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## **Technical Memorandum**

- To: Jane Reyer, Friends of the Boundary Waters Wilderness
- From: Ann Maest, PhD; Buka Environmental

Date: 14 March 2018

**Re**: Comments on PolyMet Mining's Cross-Media Report: Issues Related to Estimates of Metal Concentrations and Geochemical Behavior in the Wetland-of-Interest

### Introduction

The comments contained in this technical memorandum are presented on behalf of the Friends of the Boundary Waters Wilderness and are in response to the Draft 401 Certification for the NorthMet Project). I present a summary of my major findings and then discuss technical comments, including PolyMet Mining's conceptual model, missing or biased elements that underestimate concentrations, and the monitoring program for wetlands during mine operations. The focus of my evaluation is on hydrologic and geochemical processes and conditions related to the effects of dust on water quality.

## Summary of Major Findings

- <u>Baseline data for the wetland of interest (WOI) are severely lacking.</u> The only monitoring data available are wetland water levels and occasional specific conductance measurements. Important parameters for metals release include pH, hardness, metal, and dissolved organic carbon concentrations in the water; water inflows and outflows; metal and organic carbon content in the soils, and wetland stratigraphy. The use of an average specific conductance value from other wetlands to estimate the hardness of the WOI is unsubstantiated and should not be used to calculate hardness-dependent water quality criteria. Baseline data should be collected from the WOI and used to estimate the likelihood of water quality standard exceedences. Using actual baseline data, estimated water quality impacts from dissolution of Project mineral dust should then take the natural seasonal variability in water quality and hydrologic conditions into account.
- <u>PolyMet made a mistake by excluding nickel as an indicator metal in the cross-media</u> <u>analysis.</u> Nickel leaches preferentially from NorthMet ore and waste rock and is contained in non-sulfide minerals, especially olivine, which is abundant in the deposit and was not included in the cross-media analysis. Because the nickel water

quality standard is hardness-dependent, lower hardness values will result in lower calculated nickel water quality standards. The cross-media analysis should be redone adding nickel as an indicator metal.

- <u>Multiple-metals toxicity is not evaluated.</u> The NorthMet ore, waste, and tailings are known to leach multiple metals that are toxic to aquatic life at low concentrations, including copper, nickel, and cobalt. The effect of multiple metals on aquatic life toxicity is not adequately evaluated by comparing predicted individual metal concentrations to individual water quality standards. The additive effects of multiple metals on fish toxicity should be quantitatively evaluated as part of the cross-media analysis.
- <u>The cross-media analysis ignores the effects of organic carbon and seasonal</u> <u>hydrologic fluctuations on metal mobility and behavior.</u> Droughts, snowmelt, and metal-organic complexing can separately or in combination enhance the mobility, release, and export of metals, including methylmercury, from wetlands. Changes in wetland water levels can release previously stored sulfate, mercury, and other contaminants to downstream water systems, especially when coupled with increased atmospheric sulfate deposition. The effects of organic carbon in wetland waters and soils and seasonal flushing from wetlands needs to be more thoroughly evaluated when estimating the effects of dust on downstream water quality during mine operations.
- <u>Additional monitoring is needed.</u> To better understand and quantify the effects of atmospheric deposition on Project wetlands, additional environmental monitoring is needed before and during operations, including monitoring of more upstream locations at the Plant and Mine Sites; the organic carbon and metal composition of wetland soils and waters; and water levels, inflows, and outflows especially surrounding snowmelt and storms following extended dry periods.

## **Technical Comments**

#### 1. PolyMet's Conceptual model of Metal Transport from Mine Dust to Surface Water

The Cross-Media Report ("CMR"; Barr, 2017a) examines the effect of the NorthMet Project ("Project") air emissions on the water quality of a wetland at the mine site referred to as the wetland-of-interest (WOI). The wetland is an alder thicket. Alder thickets comprise only 12% of the Project wetlands by area, while 34% is coniferous bog or swamp, 14% is black spruce bog, and 10% is tamarack bog (PolyMet Mining, 2006, Table 4). However, according to the results of the air deposition model, the WOI is predicted to receive the highest deposition of sulfide mineral dust (CMR, Large Figure 7) and the largest atmospheric loads of sulfate (CMR, Large Figure 10) during mining.

