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Measurement of seasonal variations in stream water chemistry using a portable photometer: case histories from central and southwestern British Columbia, Canada

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INTRODUCTION

Recognising the effect of seasonal variation on chemistry is important when sampling surface and shallow groundwater, as well as considering baseflow (the groundwater component of stream flow) interaction and chemical influence on stream flow from the surface environment (Hatcher *et al.* 2004). Analyte concentrations in surface water can be affected by various factors including dilution of dissolved solids during periods of precipitation, or increased concentration by input of solutes from erosion. Typically, there is more dilution in spring and early summer caused by snow melt runoff (Bhangu & Whitfield 1997). As well, a higher component of groundwater in flowing surface water (baseflow) is expected in summer and into fall as precipitation and associated runoff decreases. This occurs even though groundwater levels tend to decrease during this time (Allen *et al.* 2008). Water pH is dependent on geology, precipitation, environmental conditions and the interactions between them, but it is important to reliably monitor these variables to understand the environment of the area we are sampling the water. Hence, it is important to consider hydrogeochemical conditions, and not necessarily only at the optimal time for water sampling. This consideration will not only help in evaluation of seasonal variation but would also assist with interpretation of the analytical results.

A large seasonal water sampling campaign in which water samples are sent to an analytical laboratory can be expensive. A more cost-effective alternative technique for water sampling involves the use of a field portable photometer. A rapid hydrogeochemistry methodology using a photometer has been discussed extensively by Yehia & Heberlein (2015) and Yehia *et al.* (2017, 2019). This low cost and rapid method for water analysis could be an attractive option for a comprehensive seasonal variation study.

In this article, we describe two surveys that use a photometer to assess seasonal variation of ground water chemistry in regional and local settings (Fig. 1). The regional survey is a Geoscience BC-funded study carried out in 2016 southwest of the Nazko community in central British Columbia (BC), Canada. The second study involves weekly measurements of water chemistry in a city storm drain with suspected groundwater influx at Vivian Creek in southeast Vancouver, BC. This sampling was carried out between June 2018 and May 2019. For both projects, analysis was performed using the Palintest Photometer 8000 and an Oakton PCSTestr 35 pH meter.

Methods to evaluate the effects of weather

One of the objectives of the Nazko study was to investigate seasonal variations in surface water chemistry. The area is hydrologically complex. It has a variety of water body types, including lakes and bogs of different sizes (natural and beaver-dammed) occurring at a

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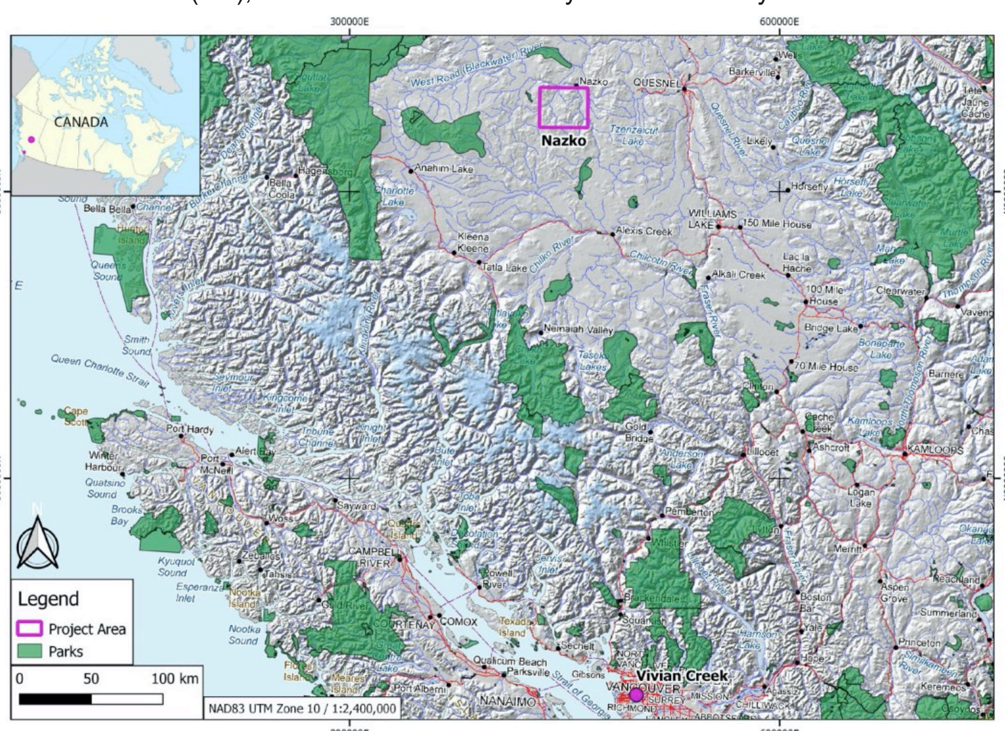

