) (i.e., background concentration + calculated incremental increase due to the project) for copper, cobalt and arsenic remain below the applicable Class 2D Water Quality Standard using either the Cross-media Analysis or MPCA calculations.

Parameter	Units	Background average concentration	Contribution from project	Potential concentration in the WOI as a result of the project	Applicable water quality standard
As (arsenic)	µg/L	1.5	0.4	1.9	53
As (arsenic)	µg/L	1.5	0.4	1.9*	2.0*
Co (cobalt)	µg/L	1.3	1.0	2.3	5.0
Cu (copper)	µg/L	3.6	0.3	3.9	6.0

* The standard listed here is applicable in Colby Lake. The estimated concentration in the WOI is 1.9, which is upstream of Colby Lake. Concentrations in Colby Lake would be expected to be less than 1.9 as a result of the considerable mixing/dilution of the WOI outflow with downstream waters prior to Colby Lake.

Mercury

Measurable Change in Fish Tissue Mercury Concentration

The following results use the concentration results in Table 6-2 of the Cross-Media Analysis and the MPCA definition of measurable change (plus or minus 10% of the background fish tissue mercury concentration):

- A measurable change is 0.122 mg/kg for Embarrass River (PM-13) and the potential change calculated in the report for Embarrass River is 0.026 mg/kg
- A measurable change is 0.0545 mg/kg for the Partridge River (SW004a) and the potential change calculated in the report for Partridge River is 0.014 mg/kg
- Therefore, neither of these potential changes in fish tissue mercury concentrations is measurable.
- The potential change expected for both the Upper St. Louis River at Forbes and at the Lower St. Louis River at Cloquet would be smaller than in the tributaries, and therefore is not measurable.

Measurable Change in Water Concentrations

MPCA staff applied its own definition of measurable change in water concentrations of mercury (see Attachment 3) to the two evaluation points that showed an increase in mercury with the project (Cross-media Analysis Table 5-5):

Wetland of Interest (WOI)

- The existing average mercury concentration at WOI is 3.8 ng/L.
- A measurable change would be any change that resulted in average concentrations greater than 5.1 ng/L.
- The cumulative average accounting for project effects reported in Table 5-5 is 4.1 ng/L
- Therefore, the projected mercury concentration in the WOI does not exceed the threshold for a measurable change (i.e., no effect).

Second Creek Headwaters site SD026 (SD026)

- The deposition of fugitive dust emissions at this site is negligible and hence, has negligible contribution to the change in mercury concentration."

All other evaluation points showed a decrease or no change in mercury concentration with the project.

MPCA RECOMMENDATIONS

Attachment 3 provides details on recommended monitoring related to mercury. As stated in Attachment 3: "Water quality monitoring will reduce the uncertainty and it will provide a better understanding of inherent (natural) variability. The monitoring recommendations will address the seasonal, annual, and spatial variability. Water quality monitoring within the surrounding wetlands, before project operation will provide a baseline dataset if stream monitoring during project operation indicates unacceptable changes in methylmercury concentrations and it becomes necessary to develop an adaptive management plan to identify the source of the higher levels."

Attachment 4 provides details on recommended monitoring of surface water in the Partridge River downgradient of the WOI and upstream of Colby Lake and monitoring in the WOI for metals.

This monitoring should be required in the MPCA 401 certification for the Project unless it is already in another MPCA permit.

The following should also be required:

- Submittal of results and analysis of those results on a specified frequency.
- Submittal of a monitoring report including:
  - The monitoring data
  - An analysis of data including any statistical assumptions and methodologies
  - Identification/interpretation/explanation/significance of any apparent data trends or anomalies
  - Conclusions regarding monitoring results
  - Recommendations for any necessary adaptive management, including items described in section 4.5.1 of the Cross-Media Analysis.

Attachment 1
Conclusions related to air emissions modeling
Jim Sullivan

To support the wetland impact assessment analysis, a simulated particle deposition data set was needed to evaluate potential air deposition impacts from the proposed NorthMet operations on the surrounding wetland assemblages. Using existing emission values for Total Suspended Particulate Matter less than 30 microns (TSP_{30}), an air quality dispersion modeling protocol was developed by NorthMet to account for the potential aerial dispersion and deposition of particulate matter by selected size fraction.

To generate a valid and reliable simulated particle deposition data set (Data), deposition methods were selected to characterize stack and non-stack emission sources. For stack-based emissions, Sulfur-bearing emissions were modeled and a pollutant-specific settling velocity was applied to each simulated concentration (by receptor) to account for gas, aerosol, and fine particle deposition. The pollutant-specific settling velocities were applied from published values. For non-stack emission sources, particle size and composition (based on mineral density), site-specific geology, published data, and the hydrological and geochemical analytical needs, informed the development of modeled deposition characteristics.

A formal MPCA air quality dispersion modeling protocol was requested to document the specific modeling methodology, including modeled input characteristics, used to create the Data. The modeling protocol also accounted for two maximum allowable emission operating scenarios that reflect the Year 8 scenario and the Year 13 scenario. The terrain elevation, meteorological, source characterization, and related modeling inputs were comparable to the data used in the regulatory ambient air quality compliance demonstration modeling and air quality risk assessment evaluation. Additional receptors were added on the NorthMet property to address potential surface water quality impacts from particle deposition. The MPCA reviewed and approved the NorthMet modeling protocol on June 28, 2017.

The MPCA reviewed the final air quality modeling files and results to determine their consistency with the June 28, 2017, approved protocol. The MPCA review consisted of an evaluation of TSP_{30} emissions, particle size characteristics, source characterization, modeling file comparisons, and receptor-based deposition. The MPCA concludes that the Data developed from the air quality modeling files is consistent with the June 28, 2017, modeling protocol and is suitable for use in hydrological and geochemical analysis.