Important geochemical and hydrologic elements of PolyMet's conceptual model include the following:

- The only minerals considered to be dissolving from Project dust are pyrrhotite and chalcopyrite.<sup>1</sup> Other sulfide minerals known to occur in the ore, waste rock and tailings were not explicitly included in the analysis, and metal release from silicate minerals was excluded completely. In their analysis, PolyMet assumes that all sulfide minerals containing copper behave like chalcopyrite, and other sulfide minerals that do not contain copper behave like pyrrhotite. They further assume that all "pyrrhotite" minerals dissolve completely in one year using a shrinking core model (CMR, p. 99), which would release the sulfur and all the arsenic and cobalt (CMR, Appendix B, p. 20) evenly throughout that year. For the "chalcopyrite" mineral release, an estimated chalcopyrite dissolution rate at pH 3 is used for the first year of weathering (CMR, p. 100), but weathering is only allowed for one year (particles are assumed to be buried and unavailable for weathering after one year; CMR, Appendix D, p. 1), and 90% removal of copper is assumed in the wetland. As a result, Project copper concentrations are not predicted to exceed water quality standards in the WOI (DMR, Table 4-10).
- The only elements of concern evaluated for their water quality impacts are sulfur, arsenic, cobalt, and copper. These "indicator metals" were included "because of their relationship with sulfur in the NorthMet ore and waste rock, and the potential release of those metals from dust deposited in wetlands due to the Project and their effect on wetland water quality" (CMR, p. 19). The indicator metals selected and rejected were discussed in the CMR, Section 2.3.3 (starting on p. 19). The metals were evaluated based on: (1) relative prevalence of elements in the sulfide minerals in the NorthMet ore; (2) relevance to compliance with applicable numeric WQS; and (3) existing water quality data in waterbodies within the Project airshed (CMR, p. 20). The only metal considered but rejected as an indicator metal was nickel. It was excluded because of the difference between its baseline concentration (1.18  $\mu$ g/L at SW004a), the fact that the lowest applicable water quality standard for the Partridge River downstream of the Mine Site (52  $\mu$ g/L), and the lower concentration of nickel in dust from ore and waste rock relative to copper, which was included as an indicator metal (CMR, p. 23). The effect of hardness on the nickel water quality standard was ignored in PolyMet's selection of indicator metals.
- The WOI is assumed to have no infiltration to groundwater and no outlet to a stream. The water balance simulation used water levels measured in well 36, which is located in the WOI. The model results were calibrated to measured water levels

<sup>&</sup>lt;sup>1</sup> Pyrrhotite is an iron sulfide mineral similar to pyrite but that dissolves more rapidly; it is the most common iron sulfide mineral in the NorthMet deposit; chalcopyrite is a copper-iron sulfide.

for the period of record (July 3, 2014 to October 22, 2016), which did not include a drought period.

#### 2. Missing or Biased Elements in PolyMet's Conceptual Model

a. Lack of Baseline Monitoring Data

#### Water Quality

According to the CMR, the factors affecting mineral weathering rates in wetlands include the redox state of the water, dissolved oxygen,  $Fe^{3+}$ , temperature, and pH (CMR, App. D, p. 7). With the exception of occasional specific conductance and pH measurements in the WOI well (Well 36) and other Project wetland wells (CMR, Appendix C), no wetland chemistry data were collected for Project wetland waters or soils. Field samplers obviously visited the many wetland wells to measure their water levels on a regular basis, but samples of surface water in the wetlands were either not collected or are not reported. During the time that groundwater level data were collected, the Cross-Media analysis was being conducted. Many opportunities existed for collecting wetland surface water samples. Instead, the analysis of the potential water quality impacts of Project dust on wetland and downstream surface water hinges on a poorly substantiated equation that relies on surrogate data from groundwater rather than surface water in the WOI. I found no discussion of possible differences between wetland groundwater and surface water, although the assumption that the surface water in the WOI does not drain to the regional aquifer suggests that groundwater and surface water quality would differ. The longer residence time of groundwater could increase the specific conductance of groundwater relative to wetland surface water.

Appendix G of the CMR describes how total hardness was estimated from specific conductance using an equation from the Minnesota Pollution Control Agency (MPCA):

Total Hardness (mg/L) = 0.48 x Specific conductivity ( $\mu$ S/cm). An r<sup>2</sup> value of 0.96 is given, but the underlying data for derivation of this equation are not provided in the CMR or elsewhere in the Project documents.

The specific conductance values used to arrive at an average hardness of 60 mg/L for the Cross-Media analysis are provided in Appendix G of the CMR (Table 1). Only six of the data points are from the well in the WOI (Well 36). In addition, one of the values from Well 33 appears to be an outlier (333  $\mu$ S/cm). Of the five wells included in the average, the WOI well, Well 36, had the lowest specific conductance on two of the six dates, and values were lower than three of the six wells on two other dates. If average hardness was calculated using *only* Well 36 data, the hardness would be substantially lower: 42 rather than 60 mg/L. The lowest calculated hardness for Well 36 is only 19.2 mg/L. Because the water quality standards for copper and nickel are hardness-dependent, the lower hardness results in lower water quality standards, as shown in Table 1. If the average estimated hardness for the WOI Well 36 is used but all other assumptions remain the same, calculated copper concentrations in the WOI under dilute conditions would exceed the water quality standard,

even assuming 90% copper removal in the wetland (estimated Project concentrations are 3.6 and 3.9  $\mu$ g/L; see CMR, Table 4-10). If the 90% removal rate is not included, the highest Project concentrations would be 6.55  $\mu$ g/L, which exceeds all copper standards in Table 1. The calculation of wetland coper concentrations is an annual average and does not take seasonal variability in hydrology or water quality into consideration. Estimated water quality impacts from dissolution of Project mineral dust should but does not take these important natural seasonal variabilities into account.

