MDAG.com Internet Case Study 46

A Case Study of High-Frequency Time Series for Individual Chemical Elements in Waste-Rock Drainage

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Abstract

The previous MDAG.com Case Study 45 looked closely at the correlation of precipitation (infiltration) and outflow from full-scale waste-rock piles. This was based on a full-scale case study including high-frequency monitoring of flow as frequently as every 15 minutes.

That previous work showed that the onset of significant rapid outflow began within hours of substantial precipitation and infiltration, with outflow increasing quickly by a factor of two or more and sometimes persisting for only 15-60 minutes. For prominent one-day peaks of precipitation, 75% or less of the volume of precipitation passed through the local waste rock in less than a day or two. Also, after drier summer months, 0.085-0.188 m of precipitation was initially needed before rapid flow began. This meant less than 1% of the waste rock had to be "wetted up" and/or saturated before rapid flow was observed.

This follow-up case study looks at time series of individual chemical elements, pH, and flow for the same time periods and for the same two monitoring stations as the previous case study on flow. The interest here lies in which elements correlate with flow, pH, and/or other aqueous elements at these two stations. Because aqueous concentrations arise when water flows over and through mine materials like waste rock, a close correlation between full-scale flow and chemistry might be expected. For example, a strong, short-term peak in rapid outflow would have a short residence time within the waste rock, and thus aqueous concentrations carried by that peak flow could be proportionally lower due to dilution. This is not observed in full-scale drainages, not even in non-mining catchments.

Correlations between time series can be statistically evaluated through cross correlation of random variables. However, minesite-drainage variables are rarely random, due to relationships such as pH-dependent solubility and aqueous complexation. In this case study, geochemical parameters and chemical elements (e.g., pH, electrical conductivity, sulphate, acidity, copper, zinc, and calcium), and flow, were significantly autocorrelated, and not surprisingly cross correlated with each other. Thus, this case study looked at finer temporal details, to see if aqueous concentrations and time series correlated or differed in some statistically minor, but geochemically important, way.

At both the downstream and upstream monitoring stations, selected time series spanning days to weeks showed no geochemical responses attributable to 1:1 dilution by flow, even during substantial peaks of flow. This should raise alarms about a standard predictive technique for minesite-drainage chemistry. The technique assumes a 1:1 inverse correlation between full-scale flow and full-scale chemistry, by dividing an estimated geochemical loading by an estimated flow to predict a full-scale concentration. This standard technique violates documented relationships between flow and aqueous concentrations on several scales and in mining-related and non-mining-related catchments.

During storms at this minesite, daily outflows at the stations often increased sharply by 400-900%. However, at the same time, aqueous concentrations of some parameters decreased by no more than 35% and often showed little correlation with flow or pH. Other elements increased substantially in concentration (the opposite of dilution) during peak diluting flows, when pH decreased as flow increased. This highlighted how quickly infiltration could accumulate chemical constituents during the hours it passed through the waste rock. Overall, trends in aqueous concentrations differed among elements and parameters, among the selected time periods, and before and after brief significant changes in pH.

This MDAG case study highlighted the unique temporal trends of individual elements and parameters identified by high-frequency monitoring. These trends did not correlate well with flow. Some did not correlate well with pH either, and some did correlate with pH in agreement with the documented power laws and the Empirical Drainage Chemistry Model (EDCM) for this minesite.

1. Introduction

For decades, full-scale waste-rock piles have been recognized as complex minesite components in all three spatial dimensions and through time. While many waste-rock investigators recognize this complexity of coarser and finer material, many ignore its reality and oversimplify water movement in the coarser material. It appears the primary reasons for this are:

(1) the lack of high-frequency monitoring data (hourly and more frequently) to characterize the rapid flow of water through full-scale waste rock,

(2) detailed studies of smaller "test piles" and laboratory columns that are unavoidably unrepresentative of full-scale waste rock, and

(3) the desire to model water flow through waste rock despite a lack of realistic equations to simulate turbulent, non-Darcian, non-capillary flow in coarse rock.

The previous MDAG.com Case Study 45 looked closely at the correlation of precipitation (infiltration) to outflow from full-scale waste-rock piles (Morin, 2017). Variations of internal temperatures, fluctuations of basal water-table elevations, spectral analysis in the wavelength-frequency domain, and high-frequency flow monitoring (as frequently as every 15 minutes) revealed many details about rapid flow passing through tens of meters of full-scale waste rock.

For example, the onset of significant rapid outflow began within hours of substantial precipitation and infiltration, with outflow increasing quickly by a factor of two or more and sometimes persisting for only 15-60 minutes. For prominent one-day peaks of precipitation, 75% or less of the volume of precipitation passed through the local waste rock in less than a day or two.

Overall, 25-50% of total annual precipitation passed through the waste rock as highly variable rapid flow. The remainder drained more slowly, within days to weeks during wetter seasons and within weeks to months during drier seasons.

After the drier summer months, 0.085-0.188 m of precipitation was initially needed before rapid flow began. This meant less than 1% of the waste rock had to be "wetted up" and/or saturated before rapid flow was observed. There was generally little additional retention of water through the remainder of a hydrologic year, and the "wetting up" water was eventually lost during drier seasons. This repeated yearly.

With high-frequency flow measurements, short periods of about two weeks were identified during which flow rates significantly oscillated on a daily cycle. Where consistent, hourly flows reached minimum values around or just after midnight, and peaked around noon or just after noon each day. The cause of these brief periods of oscillation is not known.

All the preceding findings highlighted the importance of high-frequency monitoring of full-scale waste-rock piles. This leads to the more reliable understanding, characterization, and modelling of water flow through full-scale waste-rock piles.

While this is important information on water movement, it says little about the aqueous concentrations within the flow. That is the objective of this MDAG case study.

2. The Objective of This MDAG Case Study

Put simply, in full-scale minesite drainage, there is a lack of clear correlation and cause-effect relationships between flow and the corresponding aqueous chemistry. This is strange, because flowing water dissolves and/or leaches chemical elements along its flowpath! There should be significant relationships between flow and chemistry.

For example, a strong, short-term peak in rapid outflow would have a short residence time within the waste rock, and thus aqueous concentrations carried by that peak flow could be proportionally lower due to dilution. This is not observed in full-scale drainages.

In minesite drainages around the world, aqueous concentrations typically vary much less than the flows that carry these concentrations. Thus, based on literature reviews and Internet searches, there is no 1:1 positive or inverse correlation of flow and its chemistry for full-scale minesites (e.g., Morin et al., 1995; Morin and Hutt, 1997 and 2001; Morin, 2016b). In fact, there is no reported 1:1 correlation for any full-scale non-mining catchment, and instead paradoxes between flow and chemistry exist (Kirchner, 2003). There is also no common 1:1 correlation of flow to aqueous concentrations in large-scale mine-rock tests (Li, 1999), or in small-scale kinetic mine-rock tests (Morin, 2016b).

This should raise alarms about a standard predictive technique for minesite-drainage chemistry, by which an estimated geochemical loading is divided directly by estimated flow to predict a full-scale concentration (Morin, 2013 and 2014). This is based on an assumed inverse 1:1 relationship that has not been observed anywhere on any significant scale. As a result, such common mining-related predictions are unfounded, unreliable, and thus likely often wrong.

Despite the lack of 1:1 correlations, scatterplots of full-scale flow vs. aqueous concentrations often show a weak inverse correlation (perhaps reflecting some disproportional minor dilution), a weak positive correlation (perhaps reflecting minor enhanced flushing of an element), or no correlation. Chapter 6 of Morin (2016a) showed several full-scale examples of such scatterplots for one minesite. That minesite is the focus of this MDAG Case Study 46, as it was for Case Study 45 (Morin, 2017).

Specifically, this MDAG case study looks at time series of individual chemical elements, pH, and flow for full-scale waste-rock drainage, late in operation, at the now-closed Island Copper Minesite in British Columbia, Canada. The two monitoring stations examined here, as in Case Study 45, are: (1) downstream Station WME at the confluence of two major drainage ditches capturing most drainage from the on-land waste rock, and (2) upstream Station EMO at the toe of local waste rock. The interest here lies in which elements correlate with flow, pH, and/or other aqueous elements at the two stations. This interest includes short-term peaks in rapid outflow, with short residence times within the waste rock, to see if such fast, diluting flows exceed the internal release rates of geochemical parameters and chemical elements.

