Hydrogeochemistry in a relatively unmodified subtropical catchment: Insights regarding the health and aesthetic risks of manganese

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ABSTRACT

Study region: Metal and nutrient concentrations were analysed from freshwater and soil collected from a relatively unmodified ephemeral subtropical catchment in Central Queensland, Australia. Samples were collected quarterly between December 2012 and December 2014.

Study focus: There is increasing concern about the health effects of manganese in drinking water, prompting interest in understanding manganese dynamics. This study investigated the temporal and spatial patterns of metals and nutrients, as influenced by summer rainfall; and the impacts of those variables on drinking water, associated infrastructure and concomitant health risks.

New hydrological insights for region: Results show that the hydrogeochemistry of Baffle Creek was predominantly driven by rain events, with differing responses to varying magnitudes of rain and discharge. Following a flushing event, dissolved aluminium and nitrate increased in the surface and drinking water, whereas manganese and ammonia were undetectable in the drinking water and occurred only in small concentrations in the surface waters. In contrast, when rainfall events occurred without an associated flush, manganese, iron and ammonia concentrations increased in the drinking water. The hydrochemistry of manganese and iron in the supply chain infrastructure was strongly positively correlated with ammonia, and aluminium correlated with nitrate concentrations. Currently the drinking water supply does not pose a threat to chronic manganese exposure for humans, however elevated concentrations are experienced periodically; and may become more problematic under climate change scenarios.

1. Introduction

Manganese (Mn) is found naturally in ground and surface waters, with approximately 97% of surface water sites in the USA known to contain Mn (USEPA 2002). The primary source of Mn in natural catchments is the surrounding soils, bedrock and organic matter washed into the water bodies. In surface waters, Mn occurs in both dissolved and suspended forms, with the prevalence of form depending on factors such as pH, anions present and oxidation–reduction potential (ATSDR, 2000). In most waters, the divalent form Mn²⁺ dominates at pH 4–7, however, more highly oxidised forms can arise at higher pH values, or result from microbial oxidation (ATSDR, 2000). Furthermore, Mn can be adsorbed on soil; however the extent of adsorption depends on the organic content and cation exchange capacity of the soil (WHO, 2011).

Traditionally Mn has been limited to an aesthetic concern (Sly et al., 1990), however, there has been growing concern...
from 0.001 mg/L to 0.6 mg/L, with greater concentrations occurring when polluted or anoxic conditions prevail (NHMRC 2011). At whereas treatment using activated carbon and greensands has been reported with varying results (Barbeau et al., 2011b). The use of fi enhance the oxidation process (Wang et al., 2016). Reverse osmosis and ion exchange can be used to achieve greater Mn removal, the presence of dissolved organic matter (Carlson and Knocke, 1999), though the addition of potassium permanganate can be used to oxidise and precipitate compared with other metals such as Fe (Khoe and Waite 1989). Manganese removal can also be impaired in where a greater probability of elevated Mn concentrations exists.

The treatment of water containing increased Mn concentrations can be difficult (Choo et al., 2005), as Mn takes much longer to oxidise and precipitate compared with other metals such as Fe (Khoe and Waite 1989). Manganese removal can also be impaired in the presence of dissolved organic matter (Carlson and Knocke, 1999), though the addition of potassium permanganate can be used to enhance the oxidation process (Wang et al., 2016). Reverse osmosis and ion exchange can be used to achieve greater Mn removal, whereas treatment using activated carbon and greensands has been reported with varying results (Barbeau et al., 2011b). The use of bio filters can be an efficient (Hasan et al., 2014) Mn removal method with up to 98% of Mn being removed with the pH as low as 6.3 (Hoyland et al., 2014).

Given the challenges of effective and efficient Mn treatment removal, understanding the temporal and spatial relationships of Mn will be invaluable in assisting water managers to refine or customise treatment options. For example, an early forewarning of increased Mn may signal the need to add additional steps in the treatment process, as a measure to effectively remove Mn from the water. This is particularly the case in the context of smaller treatment plants, where resources may be limited, and communities do not have ready access to alternate supplies in the event of water contamination with Mn and resulting discolouration.

The Baffle Creek Catchment is a unique modern day example of an ephemeral freshwater system in subtropical Australia pre European settlement. Unlike many other catchments throughout subtropical Australia, Baffle Creek is unique in its lack of structures obstructing flow (e.g. dams/weirs) (Gilbert and Brodie 2001), as well as its relatively unmodified condition with minimal residential and commercial development throughout the catchment. Historically, investigations into Mn in freshwater systems in Australia have taken place following the introduction of river regulation, including Mardi Dam in the Wyong Shire (Khoe and Waite, 1989) and numerous reservoirs in the South-East corner of Queensland (Bertone et al., 2016; Zaw and Chiswell, 1995, 1999; Grinham et al., 2012). This has resulted in a paucity of knowledge regarding hydrogeochemical processes in natural systems. As such, the Baffle Creek catchment represents an ideal system to ascertain the transport of metals in a natural/relatively unmodified catchment context, as well as potential impacts on human health and deterioration of the drinking water supply chain infrastructure.

The present study investigated the spatial and temporal variation of Mn and Fe in Baffle Creek. The hydrogeochemistry of Mn and Fe was compared between the surface waters and the supply chain, to establish relationships between these two water sources. The main objective was to evaluate the spatial and temporal hydrochemistry of Mn and Fe in surface waters and drinking water supply chain, as well as to ascertain any current or potential future health or aesthetic risks. The hypotheses were that (1) Increased water discharge during a flood or “flush” event will result in reduced Mn and Fe concentrations in the surface waters and drinking water supply chain; and (2) Smaller rain events that result in less or no discharge, such as “fill-shift” events, will result in increased Mn and Fe concentrations in the natural lagoon from which the drinking water is drawn and the drinking water supply chain.