Table 1. Water qualit	ty standards for $\phi$	copper and nickel	using hardness value	es estimated
using specific conduc	tance and the N	IPCA equation.		
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	Specific		Copper	
	Conductance	Hardness, MPCA	standard	Nickel standard
	(µS/cm)	equation <sup>a</sup> (mg/L)	(µg/L)	(µg/L)
Cross-Media analysis, average of five wells (n=26 <sup>b</sup> )	125	60.0	6.0	34
Average, Well 36 (n=6)	87	41.8	4.4	25
Minimum Well 36 (n=6)	40	19.2	2.3	13

n = number of samples available

a Total Hardness (mg/L) = 0.48 x specific conductivity ( $\mu$ S/cm)

b Two measurements were surrogates collected on different dates than samples for the other five wells.

#### Hydrologic conditions

No direct measures of wetland *surface water* hydrology, including seasonal wetland water inflow and outflow, have been taken. In fact, the location of the WOI outlet is highly uncertain, and it is unclear if wetland water connects to the Partridge River (CMR, Appendix C, p. 4-5). Choosing a WOI that does not directly connect to a stream underestimates the water quality effects of Project dust on downstream water quality. The western part of the WOI watershed does drain to the unnamed creek from the West Pit.

The CMR assumes that water from the WOI does not infiltrate to the regional groundwater aquifer or to a stream (CMR, Appendix C, p. 7). According to Minnesota Board of Water and Soil Resources (Eggers and Reed, 2011), alder thickets in Minnesota are on peat and underlain by alluvial material that can drain to groundwater. Wetlands with wells terminating in sand have reduced capillarity, and the water table drops quickly when precipitation drops, especially during a drought (Barr, 2010, p. 22). The stratigraphy for the WOI is not presented in the Project documents. During the extended drought in July and August 2007, water levels in many of the wetland wells dropped below the wetland threshold level (12 inches below ground surface), as shown in Figure 1.

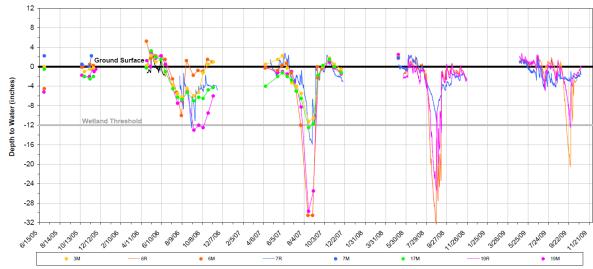


Figure 1. Wetland hydrology monitoring data for wells in the southwest mine site area from 2005 - 2009.

Source: Barr, 2010, Figure 10.

A water balance model was created for the WOI, and a calibration was run for the period 2014 to 2016 using the available water level data for Well 36. As shown in Figure 2, the modeled water levels underestimate measured maximum and minimum water levels in the WOI well. In 2014, the model underestimated water levels by over 10 inches, crossing the wetland threshold, and in late summer 2015 and 2016, the model overestimated water levels when levels were actually lower than the wetland threshold. The calibration period does not include the drought period in 2007 (CMR, Appendix C, Figure C-4). A calibration should have been run that included this drought period, using data from wetlands that were monitored during and after the drought, to evaluate how the model performs under extreme conditions that may become more common in the future with climate change. The model was used to estimate outflow from the WOI that was in turn used to estimate the potential for flushing metals and sulfur from the wetland to downgradient areas. Given the relatively poor calibration during high and low wetland water levels, a high degree of uncertainty exists in those estimates. This is especially important because the majority of particulates and metals are exported from wetlands during periods of high flow following snow melt, as discussed in the following section.

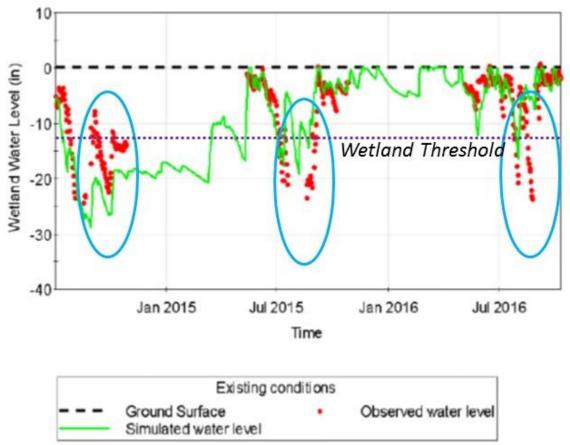


Figure 2. Water balance model results plotted against measured water level data for the WOI (Well 36) from 2014 to 2016.

