# Scaling Laboratory Sulfate Release Rates to Operational Waste Rock Piles

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## ABSTRACT

There is little agreement on scaling factors to be used for extrapolating laboratory dissolution test results for predicting solute release rates from proposed waste rock piles in the field. The scaling factor for a given solute is the ratio of its release rate in the field to that observed in the laboratory, and its magnitude is dependent on both the solute and site-specific variables. Scaling factors for sulfate release rates from Duluth Complex rock of moderate sulfur content were determined empirically by comparison of laboratory rates to field rates. The laboratory rates were calculated based on sulfate release during weeks 6 to 71 observed for 17 blast hole samples with sulfur contents of 0.18 to 1.64 percent. The samples were collected from the mine site from which comparative field data were generated. Annual field rates were determined over a period of 3 to 13 years for five waste rock piles, ranging in mass from 2,000,000 to 15,000,000 tons, with estimated sulfur contents of 0.24 to 0.97 percent. Laboratory and field rates were expressed per unit mass sulfur. Comparison of 17 laboratory rates and 42 annual field rates yielded in 714 distinct calculated scaling factors. These values were fit to a beta distribution for which the mean and standard deviation were 0.127 and 0.083, respectively.

**Keywords:** mine waste rock, mine drainage, environmental review, mine waste drainage quality prediction, laboratory scaling

## INTRODUCTION

Environmental review for proposed operations requires predicting solute release from mine waste storage facilities. Such predictions can be informed by operational phase data from mine wastes of similar composition, disposed in similarly constructed facilities, and weathering under similar climatic conditions. Such information from "analog" sites is often not available. Consequently predictions are based on the scaling of laboratory data to field conditions. The magnitude of such scaling will depend on the solute being scaled, drainage pH, rock type, rock composition, method of laboratory rate generation (e.g. humidity cells vs. column tests), method of field rate generation (e.g. test plots vs. full scale storage facilities), and reaction environment variables in both the laboratory and field (e.g. temperature, leachate to rock ratio, oxygen availability). Consequently, it cannot be assumed that scaling factors quantified will be universal.

### Previous Studies

Two approaches have been used for scaling laboratory rates to the field, the first of which applies scaling factors for individual mechanistic factors to account for differences such as rock composition, reaction environment, and solute transport. Considerable data and analysis for this approach was generated by studies focused on waste rock piles containing two varieties of both gneiss and schist in northern Sweden (Strömberg & Banwart, 1994; Strömberg et al., 1994; Strömberg & Banwart 1999a; Strömberg & Banwart 1999b). Apparent rates of pyrite, chalcopyrite, biotite, and plagioclase weathering in the field were found to be roughly 0.01 to 0.2 times those derived from laboratory batch tests on six different particle size fractions (Malmström et al., 2000). A "scale-dependence model" accounted for the differences between field and laboratory rates using quantitative contributions of particle size, temperature, pH, and hydrologic variables affecting solute transport.

Kempton (2012) included these factors as well as moisture content and pore gas oxygen concentration in a literature review of scaling factors for solute release from waste rock. This is less detailed consideration than that of scaling mineral dissolution rates but is adequate for application to predicting solute release from waste rock. He concluded that prediction of solute release rates based on reported ranges of scaling factors would have a high degree of uncertainty. For example, he stated that waste rock particle size distribution and its relationship to hydrologic factors affecting solute transport produced a scaling range covering a factor of 7.5.

A second approach is that of empirically determining scaling factor based on comparison of laboratory and field rates for the rock in question. Wagner et al. (2006) compared sulfate release rates from mafic and feldspathic gneiss in a northern Saskatchewan test pile (8 x 8 x 5 m high) to those derived from laboratory dissolution tests on five different size fractions of the rock (Hollins et al., 2001). Sulfate release rates (normalized for surface area) in the field were 0.3 times those observed in the laboratory, suggesting that factors such as temperature and solute transport limited sulfate release in the field. There were no humidity cell data for the typical -0.25-inch fraction used in humidity cell tests to calculate a scaling factor directly from this test to the test pile.

Shaw & Samuels (2012) conducted paired humidity cell and 30-gallon barrel tests on three porphyritic intrusive rocks and one metasedimentary rock. The particle size was similar in both tests and the average temperature and precipitation in the field were approximately 16 °C and 100 mm, respectively. Drainage pH from two of the field tests were 3.5 and 1 unit lower than the corresponding laboratory test, and values from the remaining two pairs were in fairly close agreement. Direct extrapolation of laboratory data yielded predicted sulfate concentrations that were roughly 0.07 to 0.3 those observed in the field tests. The comparatively low laboratory rates were attributed to higher pH conditions resulting from the higher flushing rate in the laboratory. It was speculated that the higher flushing enhanced dissolution of neutralizing minerals and prevented development of acidic micro-environments in the laboratory tests.