2. Methods

2.1. Catchment

Baffle Creek is situated on the eastern seaboard of sub-tropical Australia (Fig. 1), and is the southernmost catchment to directly discharge into the Great Barrier Reef Marine Park. The catchment is void of man-made structures regulating flow, making it the Southern Great Barrier Reef’s only remaining unregulated catchment. The catchment margins range from Tannum Sands in the north, to the mouth of the Kolan River in the south, covering an area of 4 085 km² (Department of Environment and Heritage Protection, 2016). The climate in the catchment is subtropical, with December, January and February traditionally being the wettest months (Department of Environment and Heritage Protection, 2016).

Untreated Baffle Creek water enters the Miriam Vale Drinking Water Treatment Plant from Baffle Creek and subsequently this water serves as the potable supply for the rural township of Miriam Vale, which has a population of approximately 500 people (ABS, 2011). There is minimal private or commercial development in the catchment with the primary land uses including dry land cattle grazing, dairy farming and timber plantations.
Fig. 1. Placement of Baffle Creek Catchment with surrounding hinterland. The site is located just below the Tropic of Capricorn on the Australian Eastern Seaboard. The location of the Baffle Creek catchment is indicated by the red dot on the inserted map of Australia.
2.2. Site descriptions

2.2.1. Surface waters

Due to the ephemeral nature of Baffle Creek, site selection was limited to areas that were expected to remain wet throughout the study period. These sites were interlinked by smaller, and often temporary, water bodies, which refilled and joined together during the seasons when most rainfall occurred.

2.2.1.1. Upstream. The upstream sites are located 17.5 km (U1) and 12.8 km (U2) downstream of the headwaters of Baffle Creek (Fig. 2). There is no development upstream of these sites with the land currently being used for low-intensity dry land grazing (estimated one beast per 229 ha). The riparian zones and surrounding vegetation are remnant predominantly *Melaleuca* spp., *Eucalyptus* spp. and *Lophostemon* spp.

2.2.1.2. Midstream. The midstream site was located 23.2 km downstream of the headwaters (Fig. 2). The site is a permanent lagoon surrounded by a remnant riparian zone of *Melaleuca* spp., *Eucalyptus* spp., *Callistemon* sp. and *Lophostemon* spp. There is no development upstream; the land is used for low intensity grazing (estimated 1 beast per 110 ha).

2.2.1.3. Downstream. The downstream site has been affected by more than a century of tree clearing, dairy farming and dry land
grazing (stocking rate > 1 beast per 75 ha) (Fig. 2). The downstream sections of Baffle Creek experience more frequent drying out than the upstream and midstream sites, but fortunately, the chosen site remained wet for the entirety of the study. The surrounding riparian zone consists of Melaleuca spp., Eucalyptus spp., Callistemon sp. and Lophostemon spp.

2.2.2. Drinking water supply chain

Untreated water is drawn from the midstream lagoon M1 through a bank filtration system.

2.2.2.1. Untreated water pipe. The untreated water in the pipe is drawn from the site M1. The outlet is approximately 4.5 km away from the intake pipe at M1 (Fig. 2). The pipe comprises sections of cast iron, interspersed with lengths of an asbestos product. The pipe was installed in the 1970s and has been in continuous operation for more than 40 years.

2.2.2.2. Pre-chlorinated pipe. The pipe water consists of 80% to 90% Baffle Creek untreated water mixed with up to 20% bore water sourced from a local bore. The untreated water from Baffle Creek is mixed for a number of reasons including reduction of the volume of water drawn from Baffle Creek and also to add minerals to the drinking water due to the small amounts in the Baffle Creek water supply. This water is pre-chlorinated with an average residual of 1.04 mg/L free chlorine and 1.35 mg/L total chlorine before entering the treatment plant; which aids in the precipitation of Fe and Mn. The pre-chlorinated pipe is 6.5 km from the lagoon (Fig. 2).

2.2.2.3. Treated water. This is the final site in the supply chain and represents the final potable water supply, prior to delivery to the township (Fig. 2).

2.3. Data collection

The focus of this study was to provide background information on longer-term trends and catchment-level data analyses, as compared with a short-term, event-based study, especially since this represents the first study undertaken in the freshwater sections of the catchment. The chosen design thus allowed for multiple wet seasons to be analysed in which both a “flush” and “fill-shift” event was documented.

Metal concentrations were measured quarterly in samples collected from both the surface sediment and water column, over two years between December 2012 and December 2014. The suite included dissolved and total fractions of Mn, Fe, arsenic (As), copper (Cu), Al, cadmium (Cd), chromium (Cr), lead (Pb), molybdenum (Mo), nickel (Ni), selenium (Se), silver (Ag), uranium (U), vanadium (V), boron (B) and mercury (Hg). Soil samples were collected from the sediment surface in shallow waters approximately 10 cm from the water’s edge. Five core samples were taken to a maximum depth of 10 cm using a corer of 7 cm diameter, and these samples were pooled and placed on ice. Along with metal concentrations, a series of water quality variables was also collected quarterly including nutrients, suspended solids, hardness, alkalinity, acidity, silicon (Si), sulphate, chloride (Cl$^-$), calcium (Ca$^{2+}$), magnesium (Mg$^{2+}$), sodium (Na$^+$), potassium (K$^+$), silica (SiO$_2$), fluoride (F$^-$) and chemical oxygen demand (COD). All water samples were collected and transported according to the protocols for the Queensland Government’s sampling procedures for drinking water (QGOV 2009). All dissolved metal samples were filtered in the field. The samples were then sent to a National Association of Testing Authorities (NATA) approved laboratory for analyses (Australian Laboratory Services Pty Ltd). The specific test methods and limits of reporting can be found in the appendices.

2.4. Statistical analyses

Statistical analyses were completed using PRIMER-E7 software. The series of assessments performed included principal component analysis (PCA), multi-dimensional scaling (MDS), analysis of similarities (ANOSIM), pairwise tests and Pearson Correlation Coefficients. The PCA and MDS data were first normalised and a resemblance matrix created using Euclidean distance of environmental variables. The PCA and MDS analyses were used to visualise the multidimensional data in two dimensions and the ANOSIM and pairwise tests were used to infer statistical significance. To reduce artefacts, any variables less than the limits of reporting (LOR) for the majority of the study were omitted from statistical analyses. LOR values can be found in the supplementary materials.