Source: CMR, Appendix C, Figure C-4; wetland threshold and circles of interest added.

b. Climatic, Hydrologic, and Geochemical Processes and Conditions Ignored and Effects on Water Quality

## The Effects of Droughts and Fluctuating Wetland Water Levels on Metal Retention and Water Quality

Appendix D of the CMR discusses the fate of sulfide mineral particles in wetlands (Barr, 2017c) and states that drought conditions do not occur often (CMR, Appendix D, p. 5). However, droughts will likely occur more frequently with climate change. And when they do occur, groundwater elevations will drop, conditions will become more oxidizing, and metals will be released (Szkokan-Emilson et al., 2013). Barr (2017c) states in one part of the appendix that the Szkokan-Emilson et al. (2013) study relates well to the Project (CMR, App. D, p. 8); in a later section (ibid, p. 67), it emphasizes that 99.9% of the Cu and Co were retained, "with only a small percent of the atmospheric load exported from the watershed." However, the Szkokan-Emilson et al. (2013) study of two peatlands affected by sulfur and metal aerial deposition found that following a drought period, "there was a decline in pH and a large increase in concentrations of sulfate and metal ions (Al, Co, Cu, Fe, Mn, Ni, and Zn) in water draining both peatlands, with extreme concentrations occurring over a period

of about two weeks." Szkokan-Emilson et al. (2013) further note that in the peatland with higher organic matter content, metals that bind strongly to dissolved organic carbon (DOC) (Al, Cu, Fe) had concentration increases at the onset of drought, indicating that drought conditions oxidize the organic carbon in the peat and mobilize pollutants. These very relevant findings were not mentioned in Barr (2017c), even though it is the main tenant of the Szkokan-Emilson et al. article, and they found that the research "relates well to the Project." Unlike the WOI work, the composition of the two peatlands, the behavior of metals and DOC, and linkages of geochemical behavior with hydrology were well characterized in the Szkokan-Emilson et al. (2013) research. In addition to the metals released in the Szkokan-Emilson et al. (2013) study, which examined many of the metals of interest for the NorthMet site, methylmercury (MeHg) was also released during drought conditions.

Appendix F of the CMR (Barr, 2017b) evaluates the potential for export of sulfate and MeHg from the WOI during operations. The author spends five pages discussing the effects of drought and fluctuating water levels on the potential increased export of sulfate and mercury and concludes (p. 11-12):

Overall, the estimated potential export of SO4 and MeHg from the Wetland of Interest during Project operations is likely to be similar to, but not higher than, background wetlands... the potential export of SO4 and MeHg [from other Project wetlands] is expected to be the same as background wetlands and likely no different with the Project in operation as occurs now in existing conditions.

This conclusion runs exactly counter to conclusions from an article that Barr (2017b) cites frequently and that addresses the effects of fluctuating water levels and increased sulfate deposition on sulfate and mercury cycling (Coleman Wasik et al., 2015):

Hydrologic fluctuations not only serve to release previously sequestered sulfate and Hg from peatlands but may also increase the strength of peatlands as sources of MeHg to downstream aquatic systems, particularly in regions that have experienced elevated levels of atmospheric sulfate deposition.

The earlier Coleman Wasik et al. (2012) article also emphasizes that when sulfate deposition and MeHg production are linked: when deposition is higher, MeHg levels are higher, and when sulfate deposition is reduced, MeHg levels in biota are also reduced. The findings from both Coleman Wasik et al. articles strongly imply that increase sulfur deposition from Mine and Plant Site emissions will increase the production and export of MeHg in and from site wetlands during operations, especially during times of fluctuating water levels.

The Barr (2017b) review mentions snowmelt briefly on p. 3 in terms of its effect on raising water levels in wetlands but completely ignores the effect of snowmelt on the export of sulfate, mercury, and metals from the WOI. Snowmelt has a marked effect on the export of

constituents and particles in wetlands. Snowmelt will enhance the movement of particulate metals from wetlands to streams and lakes in the spring (e.g., Scherbatskoy et al., 1998), and particulate concentrations are highest during these times. Hambly (1996) studied the behavior of nickel in a wetland receiving mine drainage and smelter emissions. He also found that, although the wetland examined efficiently retained nickel during most of the year, the export of nickel increased during periods of peak runoff, including in the spring and after heavy rains.

#### The Effects of Organic Carbon on Metal Mobility and Wetland Water Quality

The effect of total organic carbon (TOC) in wetland soils and dissolved organic matter (DOM) or dissolved organic carbon (DOC) in wetland, stream, and lake waters was ignored in the cross-media analysis. As noted previously, scarce wetland water quality information was collected, which did not include the DOC content of wetland waters or the organic carbon content of wetland soils. The Wetland Hydrology Monitoring Report (Barr, 2010) shows a Forest Service map of the extent of "lowland organic acid to neutral soils" (yellow areas in Figure 3), but only on the Mine Site; areas outside the Mine Site, including the WOI, were not mapped. The organic soils inside the Mine Site are extensive, as shown in Figure 3, suggesting that streams receiving drainage from those wetlands likely have elevated DOC concentrations at certain times of the year.