Robertson, Barazzuol & Day (2012) compared sulfate release rates from 13 humidity cell tests on fresh drill core to field rates observed for 7.6 million tonnes of rock that had been weathering for 27 years in the field, roughly 200 km northeast of Timmons, Ontario. The rock was predominantly massive and pillowed basaltic rocks, some hydrothermally altered, and felsic and mafic intrusives. Comparison of the sulfate release rate for the median sulfur content rock (0.5 percent S) in the laboratory with that observed in the field yielded a scaling factor of 0.1. The corresponding factor assuming a 95 percentile sulfur content (1.46 percent) to be controlling release in the field yielded a scaling factor of 0.05.

Hanna & Lapakko (2012) determined scaling factors for sulfate release using data generated by 26-week humidity cell tests on seven drill core samples of finely laminated, fine-grained rock, referred to by miners locally as the lower slaty member of the Biwabik Iron Formation (Severson et al., 2010). Sulfate release rates, normalized for pyrite mass, calculated for roughly 50 million tonnes of this rock in northeastern Minnesota were generally equal to or greater than the corresponding rates in the laboratory.

Lapakko (1994) compared results from laboratory dissolution tests on fine noritic and gabbroic Duluth Complex rock (0.053 < diameter ≤ 0.149 mm) from the South Kawishiwi Intrusion to those generated by roughly 1000-tonne test piles of similar Duluth Complex rock from the Partridge River Intrusion in northeastern Minnesota. Rates in the field were compared to laboratory rates for rock of similar sulfur content and yielded scaling factors of roughly 0.1 to 0.3.

## OBJECTIVE AND APPROACH

The objective of this report is to present scaling factors for sulfate release from operation scale stockpiles of Duluth Complex rock in the field relative to those that would be generated in humidity cell tests. The approach employed data that was generated in studies previously conducted by the Minnesota Department of Natural Resources (MN DNR) (Kellogg et al., 2014, MN DNR, 1996). Specifically, field data are from monitoring at the Dunka Mine and laboratory data are from dissolution tests on rock from that site. Those tests were conducted on rock with diameters in the range of 0.053 – 0.149 mm. Corresponding humidity cell rates were projected using data comparing results from the two methods.

## METHODS

### Field

Beginning in the 1960's, Duluth Complex rock was excavated at the Dunka taconite mine (Figure 1) and stockpiled at the site in order to access the underlying iron formation. In the mid-1970's it was discovered that sulfate and trace metal concentrations were elevated in Unnamed Creek, which drains the mining watershed, and the Duluth Complex rock was determined to be the source of these solutes. Due partly to concerns regarding water quality impacts from potential copper-nickel mining in the area, a program was

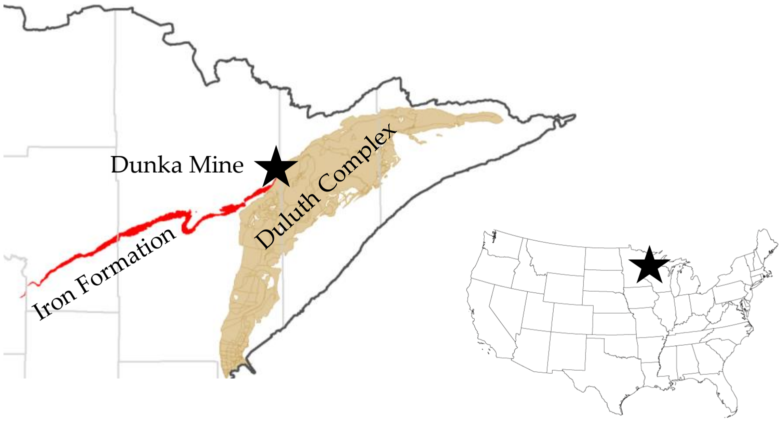


**Figure 1** Location of Dunka Mine, Iron Formation and Duluth Complex in northeastern Minnesota

initiated to monitor the Duluth Complex rock seepage at the Dunka Mine. The following information was taken from a summary of waste rock composition, flow, and drainage quality data from the site (MN DNR, 1996).

The Duluth Complex rock mass within the individual seepage watersheds ranged from roughly 2 to 15 million tons, with average sulfur contents of approximately 0.2 to 1 percent (Table 1). Sulfur contents were determined based on analyses conducted on blast hole samples from 1980 to 1988. These analyses accounted for most of the rock in stockpiles 8018 and 8031, which drain to sites W1D and W4, respectively. Therefore, there is a relatively high degree of confidence in the sulfur contents and calculations based on these contents. In contrast, sulfur contents of stockpiles 8011, 8013, and 8014 were estimated based on analyses of roughly 19, 35, and 44 percent of the rock present. No sulfur analyses were submitted by the company for rock stockpiled after 1988.

Sulfate and metals are transported from the stockpiles in several well-defined seeps, as well as in diffuse flows. The seeps (and the associated stockpiles) discussed in the present report are designated EM8 (stockpiles 8011, 8014), Seep X (8013), Seep I (8013), W4 (8027, 8031), and WID (8018, 8031). Duluth Complex drainage quantity and quality data presented in this report were collected for periods of 3 to 13 years during the time span from 1979 to 1992. Since 1976, data have been collected on the drainage quality, quantity, and chemical mass release associated with stockpile drainages at the site. The Regional Copper-Nickel Study began the data collection and after 1980 monitoring was conducted by Erie Mining Company and LTV Steel Mining Company. The seasonal flow period typically extended from the middle of April to the end of November. Weirs and flow recording equipment were installed at all sites and flow was recorded automatically from roughly mid-May to mid-November. Beyond this time period flow measurements were conducted manually. Grab samples were typically collected 15 to 20 times per year for determination of pH, sulfate concentrations, and concentrations of other solutes that are not discussed in this paper.