Figure 1. The locations of two study areas in British Columbia, Canada.

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range of elevations, and complex water courses running into and out of the lakes as well as hard to identify groundwater discharge sites. Changes in water chemistry were monitored through the analysis of repeated water samples collected at the same locations during sampling campaigns in June, August, and October. Throughout the survey, above average precipitation (Fig. 2) raised concern about the possibility of large fluctuations in analyte concentrations (see below).

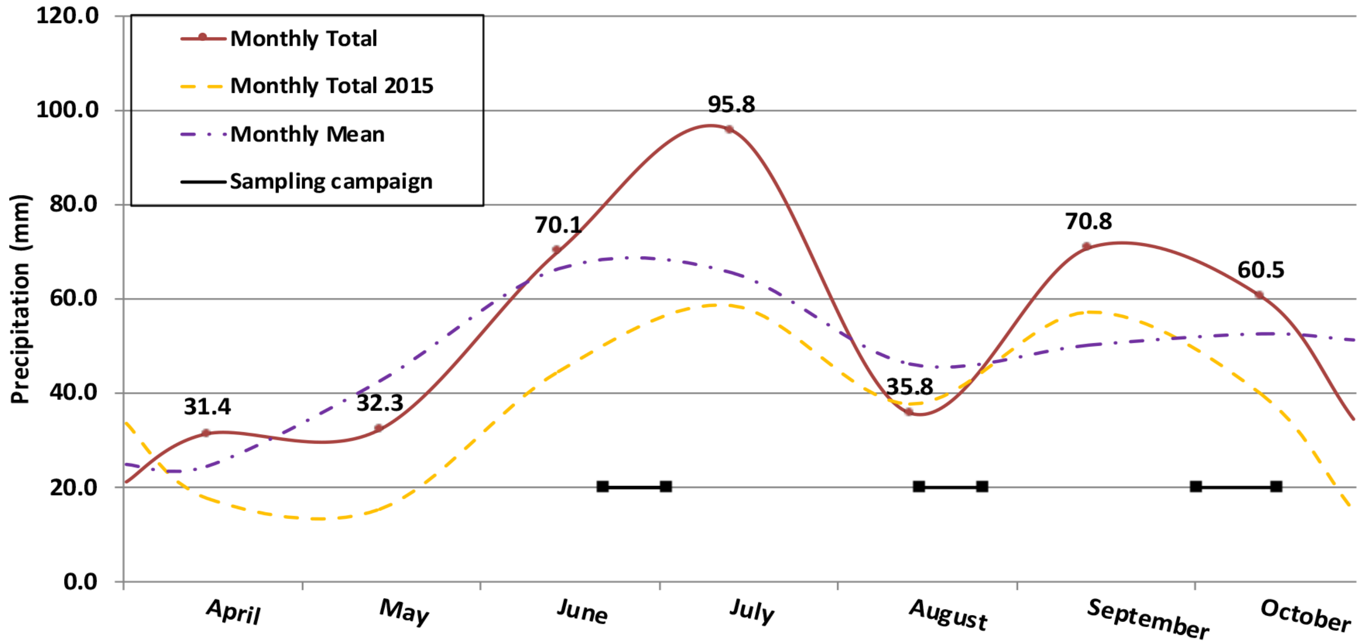

Figure 2. Nazko study precipitation chart. Values are from Environment Canada Quesnel station.

