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The ionic composition of the streams of the mid Murrumbidgee River: implications for the management of downstream salinity.

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Short title: Salt composition of the mid Murrumbidgee
Abstract

The Murrumbidgee River catchment is a major region of both dryland and irrigated agricultural production in eastern Australia. The salinity of water in the lower reaches of the river is the subject of concern; changing land management upstream is one option to minimise accessions of salt to the river but this must be done in a way that provides an adequate quantity of water for downstream users and the environment.

We examined 30 years of sporadic data on the ionic composition of water for 7 subcatchments contributing to the mid-Murrumbidgee River and for 2 gauging stations on the river itself. Despite the common local presumption that salinity, measured as electrical conductivity (EC), is primarily due to NaCl from cyclic marine salt, we found that NaCl was the dominant salt in only some streams. The presence of HCO$_3^-$ of Ca$^{2+}$ and Mg$^{2+}$ in all streams, and their dominance in 2 streams, indicates that mineral weathering is also a major contributor to the salt load of water in the catchment. However, Ca$^{2+}$ and Mg$^{2+}$ bicarbonates have limited solubility and so their concentrations will not become a cause of osmotic stress when the water is used for drinking or irrigation. Therefore in our efforts to prioritise lower order catchments of the Murrumbidgee River for changed land management, it will be necessary to examine the nature of the salts they discharge, not just EC. By distinguishing between Cl$^-$ / Na$^+$ dominated streams and Ca$^{2+}$, Mg$^{2+}$ / HCO$_3^-$ dominated streams we can refine our search for sources of osmotic stress which might potentially worsen with time. This will enable us to target particular land management units so as to obtain the maximum reduction in downstream salinity with a minimal decrease in flow volume and minimal area of land undergoing changed landuse.

Key words: land management, salt, water quality, weathering
Introduction

Understanding the processes that influence water quality, whether it be limestone weathering in India (Panigrahy and Raymahashy, 2005), magnesium silicate precipitation and dissolution in Tanzania (Deocampo, 2005) or wet season bicarbonate leaching from surface soil in the Amazon (Markewitz et al., 2001), is necessary for the sound management of river catchments. Dryland salinity is recognised as a problem in the Murrumbidgee River catchment (80,000 km²) of eastern Australia. While only 0.4% of the land area is expected to be salinized, significant quantities of salt are delivered to the Murrumbidgee River, affecting water quality for towns and irrigation industries downstream. The river has 17 subcatchments upstream of Wagga Wagga that vary widely in the amount of salt delivered to the main river, ranging between 4 and 48 tonnes of salt /km²/year and these values are expected to rise to between 6 and 74 tonne/km²/year by 2100 (Beale et al., 2000). Landuse plays a role in salt delivery; the Kyeamba and Tarcutta subcatchments have similar geology and hydrology but Tarcutta (32% forest) delivers half the salt load of the Kyeamba subcatchment (6% forest) (NSW Dept. Land & Water Resources, 2003). Changes in landscape management are considered necessary to protect the quality of the river water.

There are four possible original sources of the salt in the Murrumbidgee catchment:

1. “Cyclic” salt of marine origin, either by rain or dry deposition;
2. Inherited or “connate” salts, from sediments laid down in saline water and preserved lost during uplift and metamorphosis;
3. Aeolian dust or “parna”, a salt-bearing clay blown over the landscape from a former inland sea;
4. Weathering products from rock minerals e.g. calcite, serpentine.

\[
\begin{align*}
\text{CaCO}_3 + \text{H}_2\text{CO}_3 & \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^- \\
\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 + 6\text{H}_2\text{CO}_3 & \rightleftharpoons 3\text{Mg}^{2+} + 6\text{HCO}_3^- + 2\text{H}_4\text{SiO}_4 + \text{H}_2\text{O}
\end{align*}
\]