Attachment 2
Conclusions related to geochemistry
Zach Wenz

This memo focuses on evaluating the geochemical approach for calculating sulfur and metals release in the "Cross-Media Analysis to Assess Potential Effects on Water Quality from Project-Related Deposition of Sulfur and Metal Air Emissions" ("Cross-Media Analysis") performed by Barr Engineering for Poly Met Mining, Inc. for their NorthMet project. My review consists of five sections which summarize 1) concepts that most likely overestimate the release of sulfur and metals, 2) concepts and methods of agreement, 3) concepts and methods of disagreement, 4) analysis of the uncertainty, and 5) overall conclusions. In section 3, I offer an alternative approach for calculating chalcopyrite reaction rates that maintains consistency with the fundamentals of geochemistry and direction provided by the referenced documents and data sources. I conclude that the "Cross-Media Analysis" uses the best available data and methods to arrive at a reasonable best estimate for the potential release of sulfur and metal to surface water from sulfide mineral particulate.

Overestimation of Metals and Sulfate Release

There are three main aspects included in the "Cross-Media Analysis" that would likely overestimate sulfur and metal release.

1. The assumption that all pyrrhotite dust will react in one year likely exceeds what would occur naturally in a one-year time frame for particles larger than about 10 micrometers. This exceedance would affect releases of arsenic, cobalt, and the sulfur contributed only from pyrrhotite.
2. The one-year reaction time frame for oxidation of chalcopyrite is likely an overestimate. It is conceivable that the time period of reaction under oxidizing conditions is less than 1 year and likely varies based on the specific setting in which the sulfides are deposited.
3. Oxidation of pyrrhotite and chalcopyrite at circumneutral pH (5.5 to 7.5) of the environmental setting would lead to development of a reaction product coating. It is well documented that reaction coatings develop at the onset of reaction and increase in thickness with time. As coatings thicken, the magnitude of reaction rate inhibition increases. A reaction coating inhibiting effect is not incorporated into the Cross-Media Analysis.

Concepts and Methods of Agreement

In general, the analysis approach for estimating the overall metal and sulfur loading to the environment from dust particulates is well-defined and science-based. Three primary areas of agreement include 1) use of the Kimball et al. (2010) chalcopyrite reaction rate equation, 2) the general relationship between chalcopyrite reaction and copper release increasing with decreasing pH, and 3) the correct execution of the shrinking particle model equation.

1.) The analysis relies on an established reaction rate equation (Kimball et al., 2010) that provides the best available method to estimate chalcopyrite reaction rates in the absence of reliable data at circumneutral pH. In my opinion, it is best to use the most reputable technique and extrapolate from there rather than attempt to make predictions for conditions where there is no supporting science.
2.) The analysis shows through supporting documentation that the reaction rate of chalcopyrite and copper release decrease as pH increases. However, the extent to which the rate and concentration decreases occur is not quantified.
3.) I recreated the shrinking particle model calculations and confirmed the mathematics of the various equations and transformations was performed accurately for determining the extent of reaction for the chalcopyrite dust particles. The shrinking particle model lends itself favorably for making straightforward calculations from AERMOD deposition data.

Concepts and Methods of Disagreement

Despite agreement with the overall framework for calculating a chalcopyrite reaction rate and most of the basic geochemical principles, there are a number of instances in which I disagree with concepts and methods used for applying the reaction rate models and assumptions made regarding some geochemical principles. There are four primary areas of disagreement including: 1) assuming activity can substitute for solute concentration, 2) not accounting for all forms of dissolved ferric iron in solution, 3) using iron hydroxide solubility to calculate a ferric iron amount, and 4) excluding charge balance and the presence of relevant dissolved species (e.g., sulfate) from the geochemical system. These areas of disagreement have the potential to substantially affect the calculated chalcopyrite reaction rate used in the shrinking particle model to estimate the release of metals and sulfate. The presumed effect for each of these areas in the "Cross-Media Analysis" is described in the four bullets below.

1. Concentration is related to activity by the activity coefficient. Expressed mathematically as $a = \gamma \times m$, where $\gamma \leq 1$ and a=activity, m=concentration, and γ= activity coefficient. For a theoretically infinitely dilute systems γ=1. For highly concentrated fluids, such as the chemical systems for which the Kimball et al. (2010) chalcopyrite rate law was derived, γ is much less than one – meaning concentration is greater than activity. Therefore, using activity for the ferric iron concentration variable will lead to under-prediction of the reaction rate. Moreover, the Kimball et al. (2010) article clearly states the iron variable in the equation is concentration.
2. The Kimball et al. (2010) chalcopyrite rate law ferric iron concentration parameter is a summation of all the different species of ferric iron (e.g., Fe^{3+}, $FeOH^{2+}$, $FeSO_4^{+}$, $FeCl^{2+}$, etc.). The Cross-Media Analysis only uses Fe^{3+}, which would result in under prediction of the reaction rate.
3. The Cross-Media Analysis uses the solubility product of iron hydroxide to calculate Fe^{3+} activity. Iron hydroxide is very likely not the stable mineral phase in the chemical system for which the chalcopyrite rate law was derived. Using iron hydroxide solubility to calculate ferric iron activity likely overestimates the amount of ferric iron resulting in an over-prediction of the chalcopyrite reaction rate.
4. The sole use of iron hydroxide solubility for representing the chemical system is disparate from that used to define the Kimball et al. (2010) rate equation and conflicts with the geochemical principle that all aqueous systems must have a net neutral charge. Because the chemical system is not complete, it is difficult to surmise what effect it would have on the chalcopyrite rate calculation.