3. Results

3.1. Catchment dynamics – rainfall and hydrology

Three large rain events occurred during the sampling period, each resulting in discharge of differing magnitude (Fig. 3). The discharge event that occurred in January 2013 was the largest in recorded history for the catchment. The water flowing through the catchment reached heights between 5 and 15 m above the regular water level, the event thus “flushed” all sections of the catchment (including all study sites). The large rainfall events in March and December 2014 had comparatively modest discharges and rather than “flush” the surface waters, the outcome of these discharges resulted in a “fill” and “shift” event where waters from upstream pools moves to the downstream sites. A third hydrological event was identified, being a “filling” event, whereby the discharge is not sufficient to mobilise the waters to downstream sections, but rather, only to fill the existing pools in situ (e.g. Nov 2013 and Aug 2014). The distribution of metals, both in the lagoon from which drinking water is drawn as well as any runoff water destined for the
SGBR, was greatly influenced by these rain events (Fig. 4).

The three types of rainfall events, “flush”, “fill-shift” and “filling”, resulted in different dissolved metals dynamics within Baffle Creek. During the large “flush” event in January 2013, dissolved Mn and Fe concentrations were reduced both in the surface waters and the drinking water supply chain compared with the pre-event figures (Figs. 5–8). Conversely, during the “fill-shift” event, Mn and Fe concentrations tended to increase in the lagoon as well as the drinking water supply chain (Figs. 5–8). The “filling” events were much more local and responses were varied.

### 3.2. Surface waters

#### 3.2.1. Dissolved metals

Of the 16 dissolved metals measured, only four (Fe, Mn, As and Al) were greater than the LOR in the surface waters. The metals in greatest concentrations in surface waters were Fe and Mn, with As and Al being detected at specific sites or following rain events (Table 1; Fig. 5).

![Fig. 3. Monthly rainfall and discharge in Baffle Creek, Queensland between September 2012 and December 2014. Sampling dates denoted by red ticks on the lower axis.](image)

![Fig. 4. A multidimensional plot of Mn, Fe, Al, NH$_3$ and NO$_3^-$ concentrations recorded in the surface waters of Baffle Creek between December 2012 and December 2014. The figure depicts metric MDS of bootstrapped averages for the three hydrological events from replicate samples, including 95% region estimates for the ‘mean communities’ in Baffle Creek. Bootstrapping performed in m = four dimensional mMDS space.](image)
Dissolved Fe concentrations in the surface waters ranged from less than the LOR to 0.780 mg/L (Table 1). The greatest Fe concentration was observed at site U1 (Fig. 5). Following the ‘fill-shift’ event in March 2014, there was an increase in dissolved Fe concentrations in the midstream section of 0.460 mg/L. The ANOSIM results indicated that concentrations of Fe in the surface water sites were relatively consistent with a global R value = 0.228, p < 0.05. Dissolved Fe concentrations were generally greater at the upstream sites followed by the midstream section; with the downstream site typically having the lowest concentrations (Table 1; Fig. 5). Dissolved Fe was positively correlated with NH₃ [R² = 0.78] and Fe (total) [R² = 0.77].

Dissolved Mn concentrations in the surface waters ranged between 0.002 mg/L and 0.356 mg/L (Table 1). The highest recorded value was from D1 at 0.356 mg/L, during December 2012, prior to the large “flush” event in January 2013 (Fig. 5). Dissolved Mn concentrations were highest in the downstream section of the catchment, as compared with the other sites. The ANOSIM results indicated that the downstream sites of the Baffle Creek catchment are different from all other sites [R = 0.646 (U2), 0.500 (U1) and 0.555 (M1) (p < 0.05)]. Similar to dissolved Fe, there was also a small increase in Mn concentration during March 2014 at the midstream site, following the “fill-shift” event (Fig. 5). Dissolved Mn was positively correlated with NH₃ [R² = 0.60] and Mn (total) [R² = 0.93].

Dissolved As concentrations in the surface waters were above or at the LOR at only two sites: U2 and D1 (Fig. 5). The U2 site contained the highest concentration of As (0.003 mg/L). The ANOSIM results for As concentrations at the most upstream site (U2) were different (p < 0.05) from that at all other sites R = 0.828 (U1), 0.828 (M1) and 0.436 (D1).

The greatest concentrations of soluble Al in the surface waters were at the upstream site (U1) (Fig. 5). Dissolved Al concentrations in the surface waters ranged from less than the LOR to 0.460 mg/L (Table 1). The highest concentrations occurred following the “flush” event. The ANOSIM results indicate that Al concentrations were similar at all sites throughout the study with a significant (p < 0.05) global R value of 0.086.

Fig. 5. Selected dissolved metals, soil metals and nitrate concentrations, as measured quarterly from the surface waters of Baffle Creek between December 2012 and 2014; QWQG = Queensland Water Quality Guidelines, LOR = Level of Reporting.
Fig. 6. Selected dissolved metals and nutrients measured quarterly from the drinking water supply chain at Baffle Creek between December 2012 and 2014. LOR = Limit of Reporting.

Fig. 7. Principal Component Analysis (PCA) of environmental variables recorded in surface waters of Baffle Creek between December 2012 and December 2014. 2-dimensional PCA ordination of normalised and Euclidian distance of environmental variables during three different hydrological events within the Baffle Creek catchment. PC1 accounted for 41.8% of the total variance, PC2 accounted for 23.5% of the total variance, PC3 accounted for 12.4% of the total variance.
3.3 Drinking water supply chain

3.3.1 Dissolved metals

Of the 16 metals measured in the drinking water supply chain, concentrations of four of the metals were greater than the LOR during the study (Fe, Mn, Al and Cu) (Table 1). Arsenic was measured at the LOR in a sample collected from March 2014 at the P1 section of the pipe (Table 1).