In the Vivian Creek study, one of the main objectives was to examine if the photometer was able to identify seasonal trends in the water chemistry at a single site. Unfiltered samples (according to reagent manufacturers' procedures) and field duplicates were collected and analyzed from the city storm drain output between 10 am and noon weekly (mostly on Mondays). Weather during the sampling period was marked by a drier than usual summer followed by a wetter than average fall (September-December) and winter (December-March), with late prolonged snowfall during February, and a drier than usual spring (March-June) (Fig. 3). A weather station using a digital La Crosse wireless rain gauge was used to measure precipitation close to the study site.

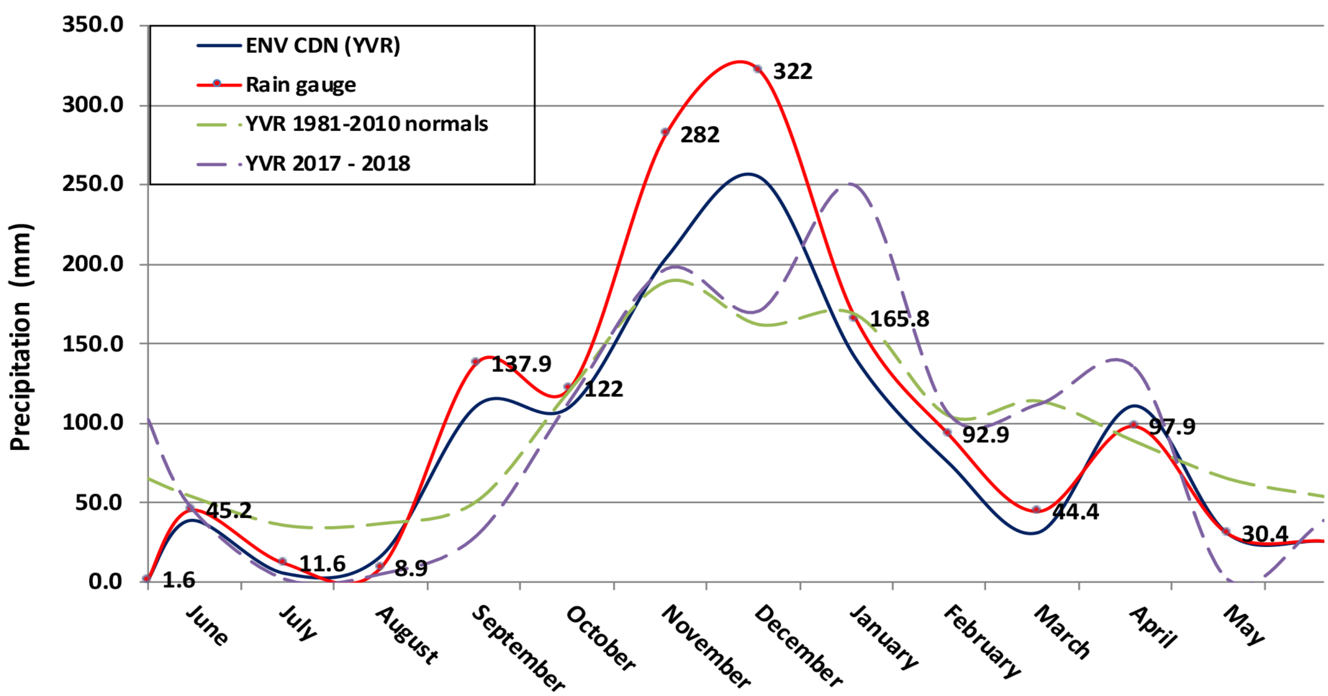

Figure 3. Vivian Creek, Vancouver precipitation chart. Environment Canada (ENV CDN) data are from the Vancouver airport (YVR) station ten kilometres west of the sample site.