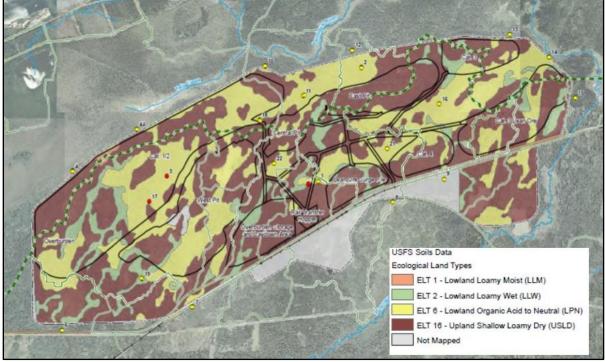


Figure 3. U.S.D.A. Forest Service map of soil types on the Mine Site.

Source: Barr, 2010, Figure 2.

The available information on TOC/DOC concentrations in area groundwaters and surface waters indicates that wetlands are contributing important amounts of organic carbon to water resources at the Mine and Plant Sites. DOC was measured in four baseline surficial aquifer locations (FEIS (MDNR et al., 2015); Table 4.2.2-22) and wells downgradient of the existing LTVSMC tailings area on the Plant Site (see FEIS, Table 4.2.2-6 for groundwater summary and Tables 4.2.2-12 – 4.2.2-15 for surface water summary). The measured DOC concentration in the four baseline groundwater samples ranged from <0.05 to 7.4 mg/L with a mean of 2.8 mg/L (FEIS, Table 4.2.2-22). The higher values suggest that DOC can be an important component of at least shallow groundwater in the area.

Wells downgradient of the existing LTVSMC tailings basin had high concentrations of TOC (from unfiltered samples), ranging from 5.4 to 25.5 mg/L with a mean of 13.5 mg/L (FEIS, Table 4.2.2-24). Elevated TOC concentrations were also found in seeps (FEIS, Table 4.2.2-13; up to 18.5 mg/L) and an unnamed creek in the tailings basin area (FEIS, Table 4.2.2-36; up to 23 mg/L), and in Trimble Creek (FEIS, Table 4.2.2-37; up to 33.7 mg/L) and Mud Lake Creek (FEIS, Table 4.2.2-38; up to 48 mg/L) in the Embarrass watershed. These high TOC concentrations are likely to enhance the movement of certain metals released in tailings leachate.

The FEIS noted the importance of DOC on the transport of mercury (p. 4-42): The MDNR has additionally conducted numerous research studies regionally and in the St. Louis River watershed specifically. The river and its tributaries frequently have mercury concentrations that exceed the 1.3 ng/L standard, especially in the weeks following major storm events. The vast majority of the mercury carried in the river is bound to dissolved organic carbon that is derived from wetland areas and riparian soils (summarized in Berndt et al. 2014).

Organic carbon can enhance the dissolution of mercuric sulfide but also inhibit its precipitation (Ravichandran, 2004). The presence of humic materials (common in wetlands) can enhance the dissolution of Cu sulfides and release copper and nickel from contaminated muds even under reducing conditions (Lehman and Mills, 1994; Lockwood et al., 2015). Grybos et al. (2007) showed that even though iron oxyhydroxide dissolution (under reducing conditions in a wetland) is important in the mobilization of metals from wetlands, the release of organic matter from soils is even more important. They found that cobalt release was more controlled by the dissolution of iron oxyhydroxides, while nickel release was controlled by reductive and organic matter mobilization processes. The myriad effects of organic matter on retaining and releasing NorthMet Project metals of concern from dust and emissions deposited in wetlands has been largely ignored in the cross-media analysis. Additional sampling and evaluation is needed before the effects of dust on wetland and downstream or downgradient water quality can be fully or reasonably evaluated.

# a. Analysis Ignores Nickel as a Primary Contaminant of Concern and Inputs from Non-Sulfide Minerals

The analysis of indicator metals in the CMR (Section 2.3.3) ignores the relative potential for leaching of nickel vs. copper, the effect of hardness on the nickel water quality standard, and the enhanced effect of multiple metals on fish toxicity. One of the stated reasons that nickel was excluded as an indicator metal was its lower concentration in dust from ore and waste rock relative to copper (CMR, p. 23). Although this is generally true, the mean concentration of nickel in Category 1 waste rock is higher than that of copper, and maximum concentrations are the same, as shown in Table 2.