I performed my own analysis to assess how much of an impact these four areas of disagreement may change the chalcopyrite reaction rate presented in the "Cross-Media Analysis." My analysis incorporated geochemical modeling to account for ferric iron concentration exceeding activity, summation of all ferric iron species, jarosite as the most soluble ferric iron bearing mineral phase, and charge balance by incorporating sulfate (a natural product of chalcopyrite oxidation) in the chemical system. I believe this approach maintains consistency with the methodology documented in the Kimball et al. (2010) document and other broad geochemical principles indicated in the four areas of disagreement. It is acknowledged that this approach is more complicated than that in the "Cross-Media Analysis." However, a geochemical modeling approach for identifying dissolved metal concentrations is relatively routine in addressing mining influenced water questions and has been performed for other aspects of the NorthMet project.
Using jarosite as a reasonable mineral for determining total ferric iron concentration was determined by inspection of mineral stability fields over a range of sulfate concentrations and pH using a geochemical modeling software and the Lawrence Livermore National Laboratories thermodynamic database (Delaney and Lundeen, 1990) encompassing the conditions from Kimball et al. (2010). An additional consideration for using jarosite to determine total ferric iron concentrations requires knowledge of the dissolved potassium concentration of a fluid. For a pH of about 3, leachate concentrations from various Duluth Complex rock piles (Dunka stockpiles and the AMAX field test piles) and laboratory rock weathering tests indicate potassium concentrations range from about 10 to 100 mg/kg.

Following the modeling approach described above and incorporating a potassium concentration of 10 or 100, the resulting total ferric iron concentrations are 0.6 and 0.3 times the values used in the "Cross-Media Analysis." These lower total

ferric iron concentrations correspond to decreasing the reaction rate of chalcopyrite by a factor between 0.6 and 0.8 times the values used in the "Cross-Media Analysis." Calculating reaction rates over a large range of potassium concentrations demonstrates the rate calculation is relatively stable regardless of the potassium concentration used from the observed range.

My analysis found that despite the "Cross-Media Analysis" not strictly following the guidance for applying the Kimball et al. (2010) rate law and some geochemical principles the net effect results in the "Cross-Media Analysis" overestimating the reaction rate and subsequent release of sulfate and copper from chalcopyrite.

Uncertainty in the Analysis

The primary source of uncertainty with defining a representative chalcopyrite reaction rate for the "Cross-Media Analysis" is the assumption that the pH 3 rate value is equal to or greater than what the rate may be in the natural environment (pH 5.5 to 7.5) where the sulfide dust falls.

The "Cross-Media Analysis" document states that the calculated reaction rate is protective because the pore water in the wetland of interest has a pH greater than the pH 3 for which the reaction rates were calculated. The difference in pH is very likely; however, the rate equation cannot be extended outside of the pH 1 to 3 range it was developed for. The Kimball et al. (2010) states that the chalcopyrite reaction rate for pH greater than about 3 is likely controlled more by dissolved oxygen concentration than ferric iron. This means the entire reaction mechanism changes as circumneutral pH conditions are approached and a rate equation for a chemical system with a pH greater than 3 would require a dissolved oxygen variable. The effect of oxygen concentration on chalcopyrite reactivity is not quantified in the available scientific literature. It is conceivable that, depending on the effect of oxygen, reaction rates at pH greater than 3 could be equal to or more than rates at a pH of 3.

Because the Kimball et al. (2010) rate equation cannot be extended beyond a pH of 3, I made an effort to gauge the uncertainty of applying the chalcopyrite rate at a pH of 3 to the anticipated natural environment pH (about pH 6) by comparing the well-defined reaction rate of pyrite to the chalcopyrite reaction rate. Reaction rate laws for pyrite span a pH range of about 1 to 10 (fig. 1). The large pH range for pyrite reaction rates offers the opportunity to assess how chalcopyrite and pyrite reaction rates compare to frame an approximate range of potential reaction rate values for chalcopyrite at more neutral pH (e.g., pH 6). The following projection was performed using my geochemical modeling approach for calculating reaction rates at a pH of 3. At a pH of 3 pyrite has a reaction rate that is about 27,291 times greater than chalcopyrite (for ferric iron concentration calculated by jarosite solubility and a potassium concentration of 10 mg/kg). Applying the rate difference at a pH of 3 to a pH of 6 results in a projected chalcopyrite reaction rate of 1.35×10^{-13}. That projected rate is 131 times less than the chalcopyrite reaction rate at a pH of 3 (fig. 1; 1.77×10^{-11}). Therefore, if the relative difference in reaction rate holds between chalcopyrite and pyrite at the anticipated natural environment pH (about pH 6), then the pH 3 rate based on jarosite solubility may be greater than the actual reaction rate at a pH of 6 (fig. 1). Although this projection of chalcopyrite rate to a pH of 6 is an indulgence of conjectural thought, the projection does help constrain the possible range of chalcopyrite rates and is in general agreement with qualitative observations that chalcopyrite reacts slower than pyrite and pyrrhotite (Plumlee, 1999; and Jambor, 1994).

Conclusion

Despite the issues discussed above, the "Cross-Media Analysis" chalcopyrite reaction rate calculation appears to over-predict the release of copper and sulfate from chalcopyrite. The lack of peer-reviewed science that is directly applicable to the natural chemical system applicable in the Cross-Media Analysis requires some assumptions to be made to reasonably estimate the potential loading of metal and sulfur to surface water from air-deposited sulfide particulate.

Collectively, the MPCA and the Cross-media Analysis use the best available data, methods, and execution of those methods to reasonably estimate the potential effects from the deposition of sulfide mineral particulate for the NorthMet project.