Dissolved Fe in the supply chain waters ranged from below the LOR up to 1.610 mg/L (Table 1; Fig. 6). In December 2013 and March 2014 there was an increase in dissolved Fe concentrations, this followed the isolated rain events in December and the "fill-shift" event that occurred in March 2014. The increase in the dissolved Fe concentrations in the supply chain occurred at the same time the highest reading was recorded for Fe concentrations in the untreated water supply M1 site (Fig. 5). Contrariwise, Fe concentrations were reduced following the "flush" event in January 2013 (Fig. 6). Dissolved Fe correlated with: Mn (total) \( R^2 = 0.87 \), \( \text{NH}_3 \) \( R^2 = 0.85 \) and Fe (total) \( R^2 = 0.62 \).

Dissolved Mn concentrations in the supply chain ranged from less than the LOR to 0.337 mg/L (Table 1; Fig. 6). Similar to dissolved Fe, Mn concentrations increased in December 2013 and March 2014. This followed the isolated rain events in December and the ‘fill-shift’ event that occurred in March. Again, similar to changes in Fe concentrations, the Mn concentrations increased in the supply chain at the same time as an increase in Mn in the untreated water supply M1 (Fig. 5). Similar to the earlier findings, Mn concentrations were reduced following the “flush” event in January 2013 (Fig. 6). Dissolved Mn correlated with: Mn (total) \( R^2 = 0.87 \), \( \text{NH}_3 \) \( R^2 = 0.85 \) and Fe (total) \( R^2 = 0.62 \).

Concentrations of dissolved Al in the supply chain sites ranged from less than the LOR to 0.110 mg/L (Table 1; Fig. 6). Following the “flush” event in January 2013 there was an increase in dissolved Al in the treated water. Dissolved Al correlated with \( \text{NO}_3^- \) \( R^2 = 0.36 \). Dissolved Cu concentrations were only detected in the supply chain sites, where concentrations ranged from less than

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Table 1

<table>
<thead>
<tr>
<th>Element (mg/L)</th>
<th>Upstream</th>
<th>Midstream</th>
<th>Downstream</th>
<th>SUP Chain</th>
</tr>
</thead>
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<tr>
<td></td>
<td>Range</td>
<td>Average (SD)</td>
<td>Range</td>
<td>Average (SD)</td>
</tr>
<tr>
<td>Al (Dis)</td>
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<tr>
<td>Cu (Dis)</td>
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<td>&lt; LOR</td>
<td>&lt; LOR</td>
<td>&lt; LOR</td>
</tr>
<tr>
<td>Mn (Dis)</td>
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<td>0.025 (0.027)</td>
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<tr>
<td>Fe (Dis)</td>
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<td>Al (Tot)</td>
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<tr>
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<tr>
<td>Cu (Tot)</td>
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<td>0.210-1.150</td>
<td>0.521 (0.315)</td>
</tr>
</tbody>
</table>

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3.3. Drinking water supply chain

3.3.1. Dissolved metals

Of the 16 metals measured in the drinking water supply chain, concentrations of four of the metals were greater than the LOR during the study (Fe, Mn, Al and Cu) (Table 1). Arsenic was measured at the LOR in a sample collected from March 2014 at the P1 section of the pipe (Table 1).

Dissolved Fe in the supply chain waters ranged from below the LOR up to 1.610 mg/L (Table 1; Fig. 6). In December 2013 and March 2014 there was an increase in dissolved Fe concentrations, this followed the isolated rain events in December and the “fill-shift” event that occurred in March 2014. The increase in the dissolved Fe concentrations in the supply chain occurred at the same time the highest reading was recorded for Fe concentrations in the untreated water supply M1 site (Fig. 5). Contrariwise, Fe concentrations were reduced following the “flush” event in January 2013 (Fig. 6). Dissolved Fe correlated with: Mn (total) \( R^2 = 0.87 \), \( \text{NH}_3 \) \( R^2 = 0.85 \) and Fe (total) \( R^2 = 0.62 \).
the LOR to 0.044 mg/L (Table 1; Fig. 6). As the water flowed through the supply chain, dissolved Cu concentrations increased (Fig. 6).

### 3.4. MDS of dissolved metals

#### 3.4.1. Surface waters

The bootstrapped MDS plot depicts that the dissolved metal concentrations varied across the different sites (Fig. 9). The stress value of 0.1 is small, which provides confidence in the data accuracy. Fig. 5 also depicts that each site in the catchment has a different range of averages for dissolved metal concentrations. The figure furthermore illustrates the influence the concentrations of metals at upstream sites, in particular U1, has on the dissolved metals in the midstream section (M1) from which the drinking water is drawn.

### 3.5. PCA of hydrological events

#### 3.5.1. Surface waters

The PCA accounted for 77.7% of the variability using the first three principal components (Fig. 7). The first principal component accounted for 41.8% of the variability and had an Eigen value of 3.35, and was negatively correlated with values obtained for Mn (dissolved and total), Fe (dissolved and total) and NH3. The second principal component accounted for 23.5% of the variability with an Eigen value of 1.88, which negatively correlated with Al (dissolved and total) and Fe (total). The third principal component accounted for 12.4% of variability and had an Eigen value of 0.99, and was positively correlated with values for Mn (dissolved and total) and NH3. Fig. 6 clearly shows differing responses to the three events, with NO3− and Al dominating during "flush" conditions and Mn, Fe and NH3 dominating following a "fill-shift" event.

### 3.6. MDS of hydrological events

The bootstrapped MDS plot depicts that the average concentrations of Mn, Fe, Al, NH3 and NO3− following different hydrological events (Fig. 4). The stress value of 0.07 is small, which provides confidence in the accuracy of the data that were used to develop this plot. This Figure depicts that each hydrological event assessed in the study has a different range of averages for concentrations of Mn, Fe, Al, NH3 and NO3−.