		Category 1 (n=38)		Category 2/3 (n=25)		Category 4 (Duluth Complex; n=16)		Ore (n=3)	
Constituent	Units	Mean	Max	Mean	Max	Mean	Max	Mean	Max
Copper	%	0.025	0.095	0.084	0.295	0.088	0.152	0.360	0.422
Nickel	%	0.032	0.095	0.035	0.072	0.034	0.071	0.106	0.139
Cobalt	ppm	57	117	51	11-94	60	119	83	94
Total Sulfur	%	0.05	0.12	0.29	0.59	1.44	4.46	0.87	0.90

Table 2. Whole rock and %S summary results for some key constituents in waste rock and ore.

Source: PolyMet Mining, 2017, Table 2-2.

More important than the relative concentrations of copper and nickel in NorthMet ore and waste, nickel leaches at higher concentrations than copper from these materials. Instead of using the voluminous leachate data for the Project, the CMR assumes that the mass of metals released (leached from the dust) is related only to the metal:sulfur ratio in the solid sulfide (CMR, p. 49 and Appendix B). The problem with this assumption is that it does not account for preferential leaching of one metal over another and does not account for metal releases from non-sulfide minerals. Additionally, it excludes metal release from metal sulfate salts that will form in the wetland from oxidation of the sulfides. Figure 4 shows the leachate concentrations from an experiment aimed at estimating metal release rates from the Category 1 waste rock. Figure 5 shows leachate concentrations of copper, cobalt, and nickel from the AMAX test piles with sulfur percentages similar to Category 4 waste rock. As noted in the CMR, while not from the NorthMet Project, the material is from the Duluth Complex and the same intrusion that hosts the NorthMet deposit (CMR, Appendix B, p. 13). For both lower and higher sulfide percentages, nickel leachates at higher concentrations than copper for Duluth Complex materials. The same increased leaching of nickel over copper was found for seepage from the Dunka Road stockpiles as well (Minnesota Division of Natural Resources, Division of Ecological & Water Resources. Electronic data deliverable. March 2014).

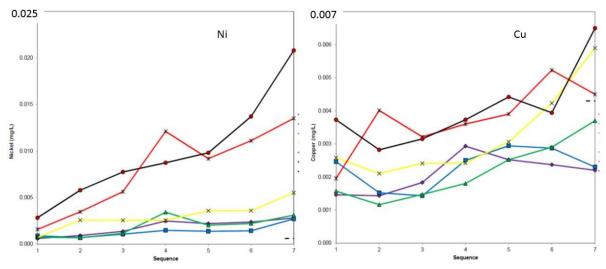


Figure 4. Leachate concentrations of nickel (Ni) and copper (Cu) (mg/L) in sequential leach tests on Category 1 waste rock.

Source: PolyMet 2015a, Attachment B. (Waste Characterization Data Package).

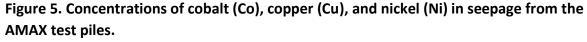
The indicator metals included in the cross-media analysis are reasonable to include, and nickel should be added to the list. The effects of multiple-metal toxicity to aquatic life should also be evaluated for all indicator metals (including nickel) because of their presence in wetlands during operations and their potential to be exported from wetlands to downstream surface water bodies. Examining the modeling concentrations relative to individual metal water quality standards will not capture the additive effects of multiple-metal toxicity (see, e.g., Playle, 2004).

The sulfur, copper, arsenic, and cobalt content of sulfide minerals used in the cross-media analysis is shown in Table 3a as weight percentages (left side of table). Using the same approach, the mean concentrations of nickel in Project sulfide minerals is listed in Table 3b; the nickel content of the two most nickel-bearing silicate minerals, olivine and biotite, is also included in Table 3b.

The minerals in mine dust from waste rock, ore, and tailings will be largely silicates, some of which contain metals. In general, the sulfide content of ore, waste rock, and tailings is <1% and the remaining ~99% is predominantly olivine and feldspars. This source is completely ignored in the cross-media analysis, which does not follow results from PolyMet's waste characterization analysis. For example, nickel is known to occur in olivine in the NorthMet deposit. Olivine is the main source of cobalt and the second most important source for nickel according to the waste characterization data report; further, olivine is a more important source for nickel in different waste categories (PolyMet Mining, 2015b, p. 65):

The nickel content of the Duluth Complex Category 4 rock is understood to be almost entirely from sulfide minerals, while lower-sulfur rock categories contain more nickel in olivine.

According to the approach used to derive non-acidic release rates for waste rock (PolyMet, 2015b, Large Table 2), nickel in Category 1, 2/3, 4 waste rock and in ore derives from sulfide minerals and olivine, cobalt derives from olivine, while sulfate derives from chalcopyrite and pyrrhotite in Category 1 waste rock and from chalcopyrite, pyrrhotite, and pentlandite in Category 2/3 and 4 waste rock and ore. Yet in the cross-media report approach, cobalt is assumed to be derived entirely from sulfide minerals (CMR, Appendix B, Table 2-1). The results from the waste characterization work (PolyMet, 2015b) argue strongly for including nickel as an indicator metal and for including olivine and possibly biotite in mineral dust as part of the cross-media analysis. If these are included in the analysis, the impact of olivine and potentially biotite weathering on nickel and cobalt concentrations in wetlands and downstream surface waters must also be examined.