**Table 1** Duluth Complex stockpile and seep watershed characteristics

| Seep | Stockpile | Deposition (start-end) | Mass in watershed, | %S | Area of pile in watershed, $ft^2 \times 10^6$ | Watershed area, | Monitoring (start-end) |
|---|---|---|---|---|---|---|---|
| Seep X[1] | 8013 | 1967-1991 | 8.44 | 0.24 | 1.3 | 1.7 | 1990-1992 |
| Seep 1[2] | 8013 | 1967-1991 | 1.86 | 0.24 | 0.50 | 0.65 | 1986-1992 |
| EM8[3] | 8011 | 1965-1986 | 12.92 | 0.23 | 3.6 | 7.7 | 1979-1991 |
| W4[4] | 8027[6] | 1979-1979 | 0.14 | 0.12 | 0.12 | 7.5 | 1980-1991 |
| W1D[5] | 8018 | 1979-1985 | 2.18 | 0.98 | 0.75 | 1.9 | 1986-1992 |

[1] Weir and continuous flow recording equipment, installed in 1991
[2] Weir installed in 1977, recorder installed in 1980
[3] Weir and recorder installed in 1976
[4] Weir and recorder installed 1981 and 1983, respectively
[5] Weir and recorder installed 1981 and 1986, respectively
[6] Mass and composition reported by MN DNR, 1996

**Laboratory**

Seventeen samples were collected from blast holes at the Dunka mine (Figure 2a). These samples were characterized (chemistry, mineral content, mineral chemistry) and subjected to dissolution testing (Kellogg et al., 2014). For 15 of the 17 samples, particle size was reduced using a bucking maul, or mechanically, with a pulverizer. These samples were subjected to dissolution tests in duplicate. The remaining two samples (0.67, 0.82 %S) were stage crushed with a jaw crusher and were not replicated in dissolution testing. Particles with diameters from 0.053 to 0.149 mm (-100/+270 mesh) were retained for experimental use. For the crushed samples, sulfur content was determined by LECO furnace, metal concentrations were determined using ICP-AES, and mineral content and mineral chemistry were determined by microprobe analysis of 100 to 125 mineral grains for each sample.

Seventy-five grams of crushed rock were placed into the upper segment of a two-stage filter unit (Figure 2b). The solids were placed on a glass fiber filter that rested on a perforated plastic plate near the bottom of the reactor. At the inception of the experiment, each reactor was rinsed three times to remove any oxidation products that accumulated between sample crushing and onset of the experiment. Each week thereafter, two hundred milliliters of distilled-deionized water was added, and remained in contact with the solids for four to seven minutes, and then vacuum-pumped from the upper stage through a 0.45- micron filter on top of the lower stage of the filter unit. This procedure changed slightly beginning in July 2002. During weeks where no sample was collected, the reactors were filled with water as before, but were then gravity drained. The procedure remained the same as before for weeks during which samples were collected. Sample pH was determined weekly using either a Radiometer 29 or an Orion SA720 meter. Sulfate concentrations were determined biweekly (R1-R20) or monthly (R29-R43) at the MN DNR lab in Hibbing, MN using an HF Scientific DRT-100 nephelometer for the barium sulfate turbidimetric method (APHA et al., 1992). The sample volume was determined by weighing the sample collection flask containing the sample and subtracting the flask mass.

(a)

(b)

(c)

**Figures 2a,b,c** The first photo (a) depicts the weir at a site used for monitoring flow and water quality at the Dunka taconite mine in northeastern Minnesota, the second photo (b) depicts an MN reactor apparatus, and the third photo (c) depicts a typical humidity cell apparatus.

Between rinses, the solids remained within the reactors, allowing evaporation of retained rinse water and continuous oxidation. The reactors were stored in individual cubicles that formed a rectangular matrix within a topless housing with a perforated base; the housing was stored in a temperature and humidity controlled room (8.5 x 10.5 x 9.5 ft). Reactor experiments were initiated at three different times. For weeks 6-71 average temperatures for the three sets of samples ranged from 25.2-26.3 °C with standard deviations of 0.5-1.3 °C. Corresponding values for average relative humidity were 55.3-59.7% and 3.4-6.8%.

**Calculations**

For waste rock piles in the field, sulfate mass release was calculated for each day sulfate concentrations were measured. Flow data from the previous and subsequent measurements were used to determine the flow volume associated with the sulfate concentration (equation 1).

$$\mathrm{SO_4\ mass\ release,\ M(SO_4)} = [\mathrm{SO_4}]_\mathrm{i}\left(\frac{\mathrm{Q_i+Q_{i-1}}}{2}\right)\left(\frac{\mathrm{t_i+t_{i-1}}}{2}\right) + [\mathrm{SO_4}]_\mathrm{i}\left(\frac{\mathrm{Q_i+Q_{i+1}}}{2}\right)\left(\frac{\mathrm{t_i+t_{i+1}}}{2}\right),\ \text{where} \qquad (1)$$

M ($SO_4$) = mass of sulfate associated with sample i, mg.