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RESULTS

Nazko

For the Nazko study, the effect of rainfall and other seasonal changes on analyte levels can be demonstrated by (1) plotting the measured concentrations at each site over time; and (2) by plotting results for each season in order of increasing concentration. The first plot is useful because it compares concentrations directly by season at each site, while the second provides an overall seasonal comparison. Charts for total Cu and SO_4 do not include data for June because June turbidity readings revealed false trends in the photometer results caused by a high load of suspended particles that were too fine to be removed by the 0.45 micron filtration. This was corrected in the August and October data after consultation with Palintest (Yehia *et al.* 2017), but not in the June data because no archived water samples were available for reanalysis.

Water pH results (Fig. 4a) are reasonably consistent despite the variable precipitation during the sampling campaigns. Of all the analytes, Al (Fig. 4b) displays the strongest response to rainfall and there is a large difference in seasonal Al concentrations, with values increasing during higher precipitation events. In contrast, total hardness (as $CaCO_3$ - Fig. 4c) displays a gradual increase with the lowest concentrations measured in June and the highest values detected in October. Unsurprisingly, Mg and K show comparable trends to hardness reflecting concentrations of other cations measured by the hardness analysis

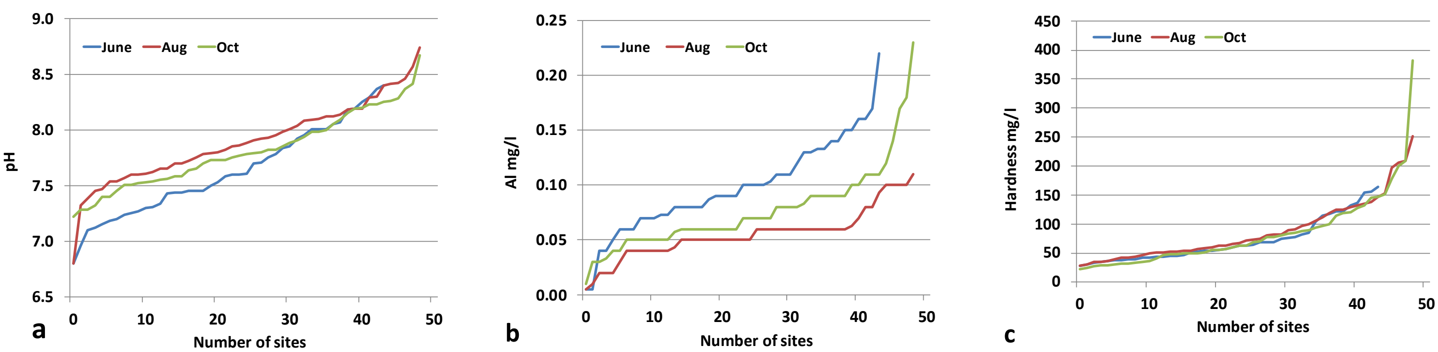

Figure 4. Nazko study seasonal variation Global Positioning System (GPS) stations and seasonal average for pH (a), and cumulative comparison for, Al (b), and total hardness ($CaCO_3$, c).

Copper displays a strong seasonal variability (Fig. 5a). As expected, concentrations were highest during the October survey when precipitation increased. This may be the result of higher concentrations caused by increased baseflow as a

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component of the surface water, in addition higher concentrations following rain known as first flush. Finally, SO_4 (Fig. 5b), an important mineralization indicator, displays low concentrations (1.0 to 14.0 mg/l) throughout the surveys.