An obvious and common approach for comparing time series is cross correlation. This is examined in Section 3 of this case study, and found to be insufficient to the level needed here. Thus, the subsequent sections look closely at time series over relatively short periods of time to discern correlations visually.

3. Cross Correlations of Autocorrelated Parameters in Minesite-Drainage Chemistry

Statistical correlation represents the deviation of two or more random variables from statistically defined independence. An important word here is “random”.

Non-random temporal variables, depicted as time series, can show combinations of long-term trends, periodicity, and residuals that may be random. To test for correlation between time series (“cross correlation”), typical approaches require long-term trends and periodicities to be removed first, such as through detrending or prewhitening. If trends and periodicities are not removed, they can lead to incorrectly enhanced cross-correlation parameters.

This typical approach leads to problems with minesite-drainage time series. First, trends between two variables can be relevant and important. For example, aqueous concentrations of some elements can rise substantially as pH falls from near-neutral to acidic values during ongoing sulphide oxidation (Morin and Hutt, 1997 and 2001; Morin and Hutt, 2007; Morin, 2015). Second, coinciding periodicities between two time series can reveal similar influences of physical, geochemical, and biological processes on the aqueous concentrations (Morin, 2016a). Thus, the removal of long-term trends and periodicities from minesite-drainage data, while meeting conditions for statistical cross correlations of the residuals, could eliminate important relationships and trends between two parameters.

A test for non-randomness of variables is autocorrelation, which compares a time series with itself, offset by an increasing number of time steps (the “lag”). By definition, at a lag of zero, the correlation is exactly 1.0. Autocorrelations were determined here using the ACF function in Version 3.3.2 of the R mathematical language (R Core Team, 2016), through the RStudio interface (RStudio Team, 2015).

At downstream Station WME at this minesite, statistically significant autocorrelations were noted for monitored parameters, including flow (Figure 3-1), pH (Figure 3-2), copper (Figure 3-3), and sulphate (Figure 3-4). The documented periodicities (Chapter 6 and Appendix A of Morin, 2016a) can also be seen, as “waves” above and below the zero lines.

Cross correlations of two time series were determined using the CCF function in Version 3.3.2 of the R mathematical language (R Core Team, 2016), through the RStudio interface (RStudio Team, 2015). Not surprisingly, the cross correlations of these autocorrelated parameters showed statistically significant values at various lags (e.g., Figures 3-5 through 3-8).

The objective of this case study is to go beyond the recognition that these time series are statistically autocorrelated and cross correlated, which is already known. The objective here is to look at fine temporal detail to see if aqueous concentrations and time series correlate or differ in some statistically minor, but geochemically important, ways. That begins in the next section, with the focus on storm events that caused outflow to vary substantially over hours.

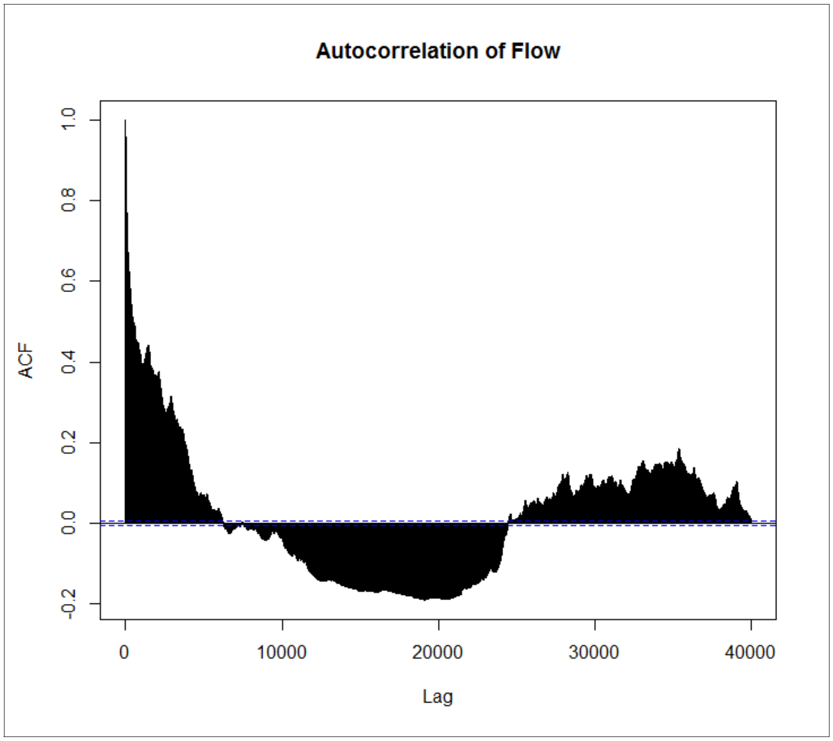

Figure 3-1. Autocorrelation of flow at Station WME; 78,685 values with a time step of 15 minutes and maximum lag of 40,000 (significant correlation exists for values above or below the zone marked by horizontal blue lines).

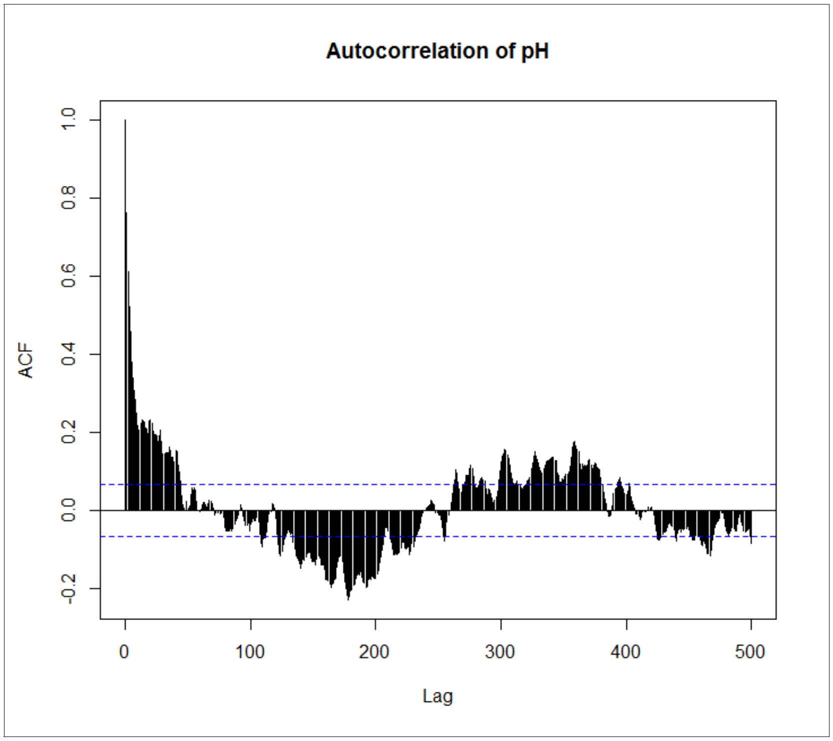

Figure 3-2. Autocorrelation of pH at Station WME; 864 values with a time step of one day and maximum lag of 500 (significant correlation exists for values above or below the zone marked by horizontal blue lines).

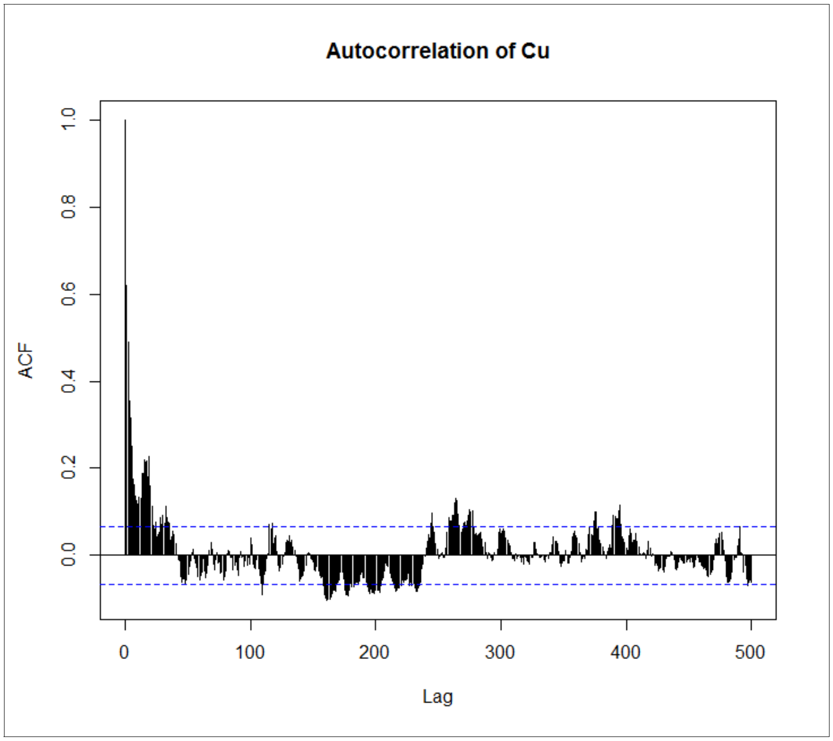

Figure 3-3. Autocorrelation of copper at Station WME; 864 values with a time step of one day and maximum lag of 500 (significant correlation exists for values above or below the zone marked by horizontal blue lines).