The first three sources yield predominantly NaCl salt while the fourth source predominantly yields bicarbonate salts. However bicarbonate is not necessarily a clear tracer for salts caused by mineral weathering as opposed to cyclic salts. Bicarbonate salts can enter soil water as a result of cation exchange in the presence of biologically elevated CO₂ concentrations. For example:

\[
\begin{align*}
\text{clay : Na}^+ + \text{CO}_2 (\text{aq}) & \rightarrow \text{clay : Na}^+ + \text{HCO}_3^- + \text{H}^+ \\
& \rightarrow \text{clay : H}^+ + \text{Na}^+ + \text{HCO}_3^-
\end{align*}
\]

Since clay: H⁺ is not stable, weathering of the clay occurs. But the initial source of Na⁺ could have been cyclic salt rather than the parent rock (sodic feldspar, for example). Therefore Na⁺ and HCO₃⁻ are not unambiguous tracers of cyclic or weathering salts respectively.

Cyclic NaCl is therefore not the only salt which might contribute to “salinity” in inland waters. Salts vary greatly in their solubility (Table 1). All of the Na⁺, K⁺ and Cl⁻ salts shown in Table 1 are very soluble and therefore have great potential to concentrate and to cause osmotic stress when water is used for irrigation or drinking purposes. However if the dominant ions in a stream are Ca²⁺ and SO₄²⁻, as in some more arid areas, then osmotic stress will remain low since the water’s electrical conductivity (EC) will not exceed about 2.4 dS/m. The concentration of HCO₃⁻, while balanced by Ca²⁺ and Mg²⁺, is unlikely to be a source of osmotic stress (Table 1) but will form the inconvenient though treatable problem of scale on taps, hot water systems and evaporative air conditioners. Therefore extrapolation of trends in EC could be accurate for Na⁺ and Cl⁻ dominated streams but might well overestimate the
future salinity of streams whose ionic composition is dominated by divalent cations and bicarbonate anions.

Management of salinity aims to minimise the leakage or discharge of salt to streams. Action is targeted on the basis of stream salinity and intervention is usually to manipulate the water balance by planting high water use vegetation. There is a recognised trade off between minimising stream salinity yet providing an adequate quantity of water for downstream users. Depending on the nature and source of the salt as outlined above, any decrease in stream flow due to revegetation carries the danger of increasing stream salinity.

A given quantity of highly soluble salt added to a stream will concentrate to higher EC than the same quantity of a less soluble salt. Therefore salinity management should be better targeted to manage the more soluble salts. The first step towards this more targeted management it to identify where in these salts enter streams. The next step will be to understand the varied hydrogeological mechanisms by which they enter our waterways (e.g. Summerell, 2004). Current salinity management based on EC will identify streams that discharge primarily Na\(^+\) and Cl\(^-\) salts as they will tend to have high EC readings. The same monitoring regime will successfully identify streams discharging bicarbonates of divalent cations as a low priority for intervention. However if the stream contains a mixture of solutes and has an intermediate EC then we need to know the spatial and temporal nature of that mix in order to understand and manage the more soluble salts.
The NSW Department of Natural Resources (DNR) has been monitoring the ionic composition of stream waters in the mid Murrumbidgee catchment sporadically for 30 years. We show how knowing the ionic composition of water is a useful step toward targeted management of salinity in the mid Murrumbidgee catchment.

Method

Data on the ionic composition of streams were available from the Triton database of DNR, with records commencing in the early 1970’s for some streams. Access to the database is by approval from DNR. Sampling was irregular over the 30 years (1973-2003) depending on the requirements of the particular projects that contributed the data. In the mid Murrumbidgee catchment the temporal density of data for 7 higher order subcatchments and for 2 stations along the Murrumbidgee River itself; Gundagai and Wagga Wagga, permitted analysis. Two of the subcatchments join the Murrumbidgee above Burrinjuck Dam, 3 more of the subcatchments enter the Murrumbidgee upstream of the Gundagai station and the remaining 2 enter between the Gundagai and Wagga Wagga stations (Fig 1). Subcatchments were sampled at, or close to, their confluence with the Murrumbidgee River.