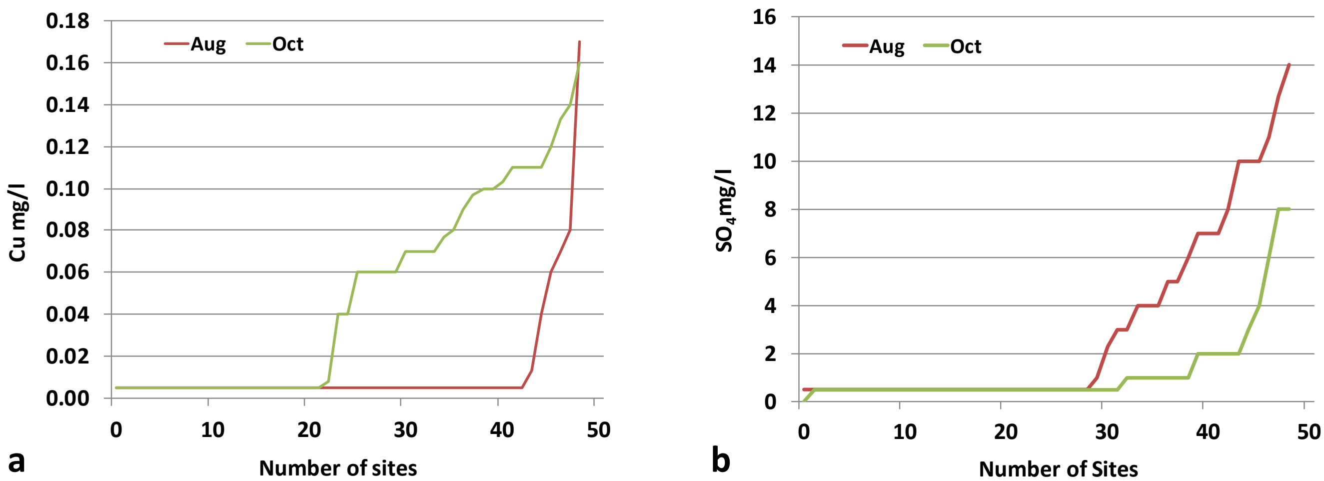

Figure 5. Nazko study seasonal variation GPS stations seasonal cumulative comparison for total Cu (a) and SO_4 (b).

Vivian Creek

In the Vivian Creek study, seasonal variations are demonstrated by (1) plotting results against weekly precipitation, (2) plotting results versus monthly precipitation and by (3) with box plot diagrams. The first charts examine in more detail the relationship between analyte concentration and precipitation. The second monthly chart provides simplified trends that show overall seasonal variation for the year of sampling. The boxplot (Krüzl, 1988) is a graphical way of visually summarizing the distribution of values in a sample or population and could aid in our comparison of water chemistry seasonal variations. Box plots provide information about the skewness of a distribution, the range of values as well as the median of the distribution.

As shown in Figure 6a-c, pH varies between neutral to slightly alkaline with a maximum value of 7.8. There is no obvious relationship between pH and precipitation (Fig. 6a). Vivian Creek pH appears to be more neutral during the summer and slightly more alkaline in the fall and winter, although the highest value recorded was in June (Fig. 6b). The box plots (Fig. 6c) show a gradual decrease in median values in late summer followed by a subtle increase from November to February followed by another gradual increase through the spring. The increase in pH in the winter occurs immediately after the period of maximum precipitation (in December), and may be attributed to increased dilution during the winter.

As seen in the Nazko study, the Al concentration in water at Vivian (Fig. 6d-f) is sensitive to precipitation and shows a strong trend of decreasing values between December and May (Fig. 6d). Although no results were measured in the summer of 2018, results for the remainder of the year show a systematic decrease in concentration starting immediately after maximum precipitation in December (Fig. 6e), which is clearly visible in the monthly chart and box plots (Fig. 6f).

