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Original Articles

Monitoring heavy metal concentrations in turbid rivers: Can fixed frequency sampling regimes accurately determine criteria exceedance frequencies, distribution statistics and temporal trends?

Jason G. Kerr*, James P. Zettel, Cynthia N. McClain, Mary K. Kruk

Alberta Environment and Parks, Environmental Monitoring and Science Division, 3115 – 12 Street NE, Calgary, Alberta T2E 7J2, Canada

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ABSTRACT

The accurate determination of water quality criteria exceedance frequencies, distribution statistics (e.g., mean, median and percentile concentrations) and temporal trends in constituent concentrations is critical to effective water resources management. Here we examine the effect of sampling regime on the accuracy of trace metal concentration, water quality criteria exceedance, and trend statistics at three sites in a turbid and highly dynamic river (mean ± 1 standard deviation total suspended solids [TSS] concentration = 56 ± 148 mg L^{-1}, 278 ± 777 mg L^{-1} and 521 ± 909 mg L^{-1}). Daily TSS data from the Red Deer River (RDR) in Alberta, Canada were used to generate a 10-year baseline data set of total Pb, Hg, Cu and Cd concentrations based on linear regression relationships. The baseline data was then sub-sampled to create fixed frequency (3-day, 7-day, 14-day, 30-day, 60-day and 90-day) and flow augmented (30-day + $Q \geq$ 90th percentile) regimes. Precision increased with increased sampling frequency for all statistics over both annual and decadal time scales. However, annual statistical estimates exhibited consistently poorer precision than estimates summarized over 10 years. For estimates of annual mean and 90th percentile concentrations, precision decreased as the variation in daily constituent concentrations in the baseline data set for each year increased. Estimates of median concentrations were generally more precise than the mean or 90th percentile, while estimates of criteria exceedance had particularly poor precision and exhibited systemic bias when the frequency of exceedance in the baseline data was low (i.e., < 10%). In terms of bias, estimates of mean, median and 90th percentile concentrations generally exhibited little to no systemic bias. Flow augmented sampling had similar or better precision than 14-day fixed frequency sampling (which had a similar sampling effort; i.e., n = 152–153) but resulted in large positive bias (median % error = 65–729%) for concentration and exceedance statistics. Considerable variation in estimates of trend statistics were observed when fixed frequency sampling was employed. Importantly, at a monthly frequency, significant trends ($p < 0.1$) were detected when a trend in the baseline data did not exist. Finally, based on a 20% error threshold, the application of fixed frequency sampling regimes (3-day, 7-day, 14-day and 30-day) failed to accurately estimate metal concentrations and criteria exceedances. Our research highlights the importance of considering the uncertainty associated with fundamental concentration statistics when designing and/or interpreting data from water quality monitoring networks in turbid river systems.

1. Introduction

Collecting and reporting on data within acceptable limits of uncertainty is a critical component of effective environmental monitoring. Potential sources of error in regular water quality monitoring programs include laboratory analyses, sample preservation/storage, discharge measurements, and sample collection (Harmel et al., 2006). In terms of sample collection, a major source of potential error is the frequency with which samples are collected (Harmel et al., 2006; Yanai et al., 2015). For many stream and river monitoring programs, water quality samples are collected at regular fixed intervals (Kirchner et al., 2004; Moatar and Meybeck, 2005; Jones et al., 2012; Horowitz, 2013). Importantly, studies have demonstrated that as the frequency of sampling decreases (e.g., from weekly to monthly), there is a concurrent increase in the error associated with the estimation of constituent loads in streams and rivers (Coynel et al., 2004; Cassidy and Jordan, 2011; Jones et al., 2012). While the estimation of constituent loads is a key goal of many monitoring programs, statistical endpoints summarizing concentration data (e.g., exceedance of water quality criteria, mean/median concentrations and temporal trends in constituent

* Corresponding author.
E-mail address: jason.kerr@gov.ab.ca (J.G. Kerr).

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concentrations) are also important. In fact, water quality thresholds which are used to initiate management actions to protect various freshwater uses (e.g., aquatic biota, recreational or agricultural uses) are frequently based on constituent concentrations (ANZECC and ARMCANZ, 2000; Smith et al., 2001; EU, 2009; AEP, 2012; AEP, 2014). Despite this, there is relatively little information on the effect of sampling frequency on the uncertainty associated with key statistical endpoints which summarize concentration data.

While much of our understanding of the effect of sampling frequency on measurement error comes from studies examining loads, there is some evidence to suggest that concentration endpoints may also be susceptible to error as a function of sampling regime. Studies have reported increased error as a function of decreased sampling frequency for estimates of mean, median and/or percentile concentrations (Pappas and Huang, 2008; Birgand et al., 2010; Skarbøvik et al., 2012; Grove et al., 2015), the proportion of samples exceeding specific water quality criteria (Jones et al., 2012; Thompson et al., 2014; Reynolds et al., 2016) and the classification of water bodies based on chemical constituent concentrations (Skeffington et al., 2015). Based on these results, a simple solution is to sample more frequently. But how much more? The collection of samples is often the most expensive component of a monitoring program (Caughlan and Oakley, 2001) and therefore an optimal sampling regime needs to provide data within acceptable limits of uncertainty while concurrently maximizing available resources (Horowitz, 2013).