[$SO_4$] = sulfate concentration (mg/L),

Q = flow (liters/sec), and

t = time (seconds).

Cumulative sulfate mass release for the year was then divided by the product of the molecular weight of sulfate, annual mass of sulfur in the watershed and the time over which release occurred to determine annual average sulfate release rates (mol $SO_4$ (g S)$^{-1}$ s$^{-1}$) for each seep (Appendix 1, Table A1.1).

Annual rate of sulfate release was calculated as follows:

$(dSO4/dt)_A = \Sigma MSO4/(96.1*M(S)_{ws} * t)$, where (2)

$(dSO4/dt)_A$ = Average annual rate of sulfate release (mg/(gS*s)),

$\Sigma MSO_4$ = sum of mass sulfate release for individual sampling periods (mg), and

$M(S)_{ws}$ = mass of sulfur in the watershed (g).

The period over which flow and sulfate concentrations were determined typically extended from mid-April to the end of November. The calculation assumed that the sulfur content in each stockpile did not change over time (the final weighted average sulfur content was used), where in reality the sulfur content added to each pile varied each year.

For the 17 laboratory tests, the average sulfate release rate and associated standard deviation were determined for weeks 6 through 71 (Appendix 1, Table A1.2). The initial five weeks were omitted to eliminate contributions of sulfate generated during sample storage. Drainage pH values for most samples were circumneutral during this period, although minimum values as low as about 4.5 were observed for some of the higher sulfur sample. The mass sulfate release for each point at which sulfate concentration was determined was calculated as the product of that concentration and sample volume. For sulfate concentrations below detection (2 mg/L) a value of 1.0 mg/L was assumed. A total of 887 sulfate measurements were made for the 17 reactors (including the replicates), out of those 93 were below the detection limit. These typically occurred in the samples with $S \leq 0.41\%$. To determine the rate of release, normalized for sulfur content, the mass release was divided by the product of 604,800 seconds/week and the mass of sulfur present in the sample. Normalizing relative to the sulfur content allowed for direct comparison among laboratory and field rates.

Scaling factors were calculated to express the ratio of field rates to a laboratory rate from a humidity cell test (Figure 2c). This required scaling rates from the MN DNR reactors to humidity cells. This was done using data generated by subjecting Duluth Complex rock samples to testing in both reactors and humidity cells (seven and ten samples, respectively) (Lapakko, Olson, & Antonson, 2013). During weeks 6 through 71 (and throughout the first three years of testing) sulfate release rates as a function of sulfur content from the humidity cells were approximately one-third those from the reactors. Thus, the observed sulfate release rates for the reactors were divided by three to represent humidity cell rates.

A set of scaling factors was then calculated using the ratio of each of 42 annual field rates to each of the adjusted 17 laboratory rates. This generated a set of 714 distinct scaling factors (42 x 17 = 714) (Figure 3a). This data set was fit to normal, beta, and log normal distributions, and the associated mean and standard deviations were determined.

## RESULTS AND DISCUSSION

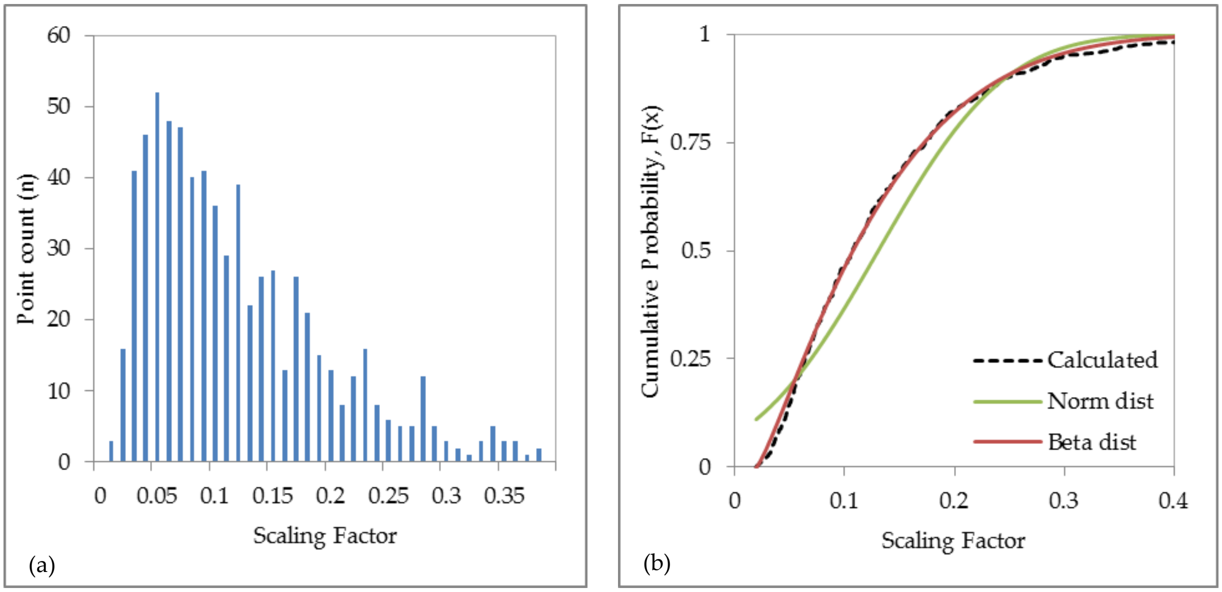
The Duluth Complex rock mass within the individual seepage watersheds ranged from roughly 2 to 15 million tons, with average sulfur contents of approximately 0.2 to 1 percent (Table 1). Because lab samples were collected from blast holes at the site, it is assumed that the mineralogy is similar to those in the lab (see below). Sulfate concentrations in the field generally ranged from 600 to 1600 mg/L and geochem equilibrium modeling of 269 seepage samples indicated that the drainages were undersaturated with respect to gypsum in all cases except one.