Total hardness shows a positive correlation with precipitation between June and November (Fig. 6g-i) but from February to May, it remains consistently high while still demonstrating a sympathetic relationship to precipitation (Fig. 6g). Monthly graphs (Fig. 6h) and box plots (Fig 6i) confirm this pattern. The higher concentrations detected from February to May are likely due to the use of road salt following snowfall in the middle of February. The snow remained on the ground until the end of the month. Although the City of Vancouver uses

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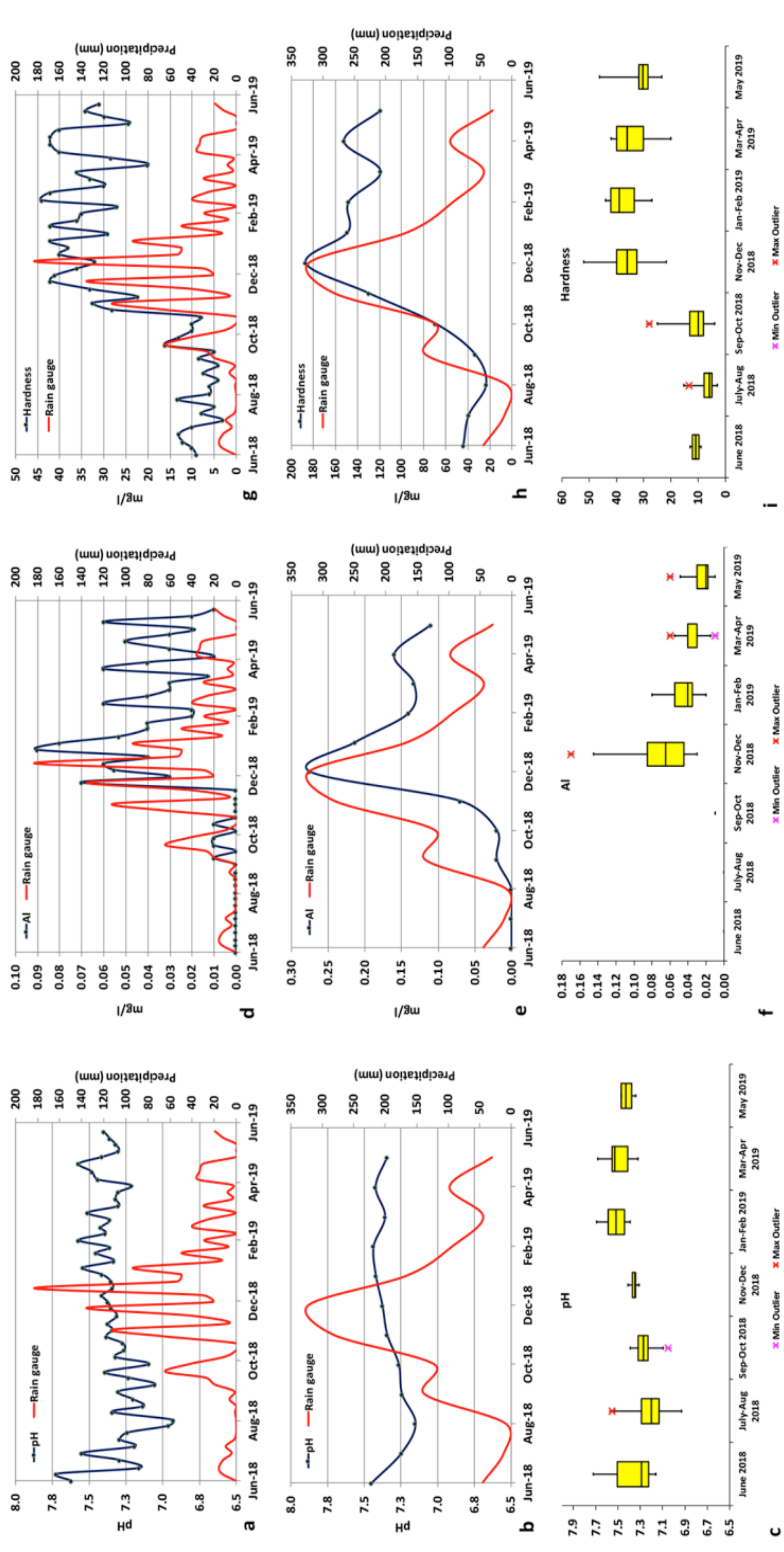