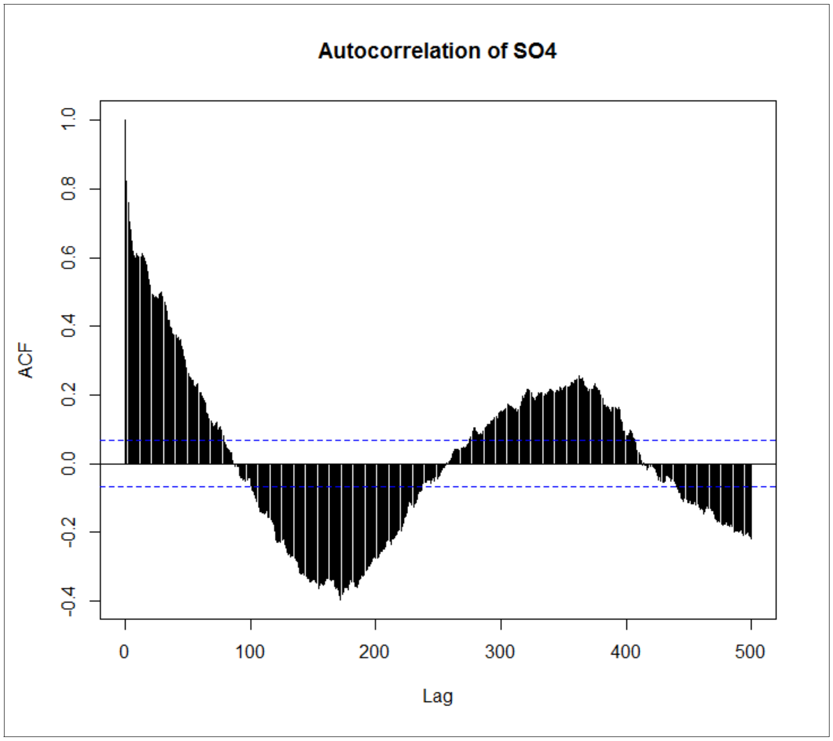

Figure 3-4. Autocorrelation of sulphate at Station WME; 850 values with a time step of one day and maximum lag of 500 (significant correlation exists for values above or below the zone marked by horizontal blue lines).

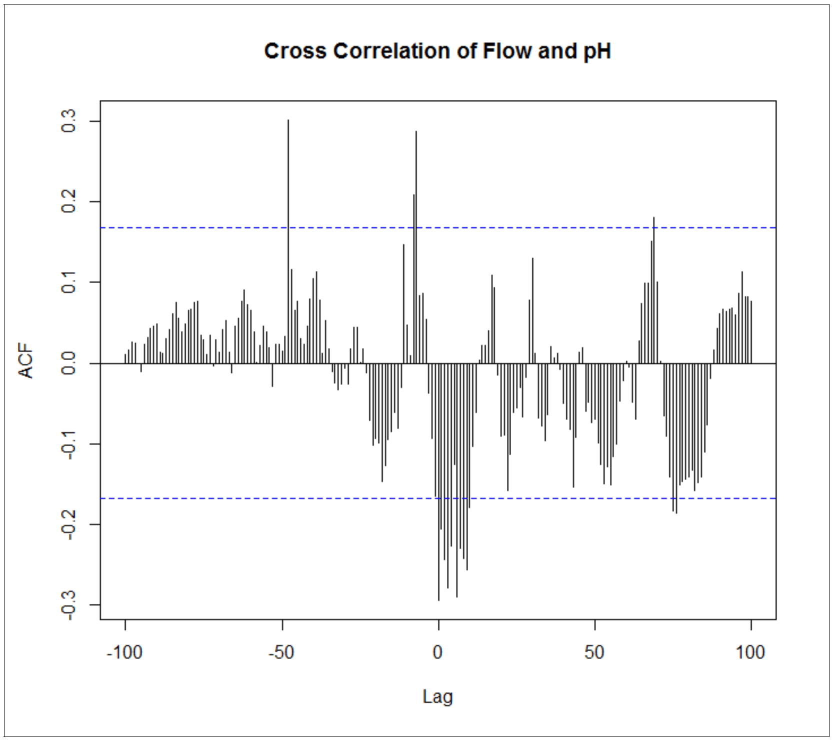

Figure 3-5. Cross correlation of flow and pH at Station WME; 137 values with a time step of one day and a lag of ± 100 (significant correlation exists for values above or below the zone marked by horizontal blue lines).

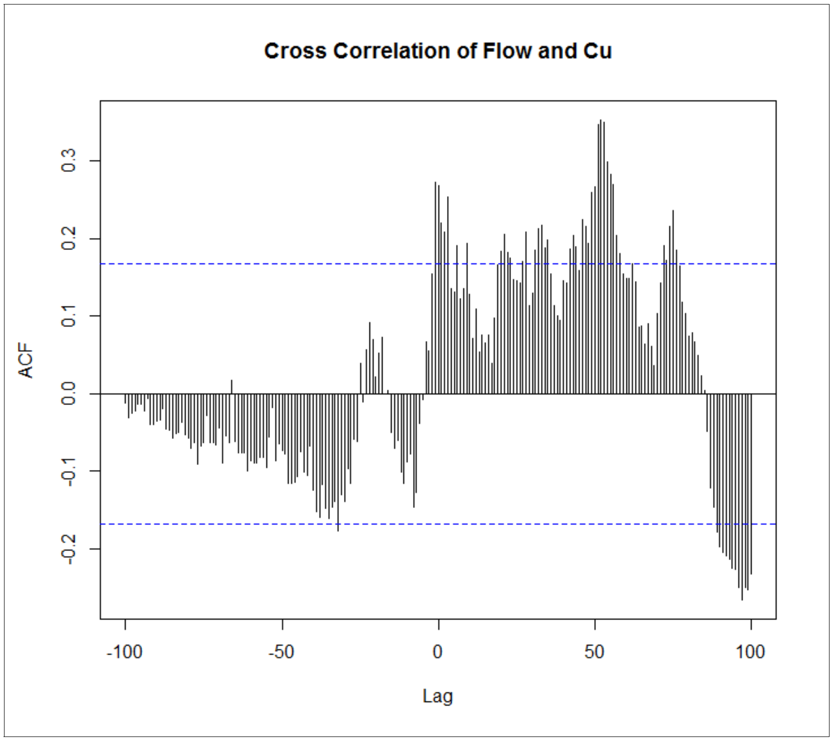

Figure 3-6. Cross correlation of flow and copper at Station WME; 137 values with a time step of one day and a lag of ± 100 (significant correlation exists for values above or below the zone marked by horizontal blue lines).