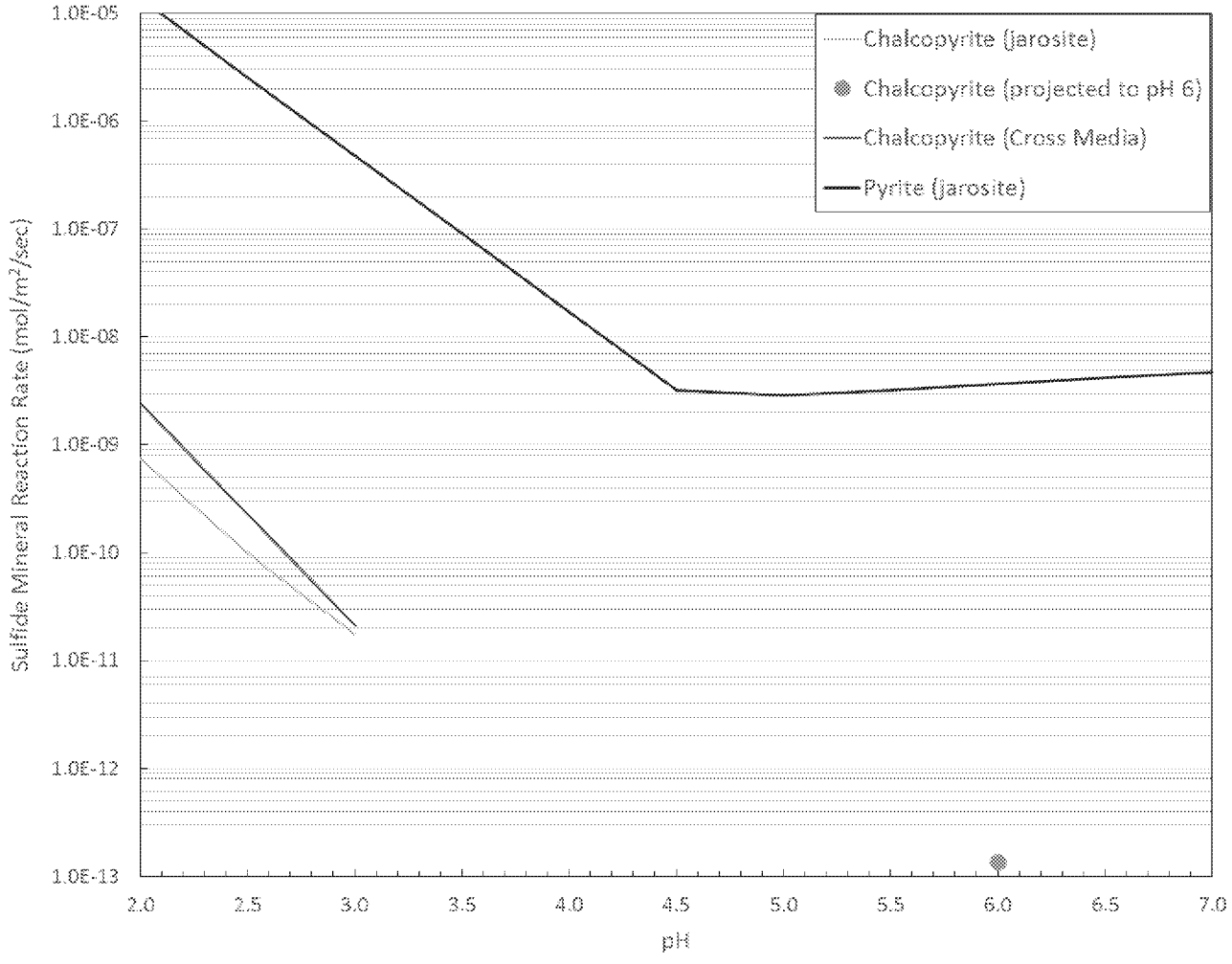

Figure 1. Chalcopyrite and pyrite oxidation reaction rates as a function of fluid pH and jarosite solubility with a potassium concentration of 10 ppm. Also shown (in blue) is the "Cross-Media Analysis" rate determination. Rates are calculated using the equations provided by Kimball et al. (2010) and Williamson and Rimstidt (1994). The green dot at a pH of 6 is the projected chalcopyrite rate if the relative difference between chalcopyrite and pyrite at a pH of 3 is applicable at a pH of 6. The projection of the chalcopyrite rate at a pH of 6 is 131 times less than the chalcopyrite rate assuming jarosite solubility for ferric iron concentration and a pH of 3.

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Attachment 3
Conclusions related to Mercury and Methylmercury
Bruce Monson

I am providing my assessment of PolyMet's report authored by Barr Engineering, "Cross-Media Analysis to Assess Potential Effects on Water Quality from Project-Related Deposition of Sulfur and Metal Air Emissions" ("Cross-Media Analysis"). As an MPCA staff mercury expert, my comments are limited to the mercury analysis, which was covered in Section 3.5 "Part 3A – Estimating Potential Effects from Project Deposition of Sulfur on Mercury Methylation and the Potential for Downstream Effects on Fish Tissue Mercury Concentrations" and Section 4.0 "Results and Discussion – Potential Water Quality Impacts from Project Air Emissions."

These sections provide a practical analysis of the potential for sulfate concentration increases due to the project that could lead to formation of methylmercury and increases in mercury concentrations in fish downstream of the mine and plant sites. Given the complexity and uncertainty of the biogeochemical processes governing the transport, methylation, and bioavailability of mercury, I agree with the conceptual approach used in this analysis.

Many of the assumptions were protective and most likely overestimated the effects of sulfate from the project (listed in Cross-Media Analysis Table 3-3). In particular, assumptions that clearly demonstrate protectiveness include:

- 100% of sulfur in pyrrhotite is released and oxidized to sulfate
- 100% of methylmercury produced in the watersheds reached SW004a in the Partridge River and PM-13 in the Embarrass River
- 100% of the estimated methylmercury is taken up by the food web and makes it to the top predator fish (no demethylation or retention of methylmercury).

Below I have some specific issues where I differ from with the Cross-Media Analysis report, recommend a monitoring plan, and give my conclusion of the analysis.