The concentration (mg/l) of Ca^{2+}, Mg^{2+}, Na^+, K^+, HCO_3^-, Cl^- and SO_4^{2-} ions had been measured on many occasions and entered into the Triton data base. Chloride was determined by potentiometric titration with AgNO_3, sulphate by reaction with BaCl_2, and bicarbonate by titration to pH 4.5. Cations were determined by atomic absorption. These concentrations were converted by us to mmolc/l and the charge balance assessed. Data were excluded where the sum of cations and the sum of anions differed by > 1.0 mmolc/l. This generally detected times of analyses when the full suite of 4 cations and 3 anions was incomplete, generally due to the absence of bicarbonate or
sulphate data. Eight data items were excluded from the Muttama Creek data set by this criterion. Additionally there were number entry errors where individual data items were an order of magnitude different to the rest of the data set. Seven such exclusions were made. Correlation and regression analyses were then used to assess relationships and infer possible balancing of pairs of ions.

The general salinity status of the streams in the mid Murrumbidgee was assessed using the mean solute data for each of the streams over the 30 years. Based on findings from this overview, one of the subcatchments was selected for more detailed investigation. The Muttama Creek subcatchment is relatively small and has a heterogeneous geology (Department of Mines, 1976). The valley runs north-south. On the eastern side of the subcatchment there are north-south trending fault lines with basic to ultrabasic volcanic rocks and frequent outcrops of serpentine. These are bound on the eastern margin by granodiorite. To the west are slates and rhyolite. The saline areas mapped for the subcatchment occur primarily in association with the sedimentary material in the west and also with rhyolite to the north west. Although the subcatchment is small and the flow rate of the creek is small, the mixed geology in this subcatchment gave us an opportunity to do two things:

1) estimate the relative contributions of *in situ* weathering versus cyclic (and geologically stored) marine salt to the ionic composition of the water,

2) test the idea that it might be possible to isolate areas of land discharging different types of salts.

The water quality of the Muttama Creek subcatchment was adequately measured 43 times over 27 years from July 1976 to August 2003.
Results and Discussion

Mid Murrumbidgee catchment

The mean data for the 7 subcatchments and 2 stations on the main river (Table 2a) show that the 7 streams ranged from low EC and high flow rate (Tumut River) to high EC and low flow rate (Kyeamba Creek). For each stream there was a decrease in EC with increase in flow rate but the pattern varied between streams. This was partly due to skewness in the range of flow rates but there was also a linkage between the solutes discharged, flow rate and EC. In the high flow, low EC Goodradigbee River, ionic composition was dominated by Ca$^{2+}$ and HCO$_3^-$ while Na$^+$ and Cl$^-$ dominated the low flow, high EC Kyeamba Creek (Table 2a). At a given flow rate the EC of the Ca$^{2+}$ and HCO$_3^-$ dominated stream (Goodradigbee) tended to be lower than that of the Na$^+$ and Cl$^-$ dominated stream (Kyeamba) (Fig. 2). The other 5 streams lay on or between these two end members.

The scatter in the EC – flow rate relationships (Fig. 2) might be an artefact of sampling at various rising, falling and “basal” stages of flow. This has been observed in ephemeral streams (Summerell 2004) and was attributed to each solute having different storage and delivery pathways. On the other hand when measuring at the outflow of a second order stream, this variation could be due to a mixing of waters from areas with different geology and hydrology.

The mean ionic composition of the streams and of the main river is dominated by Na$^+$ > Mg$^{2+}$ > Ca$^{2+}$ > K$^+$, and HCO$_3^-$ > Cl$^-$ > SO$_4^{2-}$ on an equivalent basis. On a mass basis the only change in order is that Ca$^{2+}$ > Mg$^{2+}$. K$^+$ is a minor cation in the mid Murrumbidgee catchment both in absolute concentration (Table 2a) and in relative
terms (Table 2b). Likewise the concentration of $\text{SO}_4^{2-}$ is low in absolute terms and only represents a relatively high proportion of anions in the Yass River (see also Acworth and Jankowski, 2001), possibly reflecting an exposure of reduced S compounds associated with shales in the subcatchment.