### 3.7. PCA of hydrological events

#### 3.7.1. Drinking water supply chain and lagoon

The PCA accounted for 86% of the variability using the first three principal components (Fig. 8). The first principal component accounted for 54.3% of the variability and had an Eigen value of 4.34 and was negatively correlated with values for Mn (total and dissolved), Fe (dissolved) and NH3. The second principal component accounted for 20.4% of the variation with an Eigen value of 1.63.
Table 2
Descriptive statistics relating to soil metal concentrations recorded from Baffle Creek, samples were taken quarterly between December 2012 and December 2014.

| Variable (mg/kg) | Upstream | | Midstream | | Downstream | | SUP Chain |
|------------------|---------|------------------|---------|------------------|---------|------------------|
|                  | Range   | Average (SD)     | Range   | Average (SD)     | Range   | Average (SD)     |
| Al               | 2570.0–24400.0 | 7883.5 (4891.0) | 1420.0–4660.0 | 2522.2 (1044.4) | 1190.0–10100.0 | 4580.0 (3088.6) |
| Fe               | 2680.0–67900.0 | 24207.6 (21382.9) | 4190.0–8720.0 | 6725.6 (1852.7) | 1580.0–10800.0 | 5671.1 (3434.7) |
| As               | 1.2–8.0 | 3.8 (2.4) | 0.4–2.1 | 1.0 (0.5) | 0.3–2.6 | 1.0 (0.7) |
| Cu               | 0.6–8.2 | 3.3 (2.4) | 0.4–1.3 | 0.7 (0.3) | 0.8–7.5 | 4.3 (2.6) |
| Mn               | 24.4–518.0 | 209.0 (144.0) | 30.2–178.0 | 73.2 (44.0) | 29.1–2210.0 | 534.9 (688.0) |
| Mo               | 0.1–2.2 | 0.8 (0.5) | 0.1–0.3 | 0.2 (0.1) | < LOR-0.4 | 0.1 (0.1) |
| Ni               | 0.4–6.1 | 2.3 (1.7) | 0.3–0.9 | 0.5 (0.2) | 0.8–6.1 | 3.4 (2.0) |
| Pb               | 6.7–388.8 | 15.8 (8.1) | 3.6–5.9 | 4.3 (0.9) | 1.5–6.6 | 4.0 (1.9) |
| U                | 0.2–0.7 | 0.3 (0.1) | < LOR-0.2 | 0.1 (0.1) | 0.1–1.0 | 0.5 (0.3) |
| V                | 8.0–130.0 | 48.2 (42.6) | 5.0–15.0 | 10.1 (3.0) | 5.0–26.0 | 15.4 (7.8) |
| Hg               | 0.1–0.2 | 0.1 (0.0) | < LOR | < LOR | < LOR | < LOR |
| Cr               | 1.4–25.8 | 9.4 (8.0) | 1.1–2.9 | 2.0 (0.6) | 4.2–17.7 | 10.0 (5.0) |
| Ag               | < LOR-0.7 | 0.1 (0.2) | < LOR | < LOR | < LOR-0.1 | 0.1 (0.0) |
| Se               | < LOR-4.0 | 0.8 (0.9) | < LOR | < LOR | < LOR-3.0 | 0.8 (0.8) |

Table 3
Nutrients descriptive statistics, samples were taken quarterly between December 2012 and December 2014 in Baffle Creek.

| Nutrient (mg/L) | Upstream | | Midstream | | Downstream | | SUP Chain |
|-----------------|---------|------------------|---------|------------------|---------|------------------|
|                 | Range   | Average (SD)     | Range   | Average (SD)     | Range   | Average (SD)     |
| NH₃             | < LOR-0.073 | 0.021 (0.019) | < LOR-0.024 | 0.010 (0.006) | < LOR-0.036 | 0.020 (0.012) | < LOR-0.230 | 0.039 (0.056) |
| NO₃⁻            | < LOR-0.398 | 0.094 (0.116) | < LOR-0.487 | 0.083 (0.153) | < LOR-0.442 | 0.098 (0.152) | < LOR-0.796 | 0.206 (0.256) |
| TKN             | 0.200–0.900 | 0.529 (0.214) | 0.200–0.400 | 0.256 (0.073) | 0.300–1.000 | 0.578 (0.222) | < LOR-0.500 | 0.168 (0.122) |
| TN              | 0.245–1.000 | 0.550 (0.228) | 0.200–0.400 | 0.270 (0.073) | 0.300–1.000 | 0.597 (0.212) | < LOR-0.680 | 0.193 (0.151) |
| TP              | < LOR-0.070 | 0.029 (0.020) | < LOR-0.060 | 0.021 (0.017) | < LOR-0.050 | 0.033 (0.013) | < LOR-0.110 | 0.024 (0.027) |
| TRP             | < LOR | < LOR | < LOR | < LOR-0.060 | 0.012 (0.018) | < LOR-0.040 | 0.008 (0.008) |

and was negatively correlated with values for Al (total and dissolved), Fe (total) and NO₃⁻. The third principal component accounted for 11.4% of the variability with an Eigen value of 0.91 and was negatively correlated with values for Al (total) and positively correlated with NO₃⁻. Similarly to the reported results for the surface waters, this figure clearly shows differing responses to the three events, with NO₃⁻ and Al dominating during “flush” conditions and Mn, Fe and NH₃ dominating following a “fill-shift” event.

3.7.2. Soil metals
In total, 14 of the 16 measured metals were detected in concentrations greater than the LOR (Table 2). All metal concentrations were less than the “low” ANZECC interim sediment quality guidelines (Simpson et al., 2013), with the exception of concentrations detected in March 2014 at site U2 where Hg was detected at 0.2 mg/kg. The dominant metals detected in the Baffle Creek soils were Fe, Al and Mn (Table 2). The concentrations of metals in the upstream, midstream and downstream sites were statistically different (R = 0.405, p < 0.05). The upstream section of the catchment had, on average, greater concentrations for Al, Fe, As, Mo, Pb and V; whereas the downstream section had greater average concentrations of Mn. The midstream section of the catchment had, on average, the lowest concentrations of all metals in the soil with the exception of Fe (Table 2). The Mn concentrations in the downstream soils spiked following both the “flush” event in January 2013 and the “fill-shift” event in March 2014 (Fig. 5).