Figure 6. Vivian Creek seasonal variation study weekly and monthly charts and boxplot for pH (a, b, c), Al (d, e, f) and total hardness ($CaCO_3$, g, h, i). Note that for pH, monthly values are average and for Al and hardness, monthly values are totals (weekly added). In the box plots the box, bisected by the median, extend from lower to upper hinge and contain 50 percent the values (interquartile range). The whiskers extend from the hinges to a value of hinge +/- 1.5 the interquartile range. Values beyond the whiskers are considered as outliers.

untreated NaCl as road salt in the winter (City of Vancouver, personal communication), impurities can be observed with pink and grey salt possibly containing higher Ca, Mg and Mn. Road salt input by Cl^-, Mg and Mn show comparable trends. Interestingly, although salinity increased considerably following the application of road salt (Cl^- weekly high of 45.80 ppm and salinity of 239.0 ppm), pH did not change significantly and this may be due to the increased buffering of the water chemistry by the higher dissolved Ca and Mg concentrations.

In contrast, Cu (Fig. 7a-c) and SO_4 (Fig. 7d-f) do not demonstrate a clear seasonal trend. There is no observable correlation between Cu, SO_4 and precipitation on either the weekly or monthly charts, while the box plot shows a wide range of values in January to May.

DISCUSSION

The two main objectives of this paper were to identify if seasonal variation in water chemistry could be measured by photometer and to assess those seasonal variations in regional and local settings. In both cases, we were able to observe seasonal variations in the water chemistry for some of the measured analytes and that the photometer could detect those trends.

For the Nazko study where there was above average precipitation from June to October, results reveal how the analyte concentrations responded to increased precipitation. Despite

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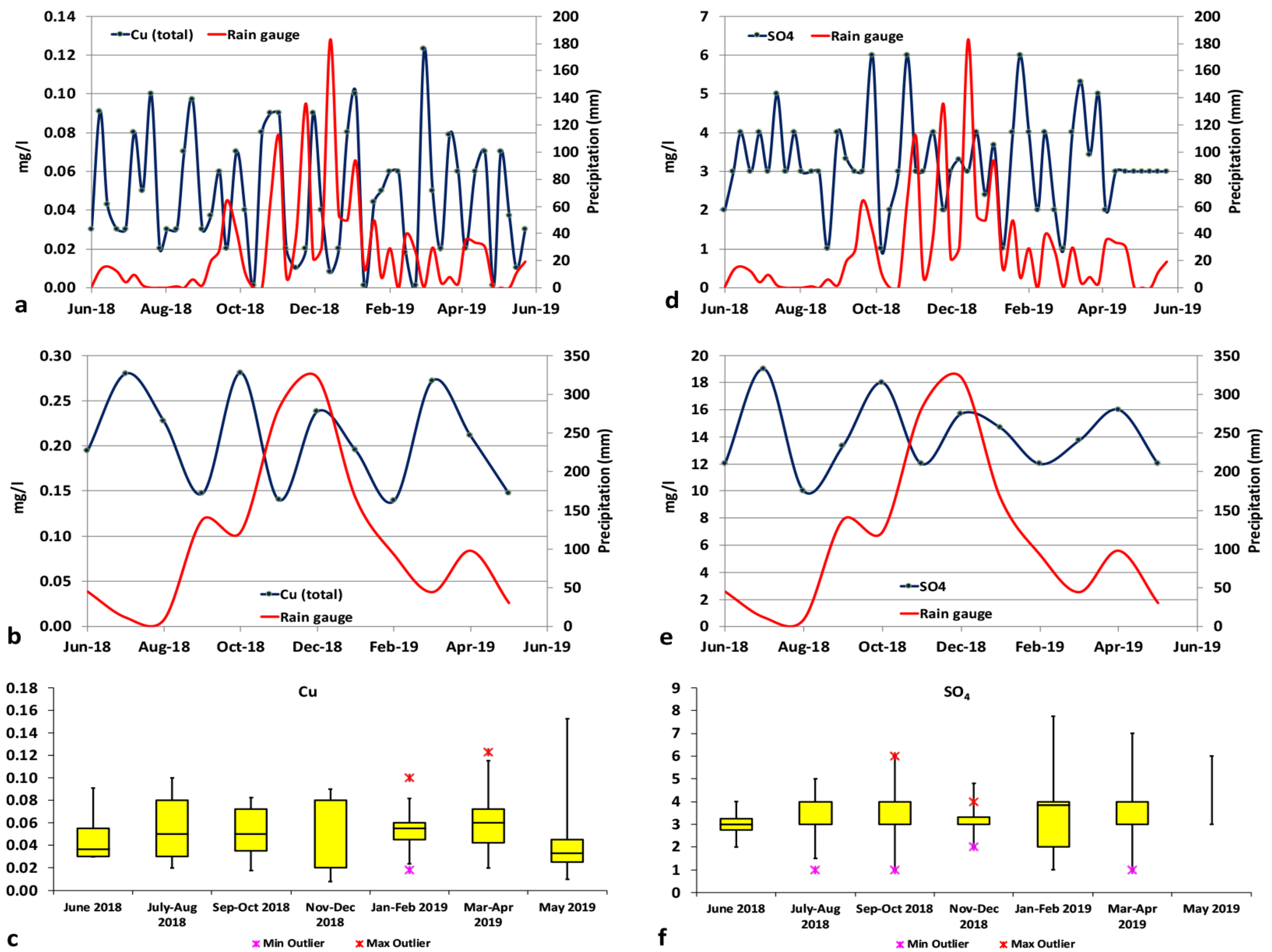