Endpoint Measurement of Impact on Fish Consumption

The Cross-Media Analysis is intended to inform the Section 401 Water Quality Certification, which assures the project will not cause a violation of water quality standards. Therefore, the MPCA should use the human health-based water quality standard (HH-WQS) of 0.2 mg/kg total mercury in edible fish tissue (Minn. R. 7050.0220) rather than the MDH's fish consumption advisories (FCA) to assess potential impact of project on fish-mercury levels. The following excerpt from the HH-WQS Technical Support Document (page 24) explains why the HH-WQS was adopted:

> *MPCA adopted a numeric fish tissue water quality standard to Minn. R. ch. 7050 in 2008. The HH-WQS is based on EPA's Water Quality Criterion for Protection of Human Health: Methylmercury (USEPA 2001). The mercury standard is 0.2 milligram of total mercury per kilogram of fish (mg/kg or parts per million, ppm). It applies to total mercury concentrations in edible fish tissue of any species of fish from Minnesota's waters. The promulgation of a 0.2 ppm mercury standard augments the current numeric CSs [chronic standards] by providing a more precise level of protection to fish consumers. This mercury HH-WQSs applies directly to the fish medium rather than the water medium.*
>
> *EPA published the mercury AWQC as a fish tissue concentration rather than a water concentration for many reasons.*
>
> - *Fish consumption is the primary source of mercury exposure to humans; the standard applies in fish tissue.*

- *Fish tissue is the medium of interest and concern; therefore, having a fish tissue standard more reliably protects fish consumers by eliminating the need to extrapolate safe mercury levels in fish from water standards by removing the uncertainty in bioaccumulation factors (BAFs).*
- *There are far more fish tissue data than water data for mercury.*

The 0.2 mg/kg HH-WQS is the threshold used by the MPCA to determine if a waterbody should be listed as impaired on the CWA 303(d) list. WQS and impairment listings have a different purpose than the FCA. FCA are non-regulatory and inform the public about what fish can be eaten at amounts that limit the potential health effects. A WQS is developed for regulatory decisions, serving as a benchmark for attainment, compliance, and enforcement purposes. An impairment listing identifies waterbodies that need additional control measures to reduce pollutant loading, with the ultimate goal of reducing or eliminating any advisories on fish consumption.

Measurable Change in Fish Tissue Mercury Concentration

Section 2.3.7 of the report, "Determining a Measurable Change in Parameter Concentrations," argues for the Laboratory Control Sample (LCS) Acceptance Criteria as the means of determining a measurable change. The LCS acceptance criteria for mercury in fish is plus or minus 20 percent. Generally, the LCS it is a fixed concentration that is continually tested in a laboratory to ensure the analytical equipment remains accurate and precise (i.e., does not drift). For the Cross-Media Analysis, PolyMet applies it to a potential range of concentrations.

Measurable change is defined in Minn. R. 7050.0255 as "the practical ability to detect a variation in water quality, taking into account limitations in analytical technique and sampling variability." An alternative quantitative interpretation of this definition is relative percent difference of duplicate samples. I calculated relative percent difference (RPD) of fish-mercury duplicates for a 2009 publication. RPD is the difference in concentrations between duplicate analyses divided by the average concentration of the duplicates. It provides a measure of analytical variability when applied to lab duplicates and additionally sampling variability when applied to sample duplicates. The Minnesota Department of Agriculture lab does the fish-mercury analysis for our Fish Contaminant Monitoring Program. The RPD for lab duplicates (two measurements of the same homogenate sample) was 9.8%, based on 100 sets of duplicates. RPD for process duplicates (two ground samples from the same fish fillet) was 11.7%, based on 260 sets of duplicates. Therefore, I recommend a measurable change be interpreted as plus or minus 10% of the background fish tissue mercury concentration.

Applying it to the results in Cross-Media Analysis Table 6-2, a measurable change is 0.122 mg/kg for Embarrass River (PM-13) and 0.0545 mg/kg for the Partridge River (SW004a). The potential changes calculated in the report are 0.026 mg/kg and 0.014 mg/kg, respectively. Therefore, using the RPD-based definition of measurable change, these potential changes in fish tissue mercury concentrations are not measurable.

Regarding estimated changes in fish tissue mercury concentrations for the St. Louis River at Forbes and Cloquet, if there were not measurable changes upstream, there is no reason to expect measurable changes at those sites. The Cross-Media Analysis calculated a cumulative mercury loading of 5.2 g/yr to the St. Louis River, which is less than 0.01% of the existing mercury load to the St. Louis River at Cloquet and Forbes; therefore, assuming a proportional change of mercury in fish, the change in fish tissue mercury concentrations would be less than 0.01%.

Measurable Change in Water Concentrations

I recommend an alternative to using the LCS acceptance criteria (proposed in the Cross-Media Analysis) as the definition of measurable change in water concentrations. Using a baseline water quality dataset, a mean concentration and 95

percent confidence limits can be calculated. The additional project contribution is added to each baseline concentration value to get a predicted mean concentration with the project in operation. The predicted concentration is a measurable change if it is outside the range of the two-tailed upper and lower 95 percent confidence interval of the mean concentration of the baseline water quality dataset. This approach has a well-established statistical basis for representing the sampling variability. It also has precedent, having been used by the Delaware River Basin Commission to assess measurable change to existing water quality (Delaware River Basin Commission 2016).

I applied this definition of measurable change to the two evaluation points (out of 12 evaluation points) that showed an increase in mercury with the project (Cross-Media Analysis Table 5-5): Wetland of Interest (WOI) and Second Creek Headwaters site SD026 (SD026). The average mercury concentration used for the WOI is 3.8 ng/L and the upper 95% confidence limit is 5.1 ng/L. The cumulative project effects average reported in Table 5-5 is 4.1 ng/L; therefore, the projected mercury concentration does not exceed the threshold for a measurable change (i.e., no effect). For SD026, potential deposition of fugitive dust emissions at this site is negligible and hence, has negligible contribution to the estimated increase in water concentration of mercury.