3.8. Nutrients

3.8.1. Surface waters
Nutrient concentrations throughout the catchment were, on average, less than the QWQG (Table 3) (Department of Environment and Heritage Protection, 2009). Organic nitrogen was in greater amounts than the other nutrient components (Table 3). Following the “flush” event in January 2013, NO₃⁻ reached the maximal concentrations that were detected during the study, however there was no corresponding increase following the “fill-shift” events in March and December 2014, rather, concentrations remained less than that of the LOR (Fig. 6).

3.8.2. Drinking water supply chain
Nutrient concentrations in the drinking water supply chain were less than the ADWG values for the entire study (Table 3). Following the “flush” event in January 2013, NO₃⁻ was in the greatest concentration as compared to other nutrients in the drinking water supply chain, whilst following the “fill-shift” event in March and December 2014 NH₃ was the nutrient in greatest concentrations (Fig. 6).
3.9. Water quality variables

Water quality variables in the upstream, midstream and downstream sites of the catchment were clearly different (p < 0.05), with an ANOSIM global R value of 0.524. The upstream section of the catchment had the least hardness, alkalinity, Cl⁻, Ca²⁺, Mg²⁺, Na⁺ and SiO₂ values (Table 4). When an ANOSIM was applied to data from the supply chain sites it was shown that P1 and P2 were statistically similar (R = 0.145, p < 0.05), which would indicate that the addition of contaminants at each section of the catchment has a small influence on the underlying water quality variables. It is possible that the suspended sediment detected in the supply chain pipes may have a small component of precipitated Mn and Fe, however, because the bulk of Mn and Fe was found to be dissolved, it is postulated that this reflects fine sediments passing through the artificial bank filtration.

The drinking water is drawn from the midstream lagoon (M1), and the water quality variables in the supply chain thus reflect natural values at this site, having a range and average for variables comparable to values recorded from water collected at the midsection site (Table 4).

3.10. Physico-chemical variables

The physico-chemical results indicated that the three different sections of the catchment were quite variable. Firstly, the temperatures of the water bodies were very similar, ranging from 11.8 to 29.4 °C. By contrast, the pH of the surface waters was different at each section of the catchment (p < 0.05; R = 0.493). The pH of the surface waters increased as the water flowed downstream (Table 5). The average turbidity was highest at the midstream section of the catchment; with the upstream section having the lowest turbidity readings (Table 5). The ANOSIM results suggested that the sites were similar (p < 0.05) (R = 0.092). The dissolved oxygen concentrations ranged between 7% and 94% at the various sites in the catchment (Table 5). The midstream section had on average the greatest DO% concentrations followed by the downstream section with the upstream site on average having the lowest DO% concentrations (Table 5).

4. Discussion

4.1. Spatial and temporal distribution of Mn

The hydrogeochemistry of Baffle Creek was predominantly driven by rain events, with differing responses to varying magnitudes

Table 4
Water quality variables descriptive statistics, samples were taken quarterly between December 2012 and December 2014 in Baffle Creek.

<table>
<thead>
<tr>
<th>Variable (mg/L)</th>
<th>Upstream</th>
<th>Midstream</th>
<th>Downstream</th>
<th>SUP Chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>Average (SD)</td>
<td>Range</td>
<td>Average (SD)</td>
<td>Range</td>
</tr>
<tr>
<td>SS</td>
<td>LOR -12.0</td>
<td>5.6 (3.3)</td>
<td>LOR -12.0</td>
<td>6.4 (3.0)</td>
</tr>
<tr>
<td>Hardness</td>
<td>LOR -25.0</td>
<td>11.0 (6.8)</td>
<td>LOR -60.0</td>
<td>30.4 (20.2)</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>LOR -32.0</td>
<td>19.5 (6.9)</td>
<td>LOR -61.0</td>
<td>31.1 (16.4)</td>
</tr>
<tr>
<td>Acidity</td>
<td>3.0 -14.0</td>
<td>6.6 (3.4)</td>
<td>2.0 -15.0</td>
<td>6.6 (3.9)</td>
</tr>
<tr>
<td>Si</td>
<td>LOR -6.4</td>
<td>2.7 (1.8)</td>
<td>LOR -10.9</td>
<td>7.2 (3.2)</td>
</tr>
<tr>
<td>Sulphate</td>
<td>LOR -5.0</td>
<td>1.1 (1.5)</td>
<td>LOR -4.0</td>
<td>1.9 (1.0)</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>7.0 -22.0</td>
<td>10.2 (4.6)</td>
<td>13.0 -97.0</td>
<td>50.3 (27.5)</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>LOR -5.0</td>
<td>2.2 (1.1)</td>
<td>1.0 -9.0</td>
<td>4.1 (2.5)</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>LOR -3.0</td>
<td>1.5 (0.8)</td>
<td>2.0 -10.0</td>
<td>5.2 (3.0)</td>
</tr>
<tr>
<td>Na⁺</td>
<td>7.0 -12.0</td>
<td>9.1 (1.6)</td>
<td>16.0 -55.0</td>
<td>34.0 (12.7)</td>
</tr>
<tr>
<td>K⁺</td>
<td>1.0 -8.0</td>
<td>3.1 (1.8)</td>
<td>1.0 -2.0</td>
<td>1.7 (0.5)</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.4 -14.4</td>
<td>6.7 (4.0)</td>
<td>12.2 -23.4</td>
<td>17.6 (3.9)</td>
</tr>
<tr>
<td>F⁻</td>
<td>LOR -0.1</td>
<td>0.1 (0.0)</td>
<td>LOR -0.1</td>
<td>0.1 (0.0)</td>
</tr>
<tr>
<td>COD</td>
<td>18.0 -53.0</td>
<td>28.8 (10.0)</td>
<td>5.0 -54.0</td>
<td>17.6 (14.4)</td>
</tr>
</tbody>
</table>