Figure 7. Vivian Creek seasonal variation study weekly and monthly charts and box plot for total Cu (a, b, c) and SO_4 (d, e, f).

the elevated turbidity and the problems caused by it in the June Cu and SO_4 readings, sufficient data were collected to provide an understanding of the behaviour of these analytes. Some of the analytes, including Mg, K and hardness, showed little variation between seasons whereas analytes such as Cu responded to changes in precipitation. Of note, the highest SO_4 measurement was in August, making it a better time for sampling streams as part of a resource exploration survey because the SO_4 peak is earlier than that of other pathfinder elements (e.g. Cu). Even though concentrations of Ca and K increased in October, their element patterns did not change significantly from August to October.

In the Vivian Creek study, some analytes such as Al and hardness displayed clear seasonal variations, whereas Cu and SO_4 did not. As with the Nazko results, Al showed a strong positive correlation with precipitation. Hardness showed a similar trend, albeit not as pronounced as Al, and we suspect that if it were not for the effect of road salt use, hardness may have continued decreasing during the second part of the year. For Cu and SO_4 no obvious seasonal trends were observed. The fluctuations in Cu and SO_4 concentrations may be attributed to: (1) precipitation and or weathering; (2) input of contaminants from city street runoff.

The photometer detection limit, sensitivity, and reliability are shown to be adequate to allow for measurement of seasonal variations in water chemistry. The low cost and rapid analysis mean that daily, or even multi-daily, variations can be investigated. The inexpensive reagents (about $0.50 per analyte) allow for customization of the analyte suite which can further reduce the cost.

An interesting implication of the Vivian Creek results is that this type of testing could be suitable for environmental monitoring. The increased water hardness after the addition of road salt could be detected well over two months after application of salt and may have had implications to base flow and ultimately groundwater contamination pH. This type of monitoring with the photometer can be extended to other types of resource industries, such as daily downstream analysis from drilling sites, tailings pond dams, landfills or forestry stream monitoring.

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CONCLUSIONS

In summary, this investigation of seasonal variability using a portable photometer shows that:

- The low cost, rapid analysis and low detection limits of the photometer make it a practical option for seasonal variability investigations, and for environmental monitoring.
- The seasonal timing for selection of various analytes, or when the samples were collected for testing, should be taken under careful consideration.
- On a regional mineral exploration water survey scale, the ideal season for sampling is late summer.
- For some analytes, two sampling campaigns in different seasons may be sufficient to demonstrate variation that will possibly be needed to be taken under consideration.

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