Sulfate release rates in the field typically ranged from 0.8 x $10^{-12}$ to 4 x $10^{-12}$ mol (g S)$^{-1}$ s$^{-1}$, with a median value of 1.7 x $10^{-12}$ mol (g S)$^{-1}$ s$^{-1}$ (Appendix 1, Table A1.1). These values were in good agreement with calculations by a slightly different method (MN DNR, 1996). Rates calculated for Seep 1 tended to be on the lower of the range and those from W4 on the higher end. Their respective mean rates were 1.2 x $10^{-12}$ and 3.3 x $10^{-12}$ mol (g S)$^{-1}$ s$^{-1}$. Rates for individual seeps showed no consistent temporal trend and values for each seep fell within a fairly consistent range over the period of record. The percent standard deviation of the mean value ranged from about 35 to 55 percent (Appendix 1, Table A1.1). Rates for Seep X, Seep 1 and EM8 were in reasonable agreement with those for W4 and W1D (Appendix 1, Table A1.1). Sulfur content of the rock in the watersheds of the last two sites was determined throughout the period of stockpiling (see Methods). The agreement among sulfate release rates suggests that estimations of sulfur content made for rock in the first three watersheds were not unreasonable. Minimum annual pH values for four of the five seeps reflected circumneutral pH conditions, typically ranging from 6.2 to 6.6. Values for Seep 1 were markedly lower, generally in the range of 4.6 to 4.8 (Appendix 1, Table A1.1).

Sulfur content of samples subjected to dissolution testing ranged from 0.18 to 1.64%. Pyrrhotite was the dominate sulfide mineral, followed by chalcopyrite, cubanite, and pentlandite. Cu and Zn sulfides were also observed in trace amounts. Plagioclase (36-65%), augite (3-17%), hypersthene (5-28%), and olivine (3-21%) contributed 65-97% of mineral content in Duluth Complex samples. Eleven samples contained the plagioclase species labradorite, while six samples contain the more sodium-rich species andesine (0.18 to 1.64%S). Unleached Duluth Complex silicate minerals had the following range of stoichiometric coefficients: plagioclase $(\mathrm{Ca}_{0.40\text{-}0.63}\mathrm{Na}_{0.32\text{-}0.55})\mathrm{Al}_{1.44\text{-}1.66}\mathrm{Si}_{2.35\text{-}2.57}\mathrm{O}_8$, augite $((\mathrm{Ca}_{0.76\text{-}0.95}\mathrm{Na}_{0.01\text{-}0.03})(\mathrm{Mg}_{0.36\text{-}0.79}\mathrm{Fe}_{0.27\text{-}0.63}\mathrm{Ti}_{0.01\text{-}0.02})(\mathrm{Si}_{1.95\text{-}2.00}\mathrm{Al}_{0.03\text{-}0.1})\mathrm{O}_6)$, hypersthene $((\mathrm{Mg}_{0.91\text{-}1.16}\mathrm{Fe}_{0.78\text{-}1.66})2\mathrm{Si}_{1.97\text{-}2.00}\mathrm{O}_6)$, and olivine $((\mathrm{Mg}_{0.72\text{-}1.00}\mathrm{Fe}_{0.96\text{-}1.25})\mathrm{Si}_{0.99\text{-}1.01}\mathrm{O}_4)$ (Kellogg et al., 2014).

Laboratory rates typically ranged from 1.1 x $10^{-11}$ to 2.3 x $10^{-11}$ mol (g S)$^{-1}$ s$^{-1}$ with three values in the range of 2.5 x $10^{-11}$ to 3.9 x $10^{-11}$ mol (g S)$^{-1}$ s$^{-1}$ (Appendix 1, Table A1.2). Rates for six of the samples included estimations of sulfate concentrations for values reported as less than detection (Appendix 1, Table A1.2). For three samples with seven or fewer below detection values this introduced a maximum error not exceeding two percent. The maximum error increased to eight percent for 15 below detection values and 19 percent for 35 sulfate concentrations reported below detection. Median pH values for the period of record ranged from 4.3 to 6.6, and minimum pH values were generally 0.6 to 1.3 units lower. There was little dependence of these rates on pH, as indicated by a correlation coefficient of 0.062 for the regression of sulfate release rate against the median pH values.