8/28/1976 5/25/1979 2/18/1982 11/14/1984 8/11/1987 5/7/1990 1/31/1993 10/28/1995 Data source: Minnesota Division of Natural Resources, Division of Ecological & Water Resources. Electronic data deliverable. March 2014.

Sulfide Minerals	Mineral Formula	S	Cu	As	Со	Category 1	Category 2/3	Category 4	Ore
Pyrrhotite	Fe <sub>(1-x)</sub> S (x=0 to 0.2)	37.67	(0.040)	(0.031)	(0.064)	28	54	79	38
Chalcopyrite	CuFeS2	34.94	34.63	(0.030)	(0.038)	51	24	11	43
Bornite	Cu₅FeS₄	25.56	63.31	(0.030)	(0.023)	2	-	-	
Covellite	CuS	33.54	66.46			1	-	-	
Cubanite	CuFe <sub>2</sub> S <sub>3</sub>	35.44	23.41	(0.030)	(0.107)	8	4	-	3
Pentlandite	(Fe,Ni)₀S <sub>8</sub>	33.23	(0.35)	(0.031)	(2.32)	8	6	9	16
Mackinawite/ Valleriite	(Fe,Ni)S <sub>0.9</sub>	33.79				1	4	-	
Sphalerite	(Zn,Fe)S	33.06	(0.103)	(0.030)	(0.111)	-	8	1	

Table 3a. Mean sulfur and metal weight percentages in sulfide minerals and percent of total sulfide mineral accounted for by the listed minerals in waste rock and ore.

Chemistry in parentheses are determined from e-probe (RS42, Appendix D.3). Mean abundances for waste rock types (Categories 1-4) are summarized from RS42, Appendix D.1 Mean abundances for ore are summarized from Table 7 of SGS (2006).

Source: CMR, Appendix B, Table 2-2.

Table 3b. Mean percent nickel in Project sulfide minerals and silicate minerals. The silicate minerals listed are olivine and biotite.

Sulfide or Silicate Mineral	%Ni
Pyrrhotite	0.22
Chalcopyrite	0.057
Bornite	0.085
Cubanite	0.94
Pentlandite	32
Olivine (Mg <sup>2+</sup> , Fe <sup>2+</sup> ) <sub>2</sub> SiO <sub>4</sub>	0.077
Biotite K(Mg,Fe) <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	0.057

Source: SRK, 2007, Table 5-1. Note: Ni percentages are not listed for covellite, mackinawite/vallerite, or sphalerite in this table.

#### 3. Important Wetland and Downstream Monitoring Elements

Many elements are missing from the wetland and downstream monitoring program that would allow for a more complete understanding of the release and movement of metals from wetlands in the Project area. Stream monitoring locations should include headwaters areas above SW-004a on the Partridge River, including Yelp Creek, and the entire length of Second Creek.

The following analytes should be measured in wetland soils and waters before, during, and after operations:

- <u>Wetland soils:</u> total organic carbon, mineralogy (especially iron oxyhydroxide and manganese coatings), total metal content, and metal associations (e.g., carbonates, iron oxyhydroxides, humic materials).
- Wetland and stream waters and shallow groundwater: total suspended solids (especially in wetland outflow); major cations and anions and hardness; dissolved and total metal concentrations at least monthly and more frequently shortly after snowmelt, after storms following extended dry periods, and during droughts (iron, nickel, copper, cobalt, arsenic, mercury, methylmercury, zinc at a minimum); dissolved organic carbon; nitrogen (nitrate/nitrite, ammonia); alkalinity; and field measurements (pH, specific conductance, temperature, Eh, dissolved oxygen).
- <u>Hydrology</u>: Ongoing measurements of depth to water; inflow, outflow locations and flows; more frequent water level measurements, especially surrounding snowmelt, droughts, and storms following dry periods.

### **References Cited**

Barr, 2010. Wetland Hydrology Monitoring Report, 2007 – 2009, NorthMet Project. Prepared for PolyMet Mining Inc. March.

Barr, 2017a. Cross-Media Analysis to Assess Potential Effects on Water Quality from Project-Related Deposition of Sulfur and Metal Air Emissions: An Analysis Conducted in Support of the NorthMet Project Section 401 Certification Request. Prepared for PolyMet Mining, Inc. October 31.

Barr, 2017b. Memorandum: Cross-Media Water Quality Analysis: An Assessment of Potential Increased Export of Sulfur and Methylmercury from Wetlands Receiving Atmospheric Inputs of Sulfate from the Project. Prepared for Christie Kearney, Poly Met Mining Inc. by Cliff Twaroski. October 25. (Appendix F of Barr, 2017a Cross-Media Report).