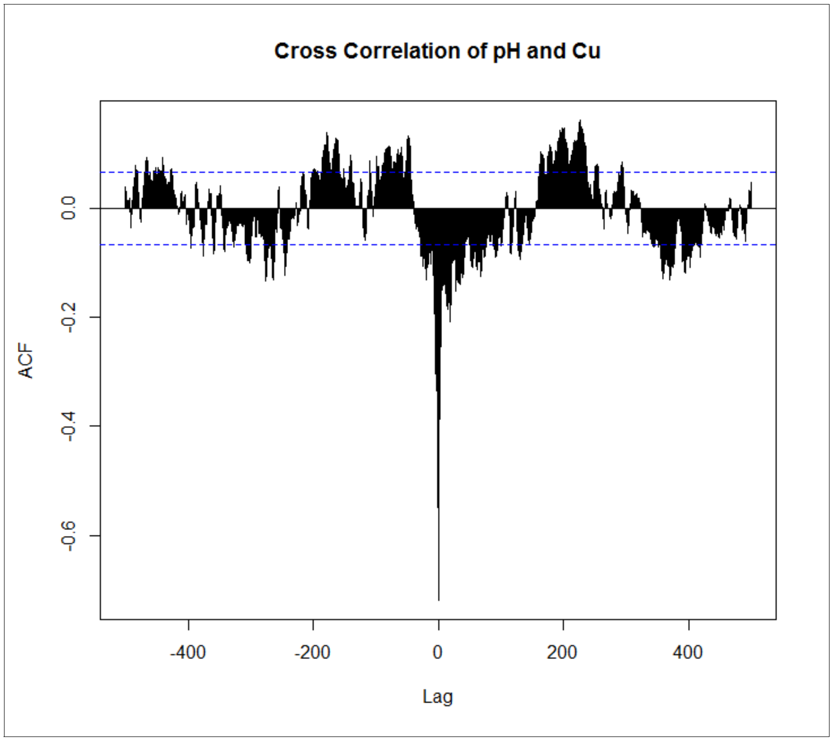

Figure 3-7. Cross correlation of pH and copper at Station WME; 864 values with a time step of one day and a lag of ± 500 (significant correlation exists for values above or below the zone marked by horizontal blue lines).

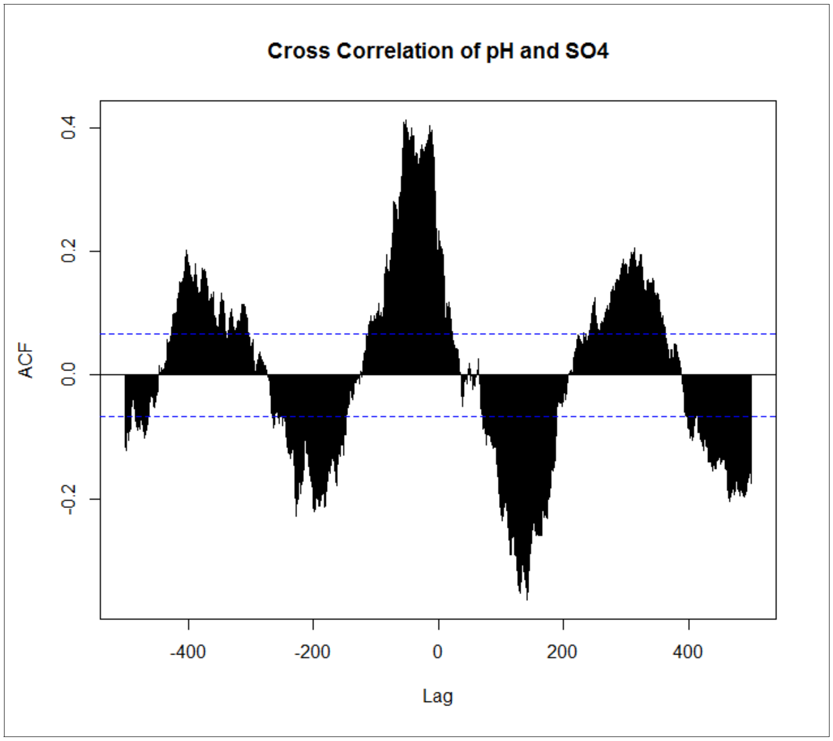

Figure 3-8. Cross correlation of pH and sulphate at Station WME; 850 values with a time step of one day and a lag of ± 500 (significant correlation exists for values above or below the zone marked by horizontal blue lines).

4. Comparisons of Time Series in Waste-Rock Drainage at this Minesite

As explained in Sections 2 and 3, this study focusses on downstream Monitoring Station WME (Section 4.1) and upstream Station EMO (Section 4.2) at the minesite. These were the same stations used to compare precipitation and outflow in MDAG Case Study 45 (Morin, 2017).

4.1 Downstream Station WME

Monitoring Station WME was located downstream of most waste rock, below the convergence of two main drainage ditches capturing most on-land waste-rock drainage. Flow was measured as frequently as every 15 minutes, and chemical concentrations were measured as frequently as daily. Due to various issues, there are many gaps of missing data in the monitoring record.

4.1.1 Late October of Mine Year 22

After a dry summer in Mine Year 22, daily precipitation generally increased in September and October. However, outflow did not increase substantially until October 18 (Figure 4-1). This represented a preceding period of "wetting up" equivalent to 0.085 m of rain, or less than 1% of the waste-rock mass.

On October 18, peak outflow occurred the same day as peak precipitation. On that day, flow increased from about 45 L/s to a maximum of 500 L/s (a 900% increase over 45 L/s) within a few hours and then began decreasing. Flow again peaked about 1.5 days later, persisting for a few hours, to a maximum of 1140 L/s, Earlier that day, flow was about 110 L/s, so this maximum was also about a 900% increase, above 100 L/s. A third major peak in flow occurred within a few hours on October 23, and then flow followed a recession curve through the rest of October. These substantial spikes in flow provided opportunities for substantial dilution in the aqueous chemistry, but this did not happen. In fact, the opposite happened for some elements.

Some parameters showed little correlation with flow or pH, notably conductivity, zinc, cadmium, sulphate, calcium, and magnesium (upper diagram of Figure 4-1). During peaks of precipitation, they decreased only by less than 25%, except zinc and cadmium that decreased by less than 35%, compared with flow increasing by 900%. This highlights how quickly infiltration can accumulate chemical constituents during the hours it is passing through the waste rock.

Some parameters showed an inverse correlation with pH and thus increased in concentration as flow increased (lower diagram of Figure 4-1). This was due to a substantial decrease in pH, from around 7 to around 5, when outflow was relatively high, and this acidic pH persisted between the two peak flows. In response to the acidic pH during high flow, concentrations of copper and aluminum increased by more than one order of magnitude; acidity became detectable; and alkalinity decreased by more than one order of magnitude. Unlike flow, these major geochemical changes and pH depression were reversed later in October, when pH recovered above 7.0.