The mixture of the major ions in the individual streams varied. $\text{Na}^+$ and $\text{Cl}^-$ were not always the dominant ions as might be expected if cyclic salt dominated (Table 2b and Fig 3). So as to be independent of differences between streams in flow rate and hence dilution, the data are expressed as the relative proportions of the ions (Table 2b). With regard to the anions, Jugiong Creek had the highest average %Cl among the seven streams at 55%Cl (and 38% HCO$_3^-$) while Goodradigbee River had the highest % HCO$_3^-$ at 89% (and 7% Cl). Only in Jugiong Creek and Kyeamba Creek, and to a lesser extent Muttama Creek, did the %Cl exceed %HCO$_3^-$ (Table 2b, Figure 3). Similarly for the cations, Jugiong Creek averaged 42% Na, 35% Mg and 21% Ca while Goodradigbee River averaged 65% Ca, 19% Mg and only 14% Na. There therefore appears to be variation in the mechanisms of saline discharge between streams.

The correlation matrix for the mean data of the mid Murrumbidgee (Table 3) shows strong associations between the cations Ca$^{2+}$, Mg$^{2+}$ and Na$^+$ and a strong association between the anions HCO$_3^-$ and Cl$^-$. The K$^+$ and SO$_4^{2-}$ were present in only low concentrations and were poorly correlated with all other ions. The cation and anion pairs that had the strongest associations ($r$) were Na:Cl (0.985), Ca:Cl (0.94), Mg:Cl (0.96), Na:HCO$_3$ (0.94), Ca:HCO$_3$ (0.97) and Mg:HCO$_3$ (0.99) (Table 3).
Associations like these which remain consistent across a range of flow rates might imply a common physical source of these salts.

Relative to sea water all subcatchments drain water which is enriched in HCO₃⁻, Ca²⁺ and Mg²⁺ (Table 2b). Therefore the proportions of Na⁺ and Cl⁻ are lower than occurs in sea water and hence in cyclic salt. The charge balance was generally within 2% with the exception of the Goodradigbee River where it was ~7% (Table 2c). Therefore the major ions within this system appear to be accounted for.

Figure 4 shows the ratio of Na/Cl plotted as a function of Cl⁻ concentration (Cartwright et al, 2004). We have modified the Cartwright et al. (2004) diagram by inserting a steady state ratio of 0.86 for sea water instead of 1.0 for halite, shown by the horizontal line with y axis value of 0.86. Values > 0.86 indicate that there is an additional source of Na⁺ e.g. mineral weathering. The mean Cl⁻ concentration of rainwater received in the catchment (Blackburn and McLeod 1983) is shown by the vertical line at 0.04 mM Cl⁻. Chloride concentrations above (to the right of) this value indicate concentration of Cl⁻ with respect to rainwater inputs. The data show that two streams (Goodradigbee and Tumut) discharge Cl⁻ which is only a little more concentrated than in rainwater. The other subcatchments (Tarcutta, Yass, Kyeamba, Muttama and Jugiong) are close to the sea water ratio of 0.86 and show concentration of Cl compared with rain water. The nearly constant ratio of Na/Cl with increasing Cl⁻ concentration has been suggested as being due to evapotranspiration (Herczeg and Edmunds, 2000). Two subcatchments (Muttama and Jugiong) show the highest concentration of Cl⁻ but exhibit lower Na/Cl ratios than sea water. Possibly a proportion of Na⁺ has been retained in the soils of these subcatchments. The two
gauging stations on the Murrumbidgee River are close to the ratio for halite (1.0) and are more concentrated with Cl⁻ than average rainwater. There is little change in ionic composition of the Murrumbidgee River from Gundagai to Wagga Wagga. Thus it appears that the high ionic concentration of the high EC streams is due in most part to the concentration of cyclic salts, with an addition of weathering salt. Although the Tarcutta and Kyeamba Creeks have relatively high Na⁺ and Cl⁻ concentrations their flow volumes are relatively low, so the composition of the Murrumbidgee water is predominantly controlled by the major flow volumes from Burrinjuck and Blowering Dams (Fig. 1).