Table 5
Selected Physico-Chemical variables recorded at the surface waters of Baffle Creek between December 2012 and December 2014. SD = standard deviation.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Upstream</th>
<th>Midstream</th>
<th>Downstream</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range</td>
<td>Average (SD)</td>
<td>Range</td>
<td>Average (SD)</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>13.2 -27.2</td>
<td>22.3 (3.7)</td>
<td>14.1 -29.4</td>
</tr>
<tr>
<td>pH</td>
<td>5.9 -7.5</td>
<td>6.6 (0.3)</td>
<td>6.3 -7.7</td>
</tr>
<tr>
<td>Turbidity (NTU)</td>
<td>1.3 -22.0</td>
<td>3.2 (3.1)</td>
<td>1.7 -29.2</td>
</tr>
<tr>
<td>Dissolved Oxygen (%)</td>
<td>7 -72</td>
<td>44 (15.0)</td>
<td>48 -94</td>
</tr>
</tbody>
</table>
of rain and discharge. As part of the Mn cycle, Mn in the water and sediment was transported from upstream sections through the midstream sections and deposited in downstream sections of the catchment following rain events. Different responses were evident depending on the magnitude of rain and associated runoff, whether it be a “flush”, “fill-shift” or a “filling” event. Previous studies investigating Mn in subtropical drinking water supplies focused on reservoirs (Khoe and Waite, 1989; Zaw and Chiswell 1995, 1999; Grinham et al., 2012; Bertone et al., 2016). The results from these studies reported different responses to rainfall with some reservoirs increasing in Mn and nutrient concentrations following a flood (Grinham et al., 2012; Zaw and Chiswell 1995, 1999; Khoe and Waite, 1989) while others reduced (Bertone et al., 2016). What appears common is that large amounts of sediment laden with metals and nutrients were washed into the reservoirs.

Increases in dissolved Al and NO$_3^-$ concentrations following the “flush” event may be attributed to the highly oxygenated environment following the “flush” and the associated mixing of sediments into the water column. Additional evidence of an oxidised environment can be realized in the soil metals profile following the “flush” event, with Mn concentrations spiking in the downstream soil samples. This can be explained by dissolved Mn precipitating out of solution and being deposited in the soils of the downstream sections of the catchment. Thus, it appears that the upstream sections of Baffle Creek are an important source of metals, whereas the downstream sections may be a sink. However, the downstream reaches are not necessarily a permanent sink because during “flush” events these metals would be carried to the downstream estuary and in turn, the SGBR.

Following the “fill-shift” events in March and December 2014 waters did not rush through each section of the catchment like the “flush” event, instead, the surface waters gradually filled before shifting downstream. This in turn led to waters moving from the upstream section of the catchment down the catchment, with less oxygenation than a “flush” event. Consequently, more Mn remained dissolved, which lead to the M1 site experiencing an increase in dissolved Mn and Fe concentration. During the “flush” event, Mn was precipitated onto the soils, whereas following the “fill-shift” event soil Mn concentrations did not immediately increase, instead months passed before the Mn precipitated onto the soil, which may have been linked to the isolated rain event in August 2014.

It is postulated that the underlying sediments were the predominant source of Mn and Fe in the surface waters. The water quality results do not strongly suggest the presence of groundwater upwelling within the sample site of Baffle Creek; nevertheless, it is possible that the ground waters have some role as a source, and future targeted studies on ground water inputs would be required to ascertain this. Micro-organisms such as reducing bacteria may contribute to the dissolution of Mn into the surface waters (Bertone et al., 2016; Ginige et al., 2011), but they are not a de novo source of dissolved metals. Given this, the present study did not measure biogeochemical processes, instead focusing on the hydrogeochemistry. Conditions in the surface waters are likely to facilitate the reducing bacteria, specifically in the upstream sections of the catchment; similar to what have been reported from other subtropical studies (Bertone et al., 2016). Future studies are required to understand the role that reducing bacteria may have in the Mn cycle of Baffle Creek.

4.1.1. Anthropogenic sources of metals

In this study, Mn, Fe and Al were shown to move throughout the catchment with rainfall and runoff being the major transporter. The other dissolved metal found in the catchment As and Cu was not part of the natural metal suite. The source of the As was a historic cattle dip, situated 400 m upstream of site U2. The cattle dip has been out of service for at least 50 years, in that time a large amount of water has washed through the dip and diluted concentrations enough so that the sites directly downstream were below LOR. However, Arsenic was also found in low concentrations in the downstream section of the catchment indicating there are likely more cattle dips downstream of the current water supply in other sections outside the study area. The source of Cu was likely from the Cu fittings within the supply chain (Harvey et al., 2016), however the reported concentrations were well below the applicable guidelines for health (2 mg/L) and aesthetic measures (1 mg/L).

Alongside the supply water as a source for Mn, the distribution network also contributed to the increased concentrations entering the treatment plant. Similar to the surface waters, Mn concentrations following rain events varied, with increases in concentrations following “fill-shift” events and reductions in concentrations following “flush” events. Supply chain infrastructures such as pipes can increase Mn concentrations in bulk water by two different means. The first is by release from built up Mn deposits (Sly et al., 1990; Gerke et al., 2016), which is particularly problematic for old pipes; and a second by way of bacterial reduction (Ginige et al., 2011). The main source of increased Mn concentration in the pipes was likely due to water quality conditions following the “fill-shift” events. This is because both the supply chain and surface waters had the same response following the differing rain events. The roles of these two release mechanisms are not fully understood and should be further investigated in future studies.

4.2. Health risks and aesthetic impacts

4.2.1. Health

The concentrations of metals recorded in the final treated water were below health-based guidelines on all occasions. On one occasion, Mn concentrations in the treated drinking water were as high as the aesthetic guideline (0.1 mg/L). This indicates that the bulk water supply alone may not be enough to represent chronic Mn exposure to infants, children or the elderly. However, during the time of elevated Mn concentrations bottle fed infants may have been exposed to increased concentrations, due to the formula and the water both having Mn inputs (Brown and Foos, 2009). It remains unclear as to whether or not short term increases in Mn concentrations can contribute significantly to long-term exposure from drinking water (Barbeau et al., 2011a), particularly where age specific drinking water intake was considered (Brown and Foos, 2009).