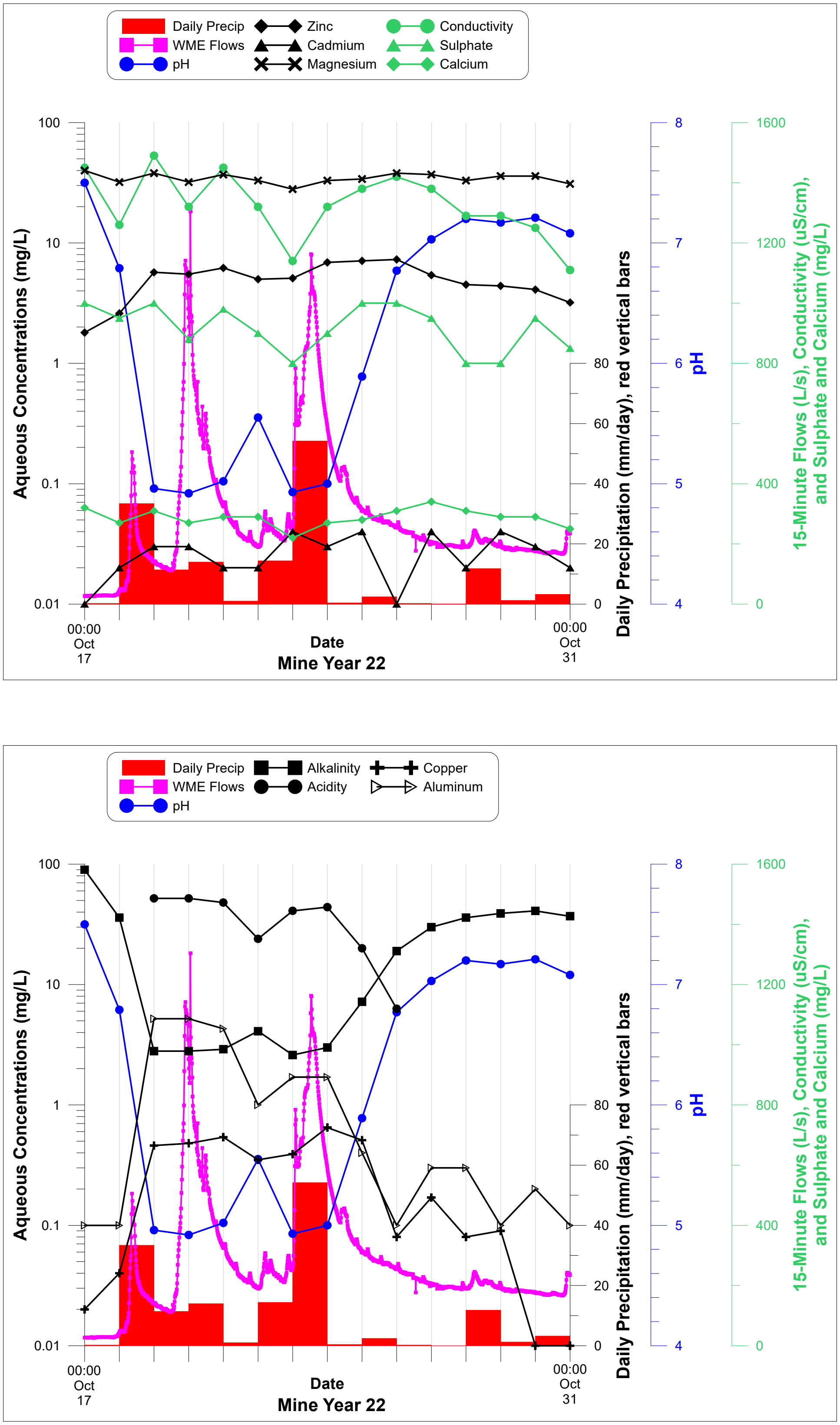

Figure 4-1. Temporal trends of precipitation, outflow, and chemistry at Station WME in late October of Mine Year 22; upper diagram shows pH-independent parameters and lower diagram shows pH-dependent parameters.

In summary, there was no geochemical response during this period attributable to 1:1 dilution by flow. As flow increased by 900%, aqueous concentrations of some parameters decreased by no more than 35%. Moreover, due to decreased pH at high flows, aqueous concentrations of some elements increased by more than 900%, but their persistence confirmed their increase was due to acidic pH and not short-term peaks of flow. Also, trends in aqueous concentrations differed among elements and parameters.

4.1.2 Early December of Mine Year 23

Over a year later, in the first half of December of Mine Year 23, peak outflow rivalled precipitation on three days (Figure 4-2). Within a few hours, flow increased from roughly 200 L/s to 1000 L/s and higher, representing an increase of at least 400% over the 200 L/s "baseline".

Unlike the previous interval (Section 4.1.1), pH did not remain around 5 during and between peak flows. Instead, pH recovered towards 7 within days after each peak in flow, and each peak in flow had less effect on pH.

The elements and parameters showing little correlation with flow or pH were conductivity, calcium, and magnesium (upper diagram of Figure 4-2). During this entire 15-day period, conductivity, calcium, and magnesium varied by less than 30%, while flow generally varied by 400% or more.

The parameters displaying some trend with pH were alkalinity, copper, zinc, cadmium, sulphate, and aluminum (lower diagram of Figure 4-2). Zinc, cadmium, and sulphate showed little correlation in the previous period (Section 4.1.1), but displayed more correlation with pH in this period. As pH decreased, alkalinity decreased, whereas the others generally increased despite a 400% or more increase in diluting flow.

Alkalinity decreased by more than one order of magnitude during the first peak of flow and the corresponding depression of pH, but varied less during the other peaks (lower diagram of Figure 4-2). The previous time period (Section 4.1.1) showed this was due to pH changes rather than flow, but this cannot be confirmed during this period because of the closer correlation of flow and pH here.

The remaining elements increased by roughly 200% (cadmium and sulphate), 500% (zinc), and more than 1000% (copper and zinc) when pH first decreased by 1-2 pH units and flow increased by 400% or more (lower diagram of Figure 4-2). Increases were generally less during the second and third peaks of flow, when pH decreased less, suggesting these elements were correlated more with pH than flow, as seen previously (Section 4.1.1).

Thus, there was no geochemical response during this period close to 1:1 dilution by flow. As flow increased by 400% or more, aqueous concentrations of some parameters decreased by no more than 30%. Due to decreased pH at higher flows, aqueous concentrations of some elements actually increased by 200% to more than 1000% (the opposite of dilution). During later similar peaks of flow, the decreases of pH and increases of some aqueous concentrations were muted, suggesting these aqueous concentrations were correlating more with pH than flow. Notably, trends in aqueous concentrations differed among elements and parameters, and some differed from the previous time period (Section 4.1.1).

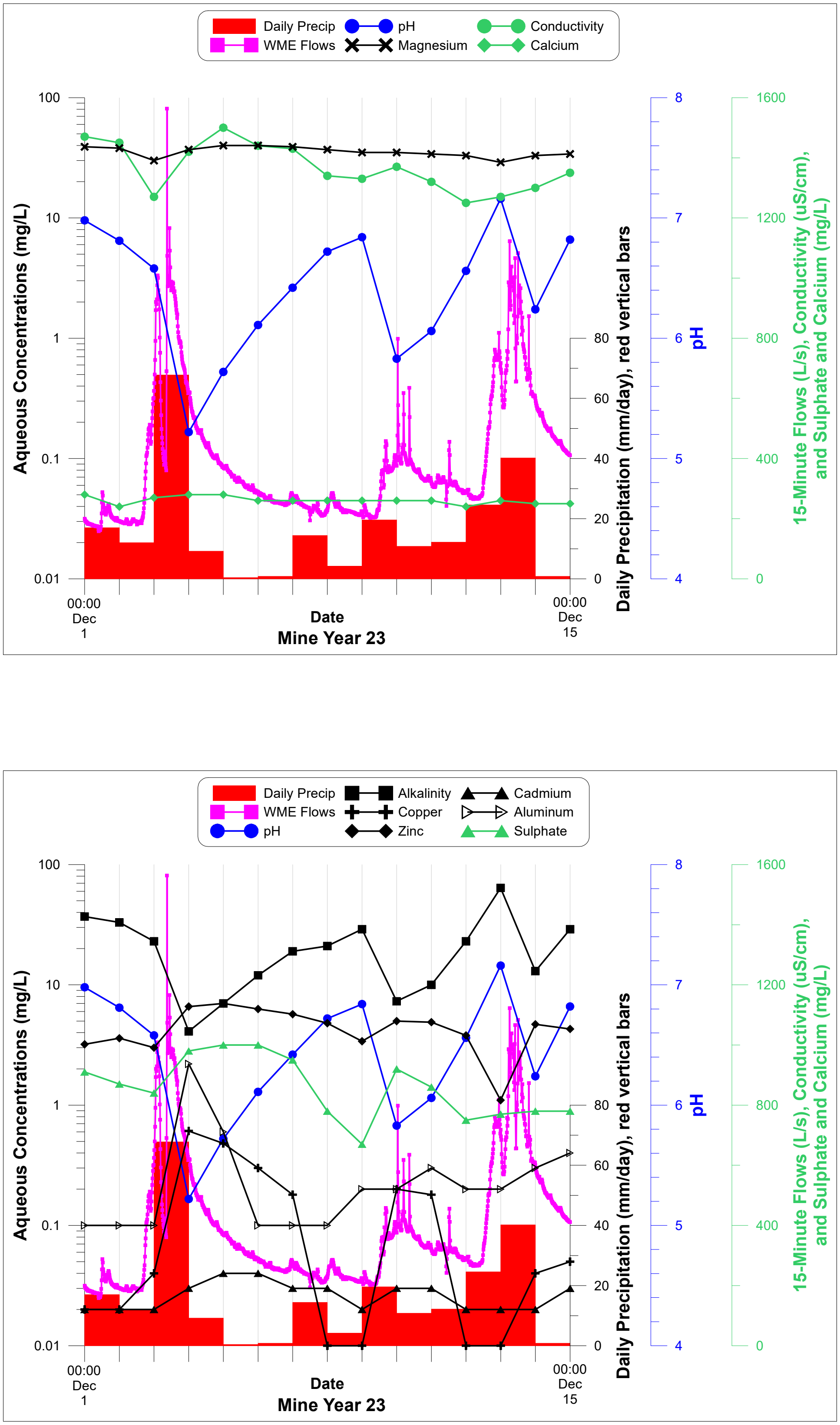

Figure 4-2. Temporal trends of precipitation, outflow, and chemistry at Station WME in early December of Mine Year 23; upper diagram shows pH-independent parameters and lower diagram shows pH-dependent parameters.