The overall range of scaling factors was 0.019 to 0.687 with about two thirds of the values falling between 0.053 and 0.21 (Figure 3a). Fitting the set of scaling factors to a normal distribution yielded respective values for the mean, standard deviation, and skewness of 0.13, 0.09, and 1.69, respectively. Given the asymmetry of the data relative to a normal distribution (Figure 3a), a beta distribution was applied for dynamic systems modeling for scaling at a proposed mining operation in Minnesota. Scaling factors for probabilities of 5, 25, 50, 75, and 95 percent were 0.034, 0.064, 0.11, 0.17, and 0.30, respectively (Figure 3b). The respective mean and standard deviation for this distribution were 0.127 and 0.083; minimum, maximum, alpha, and beta values were 0.019, 0.687, 1.25, and 6.50, respectively. A log-normal distribution also fit the data well with mean and standard deviation for ln(x) of -2.25 and 0.675, respectively.



**Figures 3a,b** a) Calculated scaling factor histogram showing point counts and b) cumulative probability of composite scaling factors compared to normal and beta distribution fits. Omitted scaling factors > 0.40 to improve resolution.

The modeling used the distribution of scaling factors to generate a corresponding distribution of sulfate release rates for the field. Such distributions are recommended by the National Academy of Sciences (National Research Council, 2007) as opposed to a single value. They are deemed more appropriate for assessment of risk by regulatory agencies, an assessment that is essential to environmental review of proposed mining operations.

It should be noted that the scaling factors presented were calculated based on field rates determined during periods of open flow (roughly April through November) and ignored winter periods when ice covered seepage areas (roughly December through March). There were few data available to compare sulfate release rates during the winter to those during the remainder of the year. The best data available were from the outflow of the watershed, site EM1, roughly 1 to 3 km downstream of the seeps. From 1975 to 1998 average sulfate concentrations during the winter were 0.71 times the average during the summer (99 and 389 measurements, respectively). From 2000 to 2014, National Pollution Discharge Elimination System (NPDES) data indicated the monthly average flow during the winter was 0.46 times that during the open flow season (52 and 116 measurements, respectively). Using these ratios allowed estimation of yearly field rate (open flow and ice cover) as 84 percent of that during open flow alone. This would in turn yield scaling factors that were 84 percent of those calculated. For example, the mean value for the beta distribution would be reduced from 0.13 to 0.11. The lower scaling factor does not, however, imply a lesser potential for environmental impact. The lower field sulfate release rates estimated for the winter months actually yielded higher sulfate concentrations in the receiving stream due to lower input flows of unimpacted water.

Beyond the statistical description of uncertainty, specific variables in the calculation were considered. First, field rates were calculated based on sulfur contents of rock within seep watersheds. As discussed above, sulfate release rates for watersheds in which sulfur content was determined throughout stockpiling were in reasonable agreement with those for watersheds with less frequent rock analyses. Thus, it appears that such estimation did not introduce substantial error.

Second, the potential role of pH was investigated. As discussed above, the laboratory rates exhibited little dependence on pH for the period of record considered. Although most of the field seeps exhibited circumneutral pH, it is possible that acidic "hot spots" with elevated sulfate release rates could develop in isolated areas of piles. However, there were no indications suggesting such areas existed. That is, there were no sudden drops in pH and release rates of sulfate remained with constant ranges (Appendix 1, Table A1.1).

Indicators of acidification were observed at Seep 3 at the Dunka mine, a seep not included in the present calculation of scaling factors. From 1975 through1988 drainage pH at the seep was near 7.0, but declined to a minimum of 4.8 in 1989 (MN DNR, 1996). Despite pH values in the typical circumneutral range, the annual release rates for nickel, copper, cobalt, and zinc increased by factors of roughly 20 to 80 from 1986 to 1988, and the sulfate release rate increased by about a factor of nine during this period. Such increases are often associated with isolated acidic zones in waste rock piles generating circumneutral pH. In contrast, sulfate release rates from each of the seeps used for scaling calculations fell within a fairly constant range (Appendix 1, Table A1.1), as discussed above. Similarly, heavy metal concentrations from these seeps did not exhibit the radical changes observed at Seep 3. Thus, it seems unlikely that acidic zones within these piles influenced rates of solute release.

Acidic drainage pH was observed at Seep 1, where minimum values were between 4.6 and 5.2 (Appendix 1, Table A1.1), but the sulfate release rate for this site was the lowest of the five sites examined. This, in conjunction with the laboratory data, suggests there is not a strong dependence of sulfate release on pH in the range of roughly 4.5 to 7.

Third, the reliability of flow measurements was considered. Flow measurements were automated from roughly the middle of May to the middle of November and measurements were made manually beyond this period. To assess the reasonability of the annual flow volumes, these values were divided by total precipitation onto the seep watershed to quantify the annual fractional yields. The average annual yield coefficients for the periods of record for EM8, Seep 1, W1D and W4 were 0.28, 0.33, 0.36, and 0.37, respectively. These values do not suggest any substantial error in flow measurement.