Regressions for cation-anion pairs using the mean data for each stream did not show any slopes ~1. Na⁺ had slopes of 0.877 with HCO₃⁻ and 1.315 with Cl⁻. Mg²⁺ had slopes of 0.87 with HCO₃⁻ and 1.20 with Cl⁻. Ca²⁺ was not clearly balanced 1:1 with any of the 3 anions on a catchment scale. Therefore the mid Murrumbidgee catchment is draining mixtures of salts. Relative to sea water the streams of the mid Murrumbidgee are enriched in Ca²⁺, Mg²⁺ and HCO₃⁻, with the data of Table 2b suggesting that mineral weathering has contributed about half of the salts in the waterways. Herczeg et al. (1993) reached a similar conclusion for the upper Murray River, which joins the Murrumbidgee downstream of our study area.

If we assume the approximation that Na⁺ and Cl⁻ are indicators of the discharge of cyclic salt and that Mg²⁺, Ca²⁺ and HCO₃⁻ indicate discharge of weathering products, then Muttama Creek is of particular interest for further study. Muttama Creek had ion concentrations where Mg²⁺ > Na⁺ and Cl⁻ ~ HCO₃⁻. Muttama Creek was chosen for further study because we know that there is a serpentine belt on the eastern side and
salt scalds below the rhyolite and shales to the west. Therefore the relative contributions of weathering ($\text{Mg}^{2+}, \text{HCO}_3^-$) and cyclic/stored marine salts ($\text{Na}^+, \text{Cl}^-$) could be investigated within this subcatchment.

*Muttama Creek*

A correlation matrix among all 10 variables across data collection times is presented in Table 4. Some of the correlation ($r$) values are low because the relationships between variables are not linear. For example, EC decreased curvilinearly with increase in flow rate (Fig 2). Similarly, $\text{Cl}^-$ and $\text{HCO}_3^-$ concentrations, which were linearly related to EC, decreased curvilinearly with flow rate i.e. a higher salt concentration occurred during lower flow periods. The pH increased exponentially with increase in $\text{HCO}_3^-$ concentration. While $\text{HCO}_3^-$ could come from respiration within the stream, such concentrations as in Table 2 would be associated with pH $< 5.7$. However this was not the case as the data range was $6.9 < \text{pH} < 8.3$ i.e. from neutral to saturation with CaCO$_3$.

The cations $\text{Na}^+$ and $\text{Ca}^{2+}$ were strongly linearly related, implying a possible common origin. The relationship between $\text{Na}^+$ and $\text{Mg}^{2+}$ did not have a high correlation because it exhibited two distinctly different trend lines, implying two possible sources. $\text{Ca}^{2+}$ and $\text{Mg}^{2+}$ were tightly correlated at low concentrations but diverged at high concentrations (low flows) where $\text{Mg}^{2+} > 5$ and $\text{Ca}^{2+} > 2$ mmol/l. The anions $\text{Cl}^-$ and $\text{HCO}_3^-$ were broadly correlated. $\text{Cl}^-$ correlated best with $\text{Na}^+$ and $\text{Ca}^{2+}$, and $\text{Mg}^{2+}$ at $< 5$ mmol/l. The anion $\text{HCO}_3^-$ correlated best with $\text{Mg}^{2+}$, while $\text{SO}_4^{2-}$ had its best correlation with $\text{Na}^+$ followed by $\text{Ca}^{2+}$. The imbalance in charge ($\sum M^+-\sum A^-$) did not correlate with flow rate ($r = 0.012, P = 0.94$). Within the correlation matrix the highest
pairwise correlations (Fig 5) were $\text{Mg}^{2+}$ with $\text{HCO}_3^-$ ($r = 0.989$) and $\text{Na}^+$ and $\text{Ca}^{2+}$ with $\text{Cl}^-$ ($r = 0.976$ and 0.963 respectively). $\text{Mg}^{2+}$ had a much weaker correlation with $\text{Cl}^-$ ($0.754$) and $\text{Na}^+$ with $\text{HCO}_3^-$ ($0.663$). This suggests ion balances which allow separation of the relative contribution of cyclic salts and mineral weathering.