Water quality monitoring recommendations

MPCA has made the best estimate of potential effects that we can reach using the best available data and MPCA's best professional judgment. Given the complexity and uncertainty of the biogeochemical processes governing the transport, methylation, and bioavailability of mercury in any particular water body, it is necessary to monitor water quality to confirm the expected outcomes. To this end, I recommend adding methylmercury, along with total mercury, to the stream water quality monitoring specified in the NPDES/SDS permit. In addition, I recommend establishing a baseline set of data in the wetlands surrounding the plant and mine site by monitoring water quality at least monthly, May through October, for two years before project operation. This baseline monitoring should occur at a subset of the wetland hydrology monitoring locations described in Monitoring Plan for Potential Indirect Wetland Impacts (Barr, February 2016). The recommended specific well numbers are listed below. Large Figures 2 and 3 in the monitoring plan show the locations of the wells. Specifically, the 22 wells proposed (out of 42 wells in the monitoring plan) for water quality monitoring are as follows:

- Mine Site (counter-clockwise beginning at Dunka Road, SW of Mine Site Perimeter)
    - 31, 33, 34, 35, 36, 37, 38, 39, 13, 47, 26, 4A, 4
- Dunka Road Wells (east to west): 40, 41, 42
- Plant Site (counter-clockwise beginning at east side of Plant Site Perimeter)
    - TB14, TB12, TB13, TB11, TB10, TB9

The air deposition modeling showed the primary impact of fugitive dust deposition will be to the south of the mine and plant site. Therefore, most of the selected wells for water quality monitoring are on the south side of the mine site. Other wells on the northwest, north, and east perimeter of the mine site are included for water quality monitoring to serve as reference sites for the south wells should any impacts be observed.

My recommended water quality parameters are listed below. Field measurements can be taken with a multiparameter sonde at the time of water sample collection. These are standard parameters measured for characterizing water quality. The primary analytes—mercury, methylmercury, and sulfate—are supplemented with ancillary analytes—base cations, alkalinity, and DOC—to determine if changes in methylmercury over time can be attributed to causes other than deposition from the project. For example, decreased dissolved oxygen, increased temperature, or the associated changes in water level could all contribute to changes in methylmercury regardless of any changes in sulfate deposition.

Field Measurements

- Temperature
- pH
- Dissolved Oxygen
- Specific conductivity

Laboratory Analyses

- Total Mercury (EPA Method 1631E) - filtered
- Methylmercury (EPA Method 1630) - filtered
- Base Cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+})
- Dissolved Organic Carbon
- Sulfate
- Alkalinity, Total

Conclusion

I have concluded the Cross-Media Analysis developed a reasonable and protective scenario showing no measurable changes of mercury in water or fish from project-related deposition of sulfur.

To check the results in the Cross-Media Analysis, I verified all calculations in Table 4-3 through Table 4-8. With the project at the maximum deposition year, the estimated potential increases in methylmercury concentration would be 0.004 ng/L in the Partridge River (at SW004a) and 0.003 ng/L in the Embarrass River (at PM-13). These are 0.7% and 0.8% increases above background. The calculated percent increase in potential future fish mercury concentration would be 0.7% at SW004a and 1.2% at PM-13, which is well below the 10% change considered necessary for a measurable change in fish-tissue mercury concentration.

Water quality monitoring will reduce the uncertainty and it will provide a better understanding of inherent (natural) variability. The monitoring recommendations will address the seasonal, annual, and spatial variability. Water quality monitoring within the surrounding wetlands, before project operation will provide a baseline dataset. If stream monitoring during project operation indicates unacceptable changes in methylmercury concentrations, the MPCA can require an adaptive management plan to identify the source of the higher levels. This plan should include more focused and detailed monitoring.

References

Delaware River Basin Commission. 2016. Lower Delaware River Special Protection Waters Assessment of Measurable Changes to Existing Water Quality, Round 1: Baseline EWQ (2000-2004) vs. Post-EWQ (2009-2011). Delaware River Basin Commission, DRBC/NPS Scenic Rivers Monitoring Program, West Trenton, NJ. Authors: Robert Limbeck, Eric Wentz, Erik Silldorff, John Yagecic, Thomas Fikslin, Namsoo Suk.

Monson, Bruce A. Trend Reversal of Mercury Concentrations in Piscivorous Fish from Minnesota Lakes: 1982–2006. Environmental Science & Technology 2009 43 (6), 1750-1755.

U. S. Environmental Protection Agency (USEPA). 2001. Water Quality Criterion for the Protection of Human Health: Methylmercury. Final. EPA-823-R-01-001. Office of Science and Technology, Office of Water, USEPA, Washington, DC 20460.

Attachment 4
Conclusions related to Estimating Potential Water Quality Changes from Project Metals
Richard Clark

This document presents MPCA staff assessments and conclusions on the "Cross-Media Analysis to Assess Potential Effects on Water Quality from Project-Related Deposition of Sulfur and Metal Air Emissions" as they relate to estimating potential water quality changes for metals from Project metals deposition.

This document addresses the following:

A. Identification of the metals of concern to be addressed in the Analysis
B. Selection of the Wetland of Interest (WOI) for evaluation
C. Process for describing existing water quality in the WOI
D. Process for calculating the potential changes in metal concentrations in the WOI as a result of deposition
E. MPCA's process for assessing whether the potential changes in metal concentrations would be in compliance with applicable water quality standards
F. Overall conclusions
G. Recommendations for future monitoring

A. Identification of the metals of concern:

- The metals identified as "indicator metals" for the Analysis – copper, cobalt and arsenic – are the primary metals of concern in this analysis. It is reasonable to conclude that a demonstration of compliance with their applicable water quality standards in the WOI provides assurance that other metals will also be below standards.