4.1.3 Early January of Mine Year 24

Less than a month later, at the beginning of January of Mine Year 24, daily precipitation increased gradually and peaked at nearly 30 mm/day on January 4 (Figure 4-3). This caused outflow to briefly peak around 400 L/s (about a 100% increase), then return to less than 200 L/s within about one day. These peaks of precipitation and flow were relatively minor compared to the past two time intervals (Section 4.1.1 and 4.1.2). Nevertheless, this was associated with a decrease in pH from around 7 to a minimum of 5.76.

As with the previous time intervals, some parameters and elements showed some correlation with pH and/or flow (Figure 4-3). In this case, alkalinity decreased by 85% as pH decreased and flow increased, cadmium decreased about 30%, aluminum increased by 50%, and copper markedly increased by more than 1000% (the opposite of dilution). The remaining parameters showed some increase during peak flow and lowest pH, but their levels remained elevated after flow subsided and pH returned to near-neutral levels. Even aluminum and copper did not return to low, pre-peak levels.

Thus, there were few geochemical responses during this period close to 1:1 dilution by flow. As flow increased by roughly 100% during this relatively minor storm, only aqueous concentrations of alkalinity decreased by a proportional amount. However, alkalinity mimics pH, so the corresponding decrease in pH likely accounted for alkalinity differences. The remaining parameters and elements generally increased as pH briefly decreased, some marginally increasing and copper increasing by more than 1000%. After pH recovered to near-neutral values and flow subsided, aqueous concentrations of many parameters and elements did not return to low, pre-peak levels.

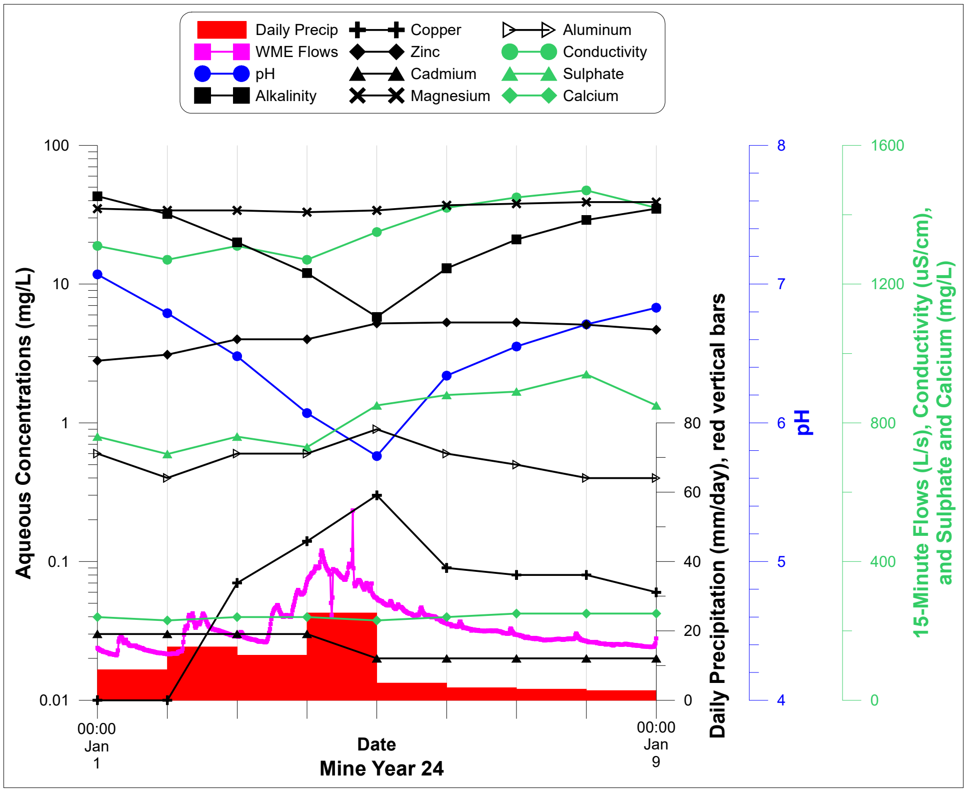

Figure 4-3. Temporal trends of precipitation, outflow, and chemistry at Station WME in early January of Mine Year 24.

4.2 Upstream Station EMO

Monitoring Station EMO was located in a drainage ditch directly at the toe of waste rock. Flow was measured as frequently as hourly, and chemical concentrations were measured as frequently as daily. Due to various issues, there are many gaps of missing data in the monitoring record.

4.2.1 The First Half of November of Mine Year 21

At upstream Monitoring Station EMO, a 14-day period early in November of Mine Year 21 experienced daily rainfall exceeding 20 mm/day on five days (Figure 4-4). Due to these daily rainfalls, outflow increased twice, from about 10 L/s to around 24-35 L/s. This high outflow was the highest to date after the preceding drier summer months, and thus represents the “first flush” from the waste rock after “wetting up”.

If 1:1 dilution were applicable, then electrical conductivity and aqueous concentrations should decrease proportionally at the same time as flow increased by about 140% to 250% relative to the low flow.

During the first half of this time interval in early November, conductivity remained relatively constant at 2100-2300 uS/cm (Figure 4-4). Thus, there was no 1:1 dilution of drainage concentrations and, in fact, there was no overall significant dilution at all based on conductivity. In turn, this highlights how quickly infiltration can accumulate chemical constituents during the hours it is passing through the waste rock as unattenuated “plug flow”.

At the same time that conductivity remained relatively constant, sulphate decreased by 15%; acidity decreased by 30%; copper, zinc, and cadmium showed no consistent decrease; and pH remained between 3.74 and 3.88 presumably reflecting the solid-liquid buffering of the Fe-OH sub-region (Morin, 2015; Morin and Hutt, 1997 and 2001). Thus, acidity and sulphate displayed a relatively minor dilution trend, but the others did display any trend, highlighting some unique responses among the aqueous elements. In all cases, the trends were not close to a 1:1 dilution upon a 140% to 250% increase in flow.

During the second half of this time interval, on November 12 (Figure 4-4), rainfall peaked at nearly 30 mm/day after a preceding wet day, flow increased from 15 to 35 L/s (increased by 130%) that day, but conductivity decreased from 2200 to only 1800 uS/cm (a 20% decrease). At the same time, sulphate decreased by 5%, zinc decreased by 15%, copper and cadmium remained about the same, and pH increased from 3.77 to only 3.80. As before, there was no geochemical response close to 1:1 dilution by flow, and trends in aqueous concentrations differed among elements and in contrast to the earlier period of November. Through the few subsequent days, sulphate and conductivity increased while acidity decreased.