The average annual yield coefficient for Seep X was notably higher at 0.74. At this site the yield coefficient decreased steadily from 1.03 to 0.56 over the three-year period of record and declined to 0.34 the following year. Visual observation of flow at the site was consistent with the high values reported. It is believed that release of stored water was responsible for the initial elevated flows, although the precise mechanism is unknown. The ultimate value of 0.34 is consistent with the annual averages from the other sites and is believed to reflect "typical flow" from the pile.

Finally, the scaling factors determined are in general agreement with values previously determined empirical scaling factors for Duluth Complex and Biwabik Iron Formation rock in northeastern Minnesota. Lapakko (1994) compared sulfate release rates from South Kawishiwi Intrusion rock tested in MN DNR reactors to rates observed for 1000 tonne test piles of Partridge River Intrusion rock. The approximate range of scaling factors reported was 0.1 to 0.3. The rates for the South

Kawishiwi rock in MN DNR reactors reported in the study can be converted to Partridge River rock in humidity cells. Subsequent research indicated that transforming these rates for influences of dissolution test type (MN DNR reactor rate/humidity cell rate ~ 3) and specific intrusion (South Kawishiwi rate/Partridge River rate ~ 0.5) (Lapakko, Olson, & Antonson, 2013). The resultant range of 0.15 to 0.45 represents that for scaling sulfate release rates from humidity cells to test piles, which is higher than the 0.127 mean for scaling humidity cell rates to operational scale piles. This seems reasonable considering, for example, that reaction product transport would likely be higher in the smaller test piles.

Hanna & Lapakko (2012) determined empirical scaling factors for waste rock piles from the lower slaty unit of the Biwabik Iron Formation waste rock piles in northeastern Minnesota. The more reliable of two methods reported yielded a range of 1.0 to 1.3, that is, field rates of sulfate release per gram pyrite were higher than those observed for drill core in the laboratory. This was largely attributed to laboratory rates determined for weeks 15 to 26 of humidity cell testing. Additional testing of weathered rock yielded rates that were roughly an order of magnitude higher than those for drill core. Using these rates for determination of scaling factors would have produced values near 0.1, which is in general agreement with the values determined in the present work. The values determined in the present work generally agree with those presented for operational scale piles by Robertson, Barazzuol, & Day (2012) and not extremely deviant from other literature values presented. However, as discussed previously, comparisons of scaling factors among different sites must be done with caution due to differences in site specific environmental conditions, rock characteristics, and test methods.

## SUMMARY AND CONCLUSIONS

Sulfate release rates from Duluth Complex rock were determined for 17 laboratory tests and five operational waste rock seepages in northeastern Minnesota. The 714 scaling factors, representing the ratio of field rates to those in the laboratory, were fit to a beta distribution that yielded a mean of 0.127 and a standard deviation of 0.083. This empirically-based distribution forms a foundation on which laboratory rates can be scaled to develop a probability distribution of predicted operational rates for the purpose of environmental review, consistent with recommendations by the National Academy of Sciences (National Research Council, 2007). It should be noted that the results were generated based on dissolution of a specific rock type in the laboratory and under specific conditions of climate and waste rock stockpile design in the field. Consequently, care must be taken when applying these results to other conditions. It does provide an example for development of empirically based scaling factors. Further application of this approach to other rock types and field conditions will reduce uncertainty in the presently tenuous extrapolation of laboratory test results to the field conditions for proposed mining operations. Consequently, it is recommended that operations and regulatory agencies generate, compile and analyze data to develop additional distributions for empirical scaling factors.

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## APPENDIX 1. Field and laboratory release rates

**Table A1.1** Annual precipitation, sulfate release rates (mol $SO_4$ (g S)$^{-1}$ s$^{-1}$), and minimum annual pH for the 5 seeps from 1979-1992