Barr, 2017c. Memorandum: Potential Fate of Sulfide Mineral Particles in Wetlands. Prepared for PolyMet Mining Inc. by Edward A. Nater. June 14. (Appendix D of Barr, 2017a Cross-Media Report)

Coleman Wasik, JK, Mitchell, CPJ, Engstrom, DR, Swain, EB, Monson, BA, Balogh, SJ, Jeremiason, JD, Branfireun, BA, Eggert, SL, Kolka, RK, and Almendinger, JE. 2012. Methylmercury declines in a boreal peatland when experimental sulfate deposition decreases. *Environ. Sci. Technol.* 46, 6663–6671. Available: https://www.fs.fed.us/nrs/pubs/jrnl/2012/nrs\_2012\_colemanwasik\_001.pdf

Coleman Wasik, JK, Engstrom, DR, Mitchell, CPJ, Swain, EB, Monson, BA, Balogh, SJ, Jeremiason, JD, Branfireun, BA, Kolka, RK, and Almendinger, JE. 2015. The effects of hydrologic fluctuation and sulfate regeneration on mercury cycling in an experimental peatland. *J. Geophys. Res. Biogeosci.*, 120, 1697–1715. Available: http://onlinelibrary.wiley.com/doi/10.1002/2015JG002993/full#abstract

Eggers, SD and Reed, DM. 2011. Alder Thickets. In: Wetland Plants and Plant Communities of Minnesota and Wisconsin. Third Edition, October. U.S. Army Corps of Engineers, Regulatory Branch, St. Paul District. Available:

http://www.bwsr.state.mn.us/wetlands/delineation/WPPC\_MN\_WI/Vb%20AlderThickets.p df

Grybos, M, Davranche, M., Gruau, G and Petitjean, P. 2007. Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxides reduction? *Journal of Colloid and Interface Science* 314:490–501.

Lehman, RM and Mills, AL. 1994. Field evidence for copper mobilization by dissolved organic matter. *Water Research* 28 #12, 2487-2497.

Lockwood, CL, Stewart, DI, Mortimer, RJG, Mayes, WM, Jarvis, AP, Gruiz, K., and Burke, IT. 2015. Leaching of copper and nickel in soil-water systems contaminated by bauxite residue (red mud) from Ajka, Hungary: the importance of soil organic matter. *Environ Sci Pollut Res* 22, p. 10800-10810.

Minnesota Department of Natural Resources (MDNR), United States Army Corps of Engineers, and United States Forest Service. 2015. NorthMet Mining Project and Land Exchange. Final Environmental Impact Assessment (FEIS). November.

Myrbo, A, Swain, EB, Johnson, NW, Engstrom, DR, Pastor, J, Dewey, B, Monson, P, Brenner, J, Dykhuizen Shore, M, and Peters, EB. 2017. Increase in nutrients, mercury, and methylmercury as a consequence of elevated sulfate reduction to sulfide in experimental wetland mesocosms. *Journ Geophy Res: Biogeosciences*. Available: <u>http://onlinelibrary.wiley.com/doi/10.1002/2017JG003788/pdf</u>

Playle, RC, 2004. Using multiple metal–gill binding models and the toxic unit concept to help reconcile multiple-metal toxicity results. *Aquatic Toxicology* 67 #4, 359-370.

PolyMet Mining, 2006. Wetland Delineation Report. November.

PolyMet Mining, 2017b. Permit to Mine Application, NorthMet Project. Appendix 2. Mine Waste Characterization Documentation and Results.

PolyMet Mining, 2015a. NorthMet Project. Waste Characterization Data Package, v. 12. Prepared by Barr Engineering Co. Feb. 13.

PolyMet Mining, 2015b. NorthMet Project. Water Modeling Data Package, Volume 1 – Mine Site. Version 14. February 27. Prepared by Barr Engineering Co.

Ravichandran, M. 2004. Interactions between mercury and dissolved organic matter—a Review. *Chemosphere* 55 #3, 319-331.

SRK Consulting, 2006b. NorthMet Project. Tailings and Hydromet Residue Testwork – Update on Sample Selection from 24 Hour Testwork. Memo from Stephen Day to Jennifer Engstrom, MDNR. January 6.

SRK Consulting, 2007a. RS53/RS42 – Waste Rock Characteristics/Waste Water Quality Modeling - Waste Rock and Lean Ore – NorthMet Project – DRAFT. February/Draft 01, March 9, 2007.

SRK Consulting, 2007b. RS54/RS46 – Waste Water Modeling – Tailings. NorthMet Project – DRAFT. Prepared for PolyMet Mining Inc. July 20.

Szkokan-Emilson, E.J., B. Kielstra, S. Watmough, and J. Gunn. 2013. Drought-induced release of metals from peatlands in watersheds recovering from historical metal and sulphur deposition. *Biogeochemistry* 116: 131-145. Abstract available:

https://www.jstor.org/stable/24716789?seq=1#page\_scan\_tab\_contents