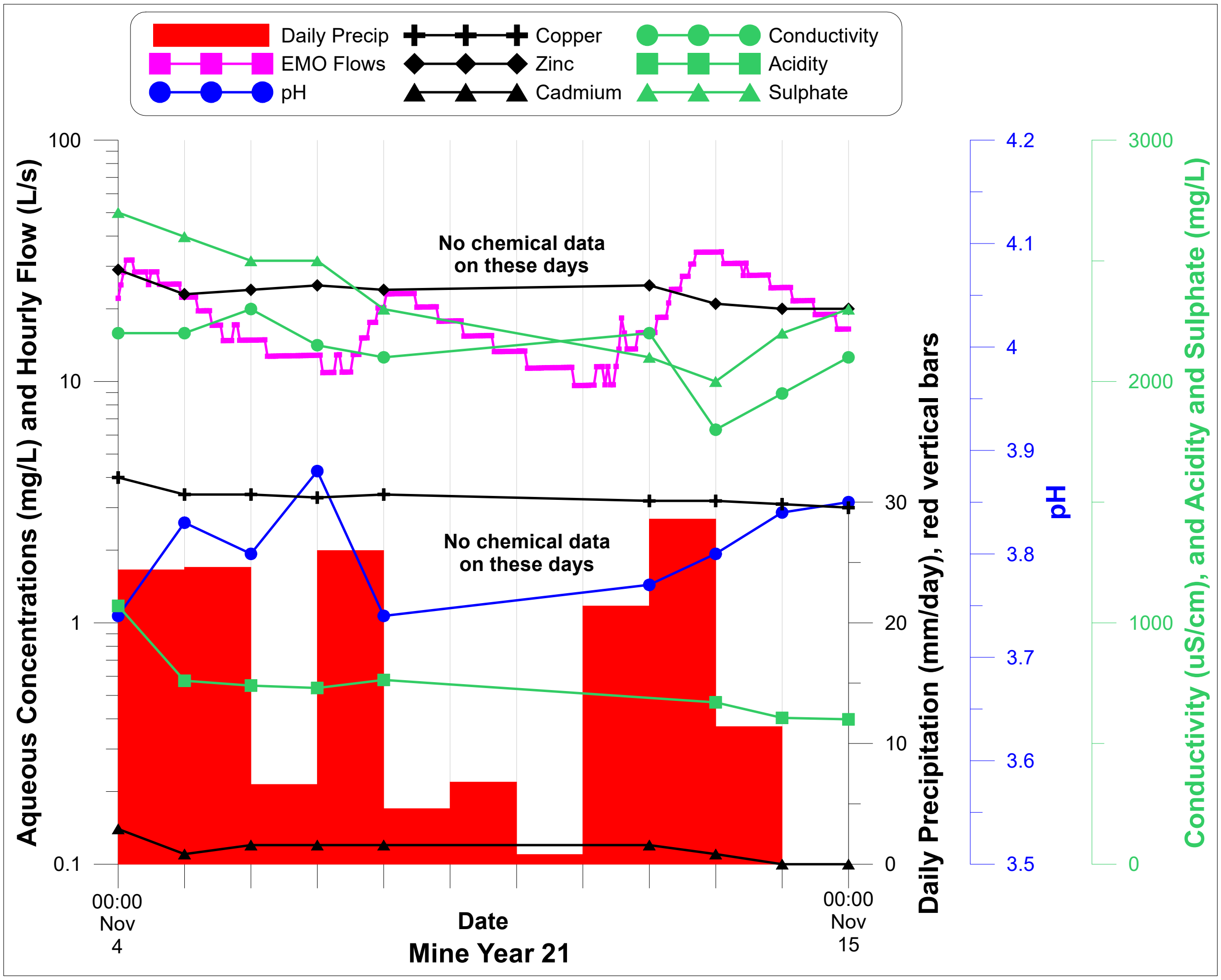

Figure 4-4. Temporal trends of precipitation, outflow, and chemistry at Station EMO in early November of Mine Year 21.

4.2.2 The Second Half of November of Mine Year 21

Turning to the second half of November of Mine Year 21 (Figure 4-5), rainfall peaked on November 16 at roughly 60 mm/day, surrounded by wet days with roughly 30 mm/day. This caused outflow to peak at 120 L/s the same day of November 15, rising from a low of 20 L/s the previous day (a 500% increase over 20 L/s) and then gradually decreasing through the remainder of the month.

That same day, electrical conductivity decreased from 2100 uS/cm to 1800 (only a 14% decrease). Conductivity continued to decrease gradually for another five days as outflow and dilution also decreased, reaching a low of 1650 (a cumulative decrease of 21% since November 15). Conductivity then began increasing and reached a seasonal maximum of 2700 uS/cm on December 2.

This suggests peak precipitation at this minesite creates a minor dilution of conductivity, which persists from the near-immediate rapid outflow through the outflow over the next five days. A similar minimum conductivity on November 27-28, with no spike in rainfall, may represent a mass of somewhat diluted water being released 11-12 days later after peak precipitation, but this is not consistent with trends in other parameters.

Through the last half of November, acidity and sulphate generally mimicked conductivity, although missing datapoints for acidity make this less certain (Figure 4-5). The somewhat lower acidity, sulphate, and conductivity around the peak outflow on November 16 should theoretically cause pH to increase due to some minor dilution. In contradiction, pH decreased slightly around November 16, from around 3.85 to 3.77. For the remainder of the month, pH erratically approached 4.0 (towards neutral) as acidity, sulphate, and conductivity generally increased.

Aqueous concentrations of copper, zinc, and cadmium decreased 20% to 25% (Figure 4-5). They reached minimums with a few days of peak rainfall on November 16, and then generally increased through the remainder of November.

As noted for the first half of November during first flush, there was no geochemical response close to 1:1 dilution by flow, and trends in aqueous concentrations differed among elements.

4.2.3 January of Mine Year 22

In the last part of January of the following year (Figure 4-6), precipitation and outflow were relatively low until January 23. On January 23, peak precipitation was roughly 60 mm/day, causing outflow to increase on the same day from about 8 L/s to about 57 L/s (600% increase above 8 L/s) within a few hours. Between January 24 and February 5, most days had precipitation above 10 mm/day and five had more than 20 mm/day. This caused flow to oscillate and remain relatively high between 20 and 70 L/s.

In response to the storm on January 23, conductivity fell from around 1800 uS/cm to 1500-1600 uS/cm for seven days until January 30 (no data for January 25 and 26). This is less than a 20% decrease as flow increased 600%. Afterwards, conductivity oscillated like flow. However, local peak flows were associated with locally high or low conductivity, so there was no strong correlation.

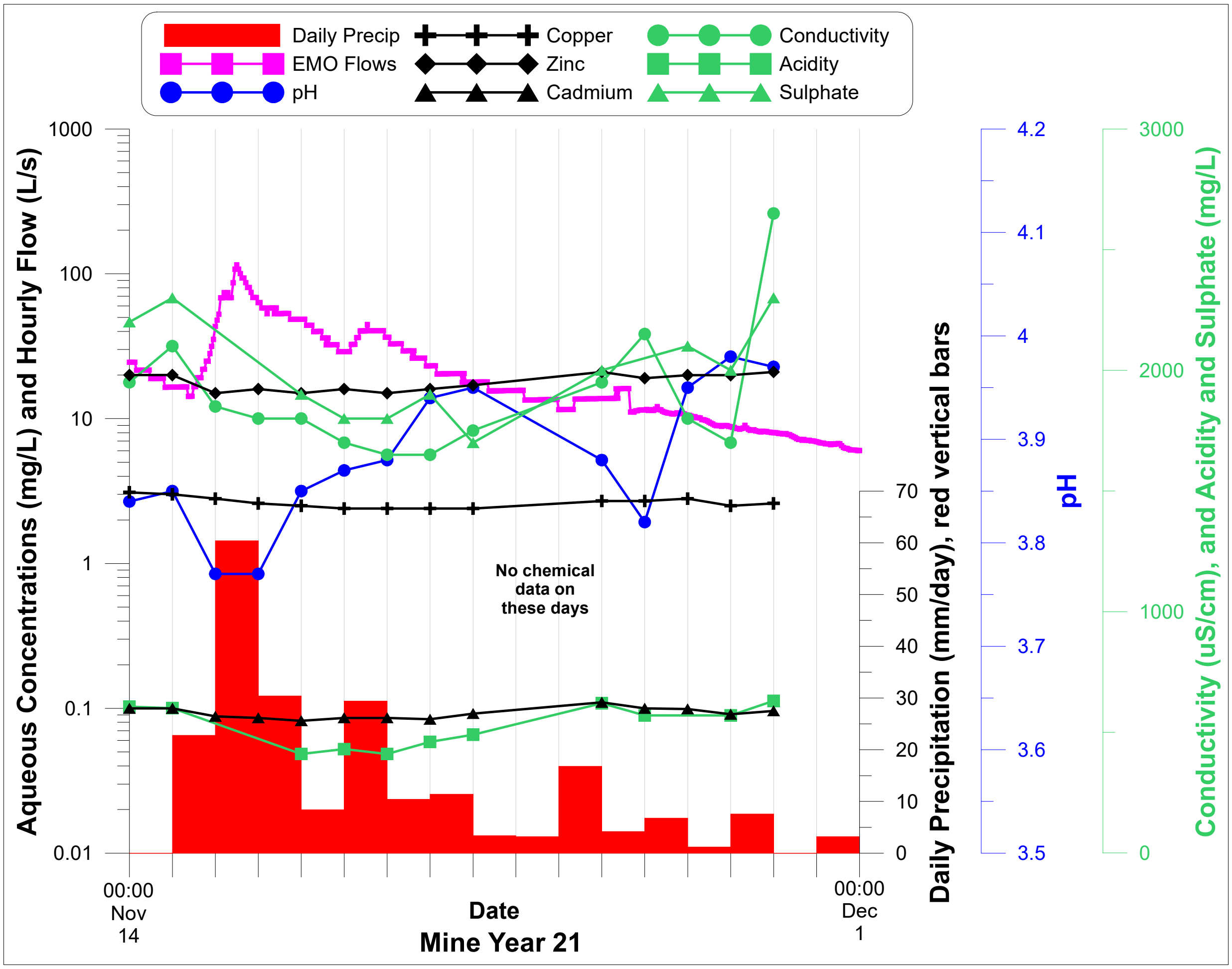

Figure 4-5. Temporal trends of precipitation, outflow, and chemistry at Station EMO in late November of Mine Year 21.