| Year | Annual precip (cm) | Seep X[1] | | Seep 1[2] | | EM8[3] | | W4[4] | | W1D[5] | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Rate | Min pH | Rate | Min pH | Rate | Min pH | Rate | Min pH | Rate | Min pH |
| 1979 | 63 | NA | NA | NA | NA | 1.6E-12 | 6.6 | NA | NA | NA | NA |
| 1980 | 68 | NA | NA | NA | NA | 2.7E-12 | 6.8 | 8.4E-13 | 7.2 | NA | NA |
| 1981 | 70 | NA | NA | NA | NA | 1.5E-12 | 6.7 | 2.4E-12 | 6.6 | NA | NA |
| 1982 | 87 | NA | NA | NA | NA | 1.8E-12 | 6.4 | 4.1E-12 | 6.4 | NA | NA |
| 1983 | 78 | NA | NA | NA | NA | 1.2E-12 | 6.4 | 3.3E-12 | 6.2 | NA | NA |
| 1984 | 56 | NA | NA | NA | NA | 1.1E-12 | 7.0 | 4.0E-12 | 6.8 | NA | NA |
| 1985 | 84 | NA | NA | NA | NA | 8.6E-13 | 6.7 | 6.5E-12 | 6.5 | NA | NA |
| 1986 | 68 | NA | NA | 9.1E-13 | 5.1 | 7.8E-13 | 6.4 | 4.3E-12 | 6.4 | 1.5E-12 | 6.7 |
| 1987 | 56 | NA | NA | 7.5E-13 | 4.8 | 7.5E-13 | 6.5 | 2.8E-12 | 6.6 | 3.2E-12 | 6.9 |
| 1988 | 79 | NA | NA | 9.1E-13 | 5.2 | 2.0E-12 | 6.4 | 2.1E-12 | 6.7 | 1.7E-12 | 6.4 |
| 1989 | 66 | NA | NA | 2.5E-12 | 4.8 | 3.1E-12 | 6.3 | 3.3E-12 | 6.7 | 2.1E-12 | 6.8 |
| 1990 | 71 | 2.8E-12 | 6.2 | 8.5E-13 | 4.7 | 2.2E-12 | 6.9 | 2.9E-12 | 6.6 | 1.3E-12 | 6.9 |
| 1991 | 74 | 4.8E-12 | 6.2 | 1.6E-12 | 4.6 | 1.7E-12 | 6.8 | 3.1E-12 | 6.6 | 2.1E-12 | 6.8 |
| 1992 | 65 | 1.9E-12 | 6.5 | 8.2E-13 | 4.8 | NA | NA | NA | NA | 1.4E-12 | 6.7 |
| Avg | 70.4 | 3.2E-12 | 6.3 | 1.2E-12 | 4.9 | 1.6E-12 | 6.6 | 3.3E-12 | 6.6 | 1.9E-12 | 6.7 |
| S.D. | 9.3 | 1.5E-12 | 0.2 | 6.4E-13 | 0.2 | 7.3E-13 | 0.2 | 1.4E-12 | 0.2 | 6.6E-13 | 0.2 |

[1] Number of annual samples collected for analysis from 1990 to 1992 was 10, 23, and 10, respectively.

[2] Number of annual samples collected for analysis from 1986 to 1992 was 15, 15, 16, 14, 12, 14, and 7, respectively.

[3] Number of annual samples collected for analysis from 1979 to 1991 was 15, 13, 11, 15, 14, 14, 13, 15, 22, 20, 23, 18, and 24, respectively.

[4] Number of annual samples collected for analysis from 1980 to 1991 was 5, 15, 21, 15, 16, 14, 16, 15, 19, 23, 19, and 18, respectively.

[5] Number of annual samples collected for analysis from 1986 to 1992 was 16, 19, 15, 16, 16, 18, and 7, respectively.

**Table A1.2** Summary of Dunka blast hole laboratory data (weeks 6-71). Average sulfate release rates (mol $SO_4$ (g S)$^{-1}$ s$^{-1}$) were determined for duplicated samples.

| Reactor(s) | %S | Median pH | Minimum pH | Sulfate count | Avg $dSO_4/dt$ |
|---|---|---|---|---|---|
| 1,2[1] | 0.18 | 6.55 | 5.97 | 65 (29<DL) | 2.29E-11 |
| 3,4[1] | 0.22 | 6.63 | 6.07 | 61 (15<DL) | 1.79E-11 |
| 5,6[1] | 0.40 | 6.30 | 4.86 | 64 | 3.89E-11 |
| 7,8[1] | 0.41 | 5.32 | 4.48 | 64 (35<DL) | 9.48E-12 |
| 9,10[1] | 0.51 | 5.01 | 4.00 | 64 (7<DL) | 1.70E-11 |
| 11,12[1] | 0.54 | 5.17 | 4.10 | 64 | 2.32E-11 |
| 13,14[1] | 0.57 | 5.34 | 4.09 | 64 | 2.28E-11 |
| 15,16[1] | 0.58 | 4.69 | 4.04 | 64 (3<DL) | 1.77E-11 |
| 40[3] | 0.67 | 5.68 | 4.04 | 17 | 1.70E-11 |
| 17,18[1] | 0.71 | 5.03 | 3.80 | 62 (4<DL) | 1.35E-11 |
| 43[3] | 0.82 | 5.42 | 4.49 | 17 | 1.19E-11 |
| 35,36[2] | 1.12 | 4.30 | 3.51 | 43 | 3.01E-11 |
| 29,30[2] | 1.16 | 4.61 | 3.63 | 44 | 1.36E-11 |
| 37,38[2] | 1.40 | 4.84 | 3.55 | 44 | 1.42E-11 |
| 33,34[2] | 1.44 | 4.43 | 3.42 | 42 | 1.15E-11 |
| 19,20[1] | 1.63 | 4.38 | 3.61 | 64 | 1.60E-11 |
| 31,32[2] | 1.64 | 4.40 | 3.64 | 44 | 2.54E-11 |
| | | | | Average | 1.90E-11 |
| | | | | St Dev | 7.52E-12 |

[1] Reactor initiated 2/14/89, average T = 26.25 ± 1.19, average R.H. = 57.77 ± 6.77.

[2] Reactor initiated 9/4/90, average T= 25.31 ± 1.32, average R.H. = 55.27 ± 5.79.

[3] Reactor initiated 8/12/97, average T= 25.23 ± 0.51, average R.H. = 59.65 ± 3.36.