    - The selection of these three indictor metals was based primarily on (a) their relative prevalence in NorthMet ore, and (b) the sensitivity of the water body to additional loading of that metal (i.e., the difference between existing background concentrations and the applicable water quality standard.)

    - Other metals that may be present in the ore either do not have applicable water quality standards against which to compare or have existing background concentrations significantly lower than applicable standards (e.g., nickel).

B. Selection of the Wetland of Interest for evaluation

- MPCA evaluated whether the WOI was the appropriate location to evaluate in this report or whether other surface water bodies, perhaps with lower loading rates but larger surface areas, would potentially be better candidates.

- Air modeling results show that the highest estimated sulfide mineral particle deposition per unit area occurred in the WOI watershed, excluding areas from which runoff is captured and treated. *See* Cross-Media Analysis § 4.1.

- A water balance analysis and hydrologic evaluation conducted on the WOI indicates that its estimated watershed yield (the proportion of precipitation that falls over the wetland's watershed that becomes wetland outflow) is similar to that of the Partridge River watershed as a whole, as determined during the EIS process. *See* Cross-Media Analysis § 3.4.3.

- Watershed yield is important for estimating the volume of water into which the metals potentially released from sulfide mineral particle oxidation would be mixed.

- Absent evidence that wetland-specific hydrologic and water balance analysis of other wetland watersheds near the Project (for which air modeling results show significantly lower sulfide mineral particle deposition per unit area) differ from the WOI, it is reasonable to conclude these other wetland areas would have similar hydrology to the WOI and would also have a watershed yield similar to that of the WOI and the larger Partridge River watershed.

- Since it is reasonable to conclude that the watershed yield for individual wetlands near the WOI are similar, it is also reasonable to conclude that the wetland having the highest estimated sulfide mineral particle deposition per unit area would have the highest potential metal concentrations. Using the WOI for the subsequent calculation of potential changes in metal concentration is therefore reasonable and appropriate.

- There are no wetlands or other water bodies adjacent to the Project to which more stringent water quality standards apply than what applies to the WOI. Using the WOI for subsequent evaluations is therefore representative in the context of comparing potential effects of sulfide mineral particle deposition against applicable water quality standards.

    - Potential effects on a downstream water body with more stringent water quality standards for arsenic and cobalt, Colby Lake, was evaluated and MPCA determined that the Project would not result in exceedance of its applicable water quality standards.

C. Process for describing existing water quality in the WOI:

- The analysis estimated existing WOI water quality for metal concentrations using data from monitoring station WP-1.

    - Water quality data for metals was not available from the wetland wells in the WOI. Instead, the average metal concentration of samples from a surface water sampling location on an unnamed creek (WP-1) flowing through a neighboring wetland complex was used to estimate background concentrations in the WOI.

    - This is the best data available and use of this data to estimate existing metal concentrations in the WOI is reasonable and appropriate.

- The estimated hardness value of the WOI (to be used in the calculation of the hardness-based water quality standard for copper applicable to the WOI) was calculated from an average of the specific conductivity values from all proximal wetland wells located in the same wetland type (alder thicket) and using an approximated conversion factor of: (Hardness = 0.48 Spec Cond).

    - The Analysis used 26 specific conductivity readings taken over three years at five wells in alder thicket wetlands in or adjacent to the WOI. Because no hardness data for the WOI exists, the Analysis averaged these 26 conductivity values to estimate the average hardness concentration of the WOI using the ratio identified above. The applicable Class 2D copper water quality standard for the WOI was then calculated using the average hardness value.

- This is an appropriate method to estimate the conductivity at the WOI. Even if the more limited data from the most restrictive individual wetland well were used for the estimation of average hardness in the WOI, the conclusions of the analysis would not change.

D. Process for calculating the potential changes in metal concentrations in the WOI as a result of deposition:

- The Analysis applied removal efficiency rates (i.e., long-term wetland sequestration rates) of 70% for cobalt and 90% for copper based on literature review and analog constructed wetlands. (No removal efficiency rate was applied to arsenic.)

  - The literature review focused on natural wetland systems impacted by atmospheric deposition and with environmental conditions similar to northern Minnesota and on analog constructed wetlands, particularly those at the Dunka Mine located near the NorthMet project.

  - These studies provide a reasonable basis to support the removal efficiency rates included in the Analysis.

- The Analysis estimated the potential changes in concentration of copper, arsenic and cobalt in the WOI using the total annual mass of each metal deposited to the WOI watershed divided by the total yield (annual flow) from the WOI and then adjusted by the wetland sequestration rates as discussed above.

  - The total annual mass of each metal was determined from the results of the air deposition modeling. Previous hydrologic modeling of the Partridge River above Colby Lake estimated that the average annual yield from the natural watershed is approximately 41% of precipitation. The hydrology of the WOI and its watershed indicates that a similar annual yield can be expected for the WOI, consistent with the findings of the Analysis.

  - MPCA relied on the incremental change identified in the Analysis in evaluating metals. Had the Analysis used the methodology described in Attachment 3, the increment would have been smaller than the one identified in the Analysis. Using the larger increment in subsequent comparisons with applicable water quality standards is protective.

- These calculations resulted in an increment of potential change in the concentration (in µg/L) of the indicator metals for the WOI.