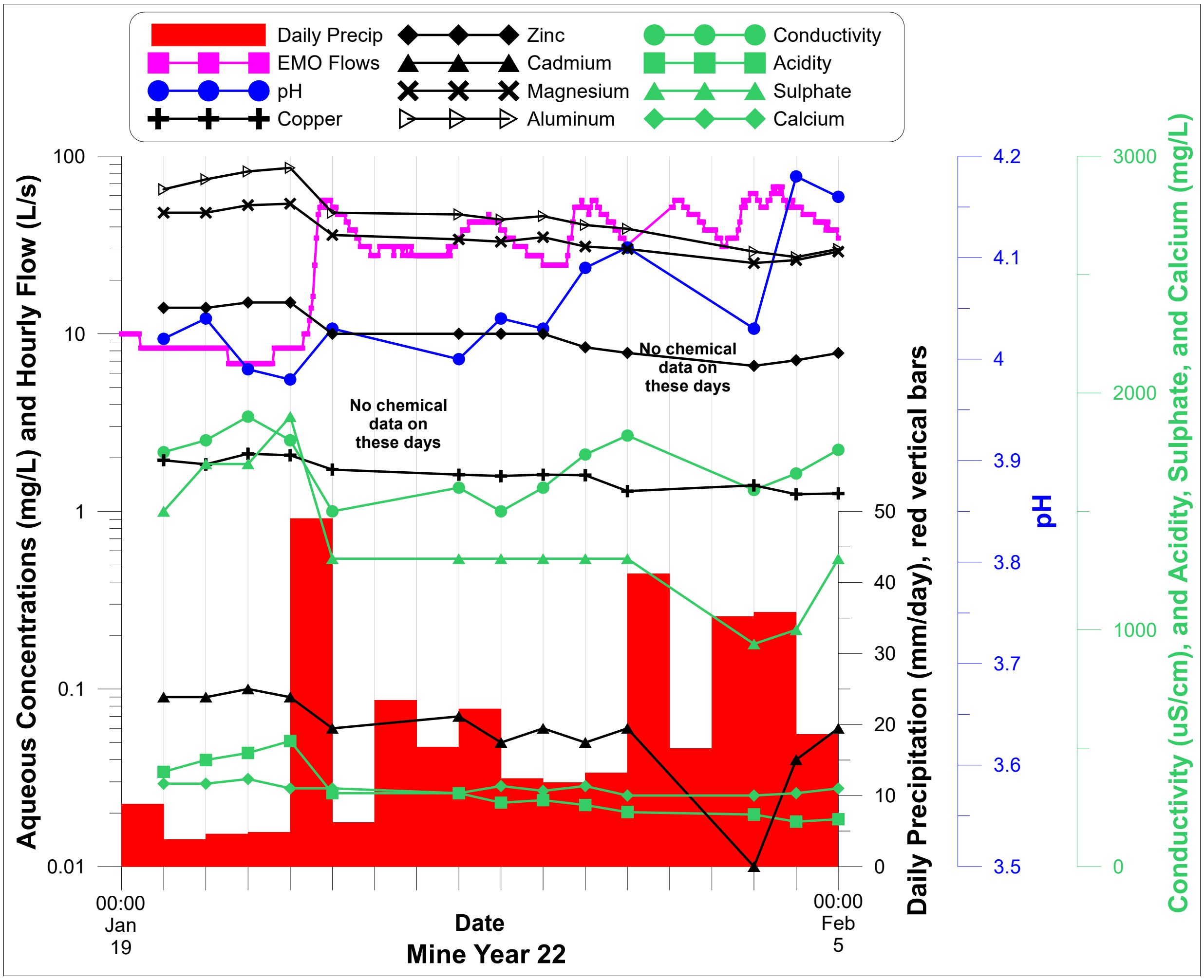

Figure 4-6. Temporal trends of precipitation, outflow, and chemistry at Station EMO in January of Mine Year 22.

On January 23, sulphate and acidity decreased more than conductivity, by 30% and 40%, respectively (Figure 4-6). Unlike conductivity, their concentrations did not recover, but fell even lower through early February.

Within a few days after January 23, copper, zinc, and cadmium decreased by 25%, 35%, and 45%, respectively, as flow increased 600%. Similar to sulphate and acidity, but unlike conductivity, their concentrations generally continued to decrease through early February.

Two newly added elements, magnesium and aluminum, also decreased in concentrations on January 23, by 35% and 45%, respectively (Figure 4-6). As with sulphate, acidity, copper, zinc, and cadmium, their concentrations generally continued to decrease through early February.

A third newly added element, calcium, showed about a 15% decrease shortly after January 23. As with conductivity, calcium showed no ongoing downward trend, unlike several other elements.

Around January 23, pH remained around 4.0 despite the large changes in flow. It then began an erratic trend of increasing towards 4.2 in early February.

As noted for November of the previous year, there was no geochemical response close to 1:1 dilution by flow, and trends in aqueous concentrations differed among elements. Nevertheless, there was a more common trend of noticeable dilution between 15% and 45% upon an increase of 600% in flow.

5. Conclusion

This MDAG case study looked at time series of individual chemical elements, pH, and flow for the same time periods and for the same two monitoring stations as the previous case study on flow. The interest here lies in which elements correlated with flow, pH, and/or other aqueous elements at these two stations. Because aqueous concentrations arise when water flows over and through mine materials like waste rock, a close correlation between full-scale flow and chemistry might be expected. For example, a strong, short-term peak in rapid outflow would have a short residence time within the waste rock, and thus aqueous concentrations carried by the peak flow could be proportionally lower due to dilution. This is not observed in full-scale drainages.

In this case study, geochemical parameters and chemical elements (e.g., pH, electrical conductivity, sulphate, acidity, copper, zinc, and calcium), and flow, were significantly autocorrelated, and not surprisingly cross correlated with each other. Thus, this case study looked at finer temporal details, to see if aqueous concentrations and time series correlated or differed in some statistically minor, but geochemically important, way.

At both the downstream and upstream monitoring stations, selected time series spanning days to weeks showed no geochemical responses attributable to 1:1 dilution by flow, even during substantial peaks of flow. The lack of 1:1 inverse correlation has also been documented at other minesites, and even in non-mining-related catchments. This should raise alarms about a standard predictive technique for minesite-drainage chemistry, which assumes a 1:1 inverse correlation by dividing an estimated geochemical loading by an estimated flow to predict a full-scale concentration.

During storms at this minesite, daily outflows at the stations often increased sharply by 400-900%. However, at the same time, aqueous concentrations of some parameters decreased by no more than 35% and often showed little correlation with flow or pH. Other elements actually increased substantially in concentration (the opposite of dilution) during peak diluting flows, when pH decreased as flow increased. This highlighted how quickly infiltration could accumulate chemical constituents during the hours it is passing through the waste rock. Overall, trends in aqueous concentrations differed among elements and parameters, among the selected time periods, and before and after brief significant changes in pH.

This MDAG case study highlighted the unique temporal trends of individual elements and parameters identified by high-frequency monitoring. These trends did not correlate well with flow. Some did not correlate well with pH either, and some did correlate with pH in agreement with documented power laws and the Empirical Drainage Chemistry Model (EDCM) for this minesite.

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