The catchment level study indicated that each rain event can pose differing risk with respect to Mn concentrations. There are a number of scenarios that could lead to increased concentrations of Mn and Fe. The extent of Mn and Fe concentrations in the surface
water and supply chain are conservative at best, given that a large ‘flush’ event occurred during the study. This resulted in metals and other pollutants that had built up over time flushing from the system. The resulting increases in Mn following the “fill-shift” events were again conservative due to it only recently being flushed. It is anticipated that the metal concentrations in the future could be much higher in the years without recent flushing.

4.2.2. Aesthetic

The concentrations of Mn and Fe found in the surface waters can lead to the deterioration and build-up of Mn deposits in the supply chain pipes (Sly et al., 1990), which results in reduced carrying capacity (Griffin 1960) and a reduced quality of the water entering the treatment plant (Gerke et al., 2016; Cerrato et al., 2006a). Water with high Mn and Fe is often discoloured, smells earthy and tastes metallic (Ginige et al., 2011); which is one of the major reasons water managers receive complaints (Ginige et al., 2011). To reduce or potentially eliminate Mn deposits building up in the supply chain, future targets for Mn concentrations should be reduced to 0.01 mg/L, supplying water treated to this level would decrease Mn build up in the distribution network as well as reducing consumer complaints (Sly et al., 1990).

4.3. Treatment

Manganese treatment in drinking water can be challenging due to the high levels of oxidation required to precipitate the dissolved form from solution. Treatment can be further complicated by the presence of low pH and DO% and increased concentrations of humic and fulvic acids (Carlson and Knocke 1999). Anticipating increased Mn concentrations allows water managers to make informed decisions about treatment. If the demand for water is not time-sensitive, simple aeration techniques can be added, which require more time for the Mn to precipitate out. On the other hand, if water delivery is time sensitive a faster treatment may be the addition of permanganate as an oxidative choice, the benefit of permanganate is that it has also been shown effective when pH and DO% are reduced and humic and fulvic acid concentrations are increased (Carlson and Knocke 1999).

Small regional treatment plants may not be staffed as frequently, or sampled as regularly, as larger centres, meaning that understanding the hydrogeochemistry of their water supply and being able to predict changing water quality following rain events can critically improve the treatment process. Using the information on its spatial and temporal variation it is possible to start predicting Mn spikes and to increase treatment steps in order to reduce concentrations below health and aesthetic guidelines. This would have positive outcomes for the health of infants and small children, and also in reducing the amount of Mn able to deposit in the distribution and the associated customer complaints. This predictive model appears to represent a novel application of temporal and spatial data to predict Mn peaks in an unregulated freshwater system.

4.4. Predicted scenarios with climate change and flow regulation

With the onset of climate change it is predicted average temperatures will increase (Jimenez Cisneros et al., 2014). For freshwater environments this will lead to increased evaporation and water temperatures with a reduction in pH and DO% concentrations in turn increasing the amount of metals able to dissolve into the water (Delpla et al., 2009). Additional pressures due to climate change include a shift in duration, frequency and intensity of rainfall events (Jimenez Cisneros et al., 2014). Palmer et al. suggests that it is imperative individual watersheds such as Baffle Creek obtain sufficient baseline information on water flows and quality to support water managers in prioritising activities and evaluating their effectiveness and developing comprehensive scenarios of the likely impacts of climate change (Palmer et al., 2009).

Currently the catchment is unregulated, but there are plans to introduce regulation in the future (Corder and Moran, 2006). In Baffle Creek specifically, the possibility that regulation will exacerbate risks is high. Currently, under natural conditions, the downstream sections of Baffle Creek are higher in Mn, both in solution and in the soil. If Baffle Creek is regulated, it would reduce if not eliminate the flushing effect caused by large rainfall events, in turn there would be a build-up of sediments high in metals particularly Mn and Fe. Other metals that are at present being cycled out of Baffle into the marine environment would also accumulate in the impoundment, with potential problems arising from metals such as Arsenic. To reduce the risks associated with regulation, construction work should include design features that allow flushing.

5. Conclusions

The hydrogeochemistry of Baffle Creek was predominantly driven by rain events, with differing responses to varying magnitudes of rain and discharge.

- Extreme floods or “Flush” events reduce Mn concentrations in the surface waters and the drinking water supply chain.
- Small floods or “Fill-Shift” events increase Mn concentrations in the drinking water supply and the drinking water supply chain.
- Currently the drinking water supplied to the small regional town does not pose a threat to chronic exposure to Mn, however there are times that Mn concentrations are increased. It is still unknown as to the effects of short term exposure and the long-term effects it may have on an individual’s health; specifically infants, small children and pregnant mothers.
- Additional aeration or oxidation treatment steps are recommended following “fill-shift” events, to reduce Mn concentrations below 0.01 mg/L. This would assist in the elimination of build-up of Mn in the distribution system and over time reduce consumer complaints.
- It is anticipated that Mn will become increasingly problematic for water managers in the future, with a combination of effects from climate change and river regulation. Therefore it was crucial to obtain sufficient baseline information on water flows and metal concentrations to assist water managers to prioritise activities particularly around times of summer rainfall.
- Future studies are recommended to obtain responses to drought conditions.
- Future studies are recommended to ascertain the ground water influence on the metal and nutrient cycle, as well as the role reducing bacteria have in the increase of dissolution of Mn.

Conflict of interest

There is no conflict of interest. The Gladstone Regional Council did not have input on the design, collection, analysis and interpretation of data or in the writing of the manuscript and did not have any part in the decision to submit with the Journal of Hydrology: Regional Studies.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.ejrh.2017.08.008.

References