E. MPCA's process for assessing whether the potential changes in metal concentrations would be in compliance with applicable water quality standards:

- MPCA utilized the methodology described in MPCA's "Guidance Manual for Assessing the Quality of Minnesota Surface Waters for Determination of Impairment: 305(b) Report and 303(d) List" (2016) for assessing whether the potential changes in metal concentrations in the WOI would be in compliance with water quality standards. Because the indicator metals, copper, cobalt and arsenic, are subject to aquatic life toxicity-based chronic water quality standards, MPCA followed the procedures in the Guidance Manual for evaluating toxic pollutants. Specifically, Section V.A.2 of the Guidance Manual states that "two or more exceedances of the chronic standard in three years is considered an impairment" and "one exceedance of the maximum standard is considered an impairment."

- MPCA's assessment process included the following:

- As stated in Item B above, an existing data set exists for sampling location WP-1 that is representative of the WOI; this includes sampling results for copper, cobalt and arsenic.
- The potential incremental change in metal concentration (in µg/L) calculated from the process described in Item C above was then added to the individual WP-1 sample results for copper, cobalt and arsenic thereby creating an "adjusted" dataset that reflects the potential additional contribution from deposition.
    - Adding the increment to the individual existing values maintains a consideration of the variability of water quality that is evident in the existing water quality data from WP-1.
- The "adjusted" data from the most recent three-year monitoring period was assessed as to whether there would be exceedances of the applicable water quality standard.
    - Monitoring results from the most recent three-year period includes those from approximately monthly sampling during spring, summer and fall months as well as results from winter sampling.
    - These are the most representative data available that best provides adequate representation of pollutant concentrations over the three-year time period and includes the time periods when exceedances are most likely to occur.

- The results of MPCA's assessment of the "adjusted" data set (that represents the potential additional contributions from the project) are as follows:
    - One of 24 values of the "adjusted" data set for copper exceeded the chronic water quality standard.
    - One of 24 values of the "adjusted" date set for cobalt exceeded the chronic water quality standard.
    - None of 24 values of the "adjusted" date set for arsenic exceeded the chronic water quality standard.
    - None of 24 values of the "adjusted" date set for any of the metals exceeded the maximum water quality standard.
- Based on these results, the MPCA determined that the WOI would remain in compliance with applicable water quality standards.

F. Overall conclusions

- MPCA staff concludes that the Analysis methods for determining the increment of potential change (including evaluation of existing concentrations, removal rates, and water yield) as applied to the concentration of copper, cobalt and arsenic in the WOI rely on the best available data and are reasonable. Staff also concludes that potential changes in metal concentrations would be greatest in the WOI and focusing this portion of the Analysis on the WOI is reasonable and protective.

- MPCA staff has determined that the estimated project concentrations (i.e., background concentration + calculated incremental increase) in the WOI for copper, cobalt and arsenic would remain in compliance with the applicable Class 2D Water Quality Standards.

- MPCA staff concludes that the assumptions on unknowns incorporated into the Analysis, including those related to the contribution of metal loading to the WOI from upland areas within the WOI watershed and the exposure of the deposited metal particles to oxidizing conditions for a full year prior to their removal to an anaerobic environment are protective.

- MPCA staff concludes that the project would not result in exceedance of downstream water quality standards in Colby Lake (where more stringent standards apply for arsenic and cobalt), since the average of the estimated project concentrations in the WOI for these two metals are below the Colby Lake standards. This conclusion was reached without accounting for the considerable mixing/dilution of the WOI outflow with downstream waters prior to Colby Lake.

- MPCA staff agrees with the calculation methods and the conclusions of the supplemental memorandum submitted by PolyMet's consultant (Barr Engineering Memorandum: "Estimated Potential Concentrations of Arsenic, Copper and Cobalt in the St. Louis River at Forbes, November 29, 2017") that due to the effects of dilution, potential changes in metal concentrations in the WOI would not result in any measureable changes to water quality downstream of the project in the St. Louis River at Forbes.

- MPCA staff concludes that the overall approach, assumptions, and methods for determining the potential change in the concentration of copper, cobalt and arsenic in the WOI provides protectiveness to the calculations and results (i.e., provide an overestimation of actual impacts).

- Finally, MPCA staff concludes that the adaptive management process described in the Analysis that would be implemented in the event that monitoring indicates unacceptable concentrations of metals in the WOI is reasonable and that the potential options for contingency mitigation identified in the Analysis are currently available and should be effective if employed.

G. Recommendations for Future Monitoring

- Given the uncertainties associated with the geochemical processes on which the calculation of potential changes in metals concentration were made, water quality monitoring of the WOI and downstream waters is recommended.

- Monitoring of wetland water quality in the WOI should include, at a minimum, sulfate, copper, cobalt and hardness to provide confidence that the Class 2D water quality standards for copper and cobalt will not be exceeded in the WOI as a result of the project.

    - Monitoring should be conducted at two locations in the WOI, one at or near existing monitoring location 36 in the northern portion of the wetland (closest to Mine Site sources of dust) and one in the southern portion of the wetland near its outlet to downstream wetland complexes.

    - Monitoring at each location should be conducted at least once every other month to address any seasonal variability, and should include, at a minimum, sulfate, copper, cobalt and hardness.

- Monitoring at each location should be conducted during facility operation and for approximately one year after operations cease. (Once operations cease, little dust containing metals, especially copper or cobalt, is expected to be generated.)

- If monitoring demonstrates that concentrations of copper and cobalt in the WOI are in compliance with their respective water quality standards, then it is reasonable to conclude that concentrations in surface waters downgradient of the WOI will also be in compliance with standards due to the effects of dilution.

- Monitoring of surface water monitoring station SW004a, located in the Partridge River downgradient of the WOI and upstream of Colby Lake, should include arsenic and cobalt to provide confidence that the Class 2Bd water quality standard for these metals in Colby Lake will not be exceeded as a result of the project. (Monitoring for arsenic and cobalt in Colby Lake itself is not as informative on project effects because non-project sources contribute arsenic and potentially cobalt to Colby Lake.)