There are two key challenges in terms of defining an optimal sampling regime. Firstly, the relationship between sampling regime and error is often very constituent and/or site specific making extrapolation of error values beyond a specific study area and/or constituent problematic. In particular, site specific hydrology has been shown to be important. Specifically, streams which exhibit a high degree of variability in flow often require a higher frequency of sampling relative to systems where flow is less variable (Stelzer and Likens, 2006; Moatar et al., 2006). Furthermore, not all constituents are equally susceptible to error. Sediment and sediment bound-constituent concentrations are generally very responsive to changes in flow and are therefore particularly susceptible to error when fixed frequency sampling is employed (Kronvang and Bruhn, 1996). The second major challenge in determining an optimal sampling regime is that monitoring programs, and in particular long-term monitoring programs, are rarely established to do just one thing. Monitoring data are frequently used to summarize constituent concentrations and water quality criteria exceedances at multiple sites over seasonal to decadal time scales and in the case of long-term programs, to examine temporal trends. As such, an important but poorly understood question is: to what extent do commonly employed sampling regimes accurately deliver on these fundamental information requirements?

An important although frequently overlooked consideration in the design of monitoring networks is the extent to which different statistical endpoints (e.g., mean concentrations, percent guideline exceedances and trend statistics) vary in their sensitivity to sampling regime. Birgand et al. (2010) demonstrated that estimates of upper percentile concentrations were more sensitive to reduced sampling frequency than either mean or median estimates. While this suggests that differences among endpoints are important, studies comparing error as a function of sampling frequency across a suite of statistics summarizing concentration data are rare. Furthermore, in the case of trend statistics, there is a paucity of information relating sampling frequency to error, despite the central role that trend assessment plays in water resources monitoring and management. Finally, based on studies examining the effect of sampling regimes on loads, the duration over which data are summarized may also be important. For estimates of loads, it has been demonstrated that as the duration of the estimate decreases (e.g., from decadal to annual), the error associated with these estimates increases (Alewell et al., 2004; Aulenbach and Hooper, 2006; Kerr et al., 2016). However, the extent to which this applies to estimates of concentration based statistics is unclear. This is an important knowledge gap given that many jurisdictions require concentration data be assessed on an annual basis (e.g., EU, 2009; AEP, 2014).

An optimal sampling regime should provide data within acceptable limits of uncertainty for all sites, constituents and summary statistics upon which the program is designed to address. This requires an understanding of the relationship between sampling regime, statistical endpoints, reporting duration, and error. The objective of this study is to address the question of whether commonly employed sampling regimes can accurately estimate fundamental concentration and criteria exceedance statistics for sediment bound constituents in a turbid and highly dynamic river system. Specifically, we focus on heavy metals and examine the accuracy of mean, median and 90th percentile concentrations, water quality criteria exceedances, and temporal trend estimates as a function of sampling regime over annual and decadal time scales.

2. Methods

2.1. Study sites and data sets

The study was conducted using data from the Red Deer River (RDR), Alberta. The RDR watershed (49,650 km^2) includes the Alberta badlands which are a source of substantial sediment to the RDR, particularly during convective rainstorms (Campbell, 1970). Heavy metal concentrations in the RDR are closely related to the concentrations of suspended sediments. As such, sediment fluxes from the badlands frequently result in elevated heavy metals in the RDR and exceedances of water quality criteria for the protection of aquatic biota (Kerr and Cooke, 2017). The relationships between heavy metal concentrations and total suspended solids (TSS) in the RDR were used to generate a baseline data set of metal concentrations from daily TSS data. Daily TSS data were obtained from Water Survey of Canada (www. wateroffice.ec.gc.ca) for the open water (i.e., ice free) period (Apr-Oct) from 1975 to 1984. Samples were collected by Water Survey of Canada using depth integrated samplers every few days during average flow conditions and more frequently during event flows (% of days sampled at each station = 42–57%; Supplementary Table 1). Mean daily TSS concentrations were subsequently generated by interpolation between samples (Ashmore and Day, 1988). Three stations were included in our analysis: one upstream of the badlands and the city of Red Deer (RDR-RD; mean ± 1SD TSS = 56 ± 148 $mg\,L^{-1}$); one downstream of the badlands near the town of Drumheller (RDR-DH; mean ± 1SD TSS = 278 ± 777 $mg\,L^{-1}$); and one downstream of the badlands near the Alberta-Saskatchewan border at Bindloss (RDR-BL; mean ± 1SD TSS = 521 ± 909 $mg\,L^{-1}$) (Supplementary Table 1).

A second data set obtained from Alberta Environment and Parks (AEP; www.aep.alberta.ca) was used to generate linear least squares regression models describing total mercury (THg), lead (TPb), cadmium (TCd) and copper (TCu) concentrations as a function of TSS in the RDR watershed (Supplementary Fig. 1). TSS and metals data were obtained from grab samples collected at nine locations within the RDR watershed at weekly to monthly sampling frequencies during the open water season from 2007 to 2015. For each metal, a single regression model derived from the 2007–2015 data set was then applied to daily TSS concentrations (1975–1984) obtained from Water Survey of Canada to generate daily metal concentrations over a 10-year period for all three stations. We refer hereafter to this data set as the “baseline” data set. There are two important caveats in regards to the baseline data set. Firstly, the relationships for total metal concentrations *vs*. TSS generated from 2007–15 may not be applicable to the 1975–1984 period due to unknown factors that may have changed this relationship over time. Secondly, daily variation in modelled metal concentrations reflect only variation related to changes in TSS concentration and do not include potential variation associated with other factors (e.g., changes in dissolved metal concentrations or changes in the concentration of metals

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