The regression analyses for these highest 3 cation:anion correlations over the flow rates showed that all had intercepts not significantly different to zero and slopes which were significant at $P<0.001$ (Fig 5). Subsequent t-tests showed that the slope of the ion pair $\text{Mg}^{2+}$ and $\text{HCO}_3^-$ was not statistically different to $1.0$ ($t_{42} = 1.35$). The implication is that the ion pair $\text{Mg} : \text{HCO}_3$ is in a 1:1 relationship across the range of flow rates. This implies discharge in base flow.

Our hypothesis that $\text{Mg(HCO}_3)_2$ is discharged by base flow is further supported by the finding that the highest concentration (at the lowest flow rate) (Fig 5c) corresponds with saturation with $\text{MgCO}_3$ in well aerated water. The concentration of $\text{Mg}$ sourced from serpentine is likely to have an upper limit in water due to equilibrium with atmospheric $\text{CO}_2$ once it reaches surface waters. The solubility of $\text{MgCO}_3$ is listed in the CRC Handbook (1994) at 0.11 g/l equating to a maximum concentration of 2.6 mmol$_c$ $\text{Mg}$/l. However Aylward and Findlay (2002) list the solubility at 0.6 g/l, equating to a maximum concentration of 14.2 mmol$_c$ $\text{Mg}$/l in well aerated water. This latter value is indicated by the open circle in Figure 5c. That is, the highest concentration data point, which occurs at the lowest flow rate, is near saturation with respect to the solubility of $\text{MgCO}_3$ as listed by Aylward and Findlay (2002). Since concentrations of both $\text{Mg}^{2+}$ and $\text{HCO}_3^-$ (and pH) decrease concurrently as flow rate increases, we suspect that the $\text{Mg(HCO}_3)_2$ is discharged in base flow and that this
concentration is diluted by event flows. Therefore although the concentrations of Mg\(^{2+}\) and HCO\(_3^-\) currently exceed that of Na\(^+\) and Cl\(^-\) (Figures 5a vs 5c), we predict that the concentrations of Mg\(^{2+}\) and HCO\(_3^-\) will only increase beyond current base flow concentrations in certain circumstances: 1) if a stronger acid than carbonic acid enters the soil or stream water, then the concentration of Mg\(^{2+}\) can increase exponentially as pH falls, rather than being capped by the solubility of MgCO\(_3\) in well aerated water. This means that acidification of the solum could increase the concentration of salts which are sourced from weathering. 2) A spatially concurrent source of Cl\(^-\) could continue to increase in concentration by evaporation and increase the mobilisation and discharge of Mg\(^{2+}\).

The absence of a 1:1 relationship between other ion pairs prevented the application of this simple dilution hypothesis to other ions. Mixing within the stream might generally disguise any 1:1 association between the ions. In Muttama Creek this mixing involves both sides of the catchment and involves both subsurface and surface flows. While the Mg : HCO\(_3^-\) association survived this mixing, it is possible that the apparent close balance between [Ca\(^{2+}\) + Na\(^+\)] and Cl\(^-\) (Fig 5a,b) is an artefact of this mixing.

\[ \text{Cl} = 0.89(0.03)[\text{Ca} + \text{Na}] - 0.04(0.2) \quad r^2 = 0.966 \quad n = 43 \]

P<0.001 ns

where standard errors are given in parentheses and P and ns refer to the significance level for the slope and intercept. The Ca\(^{2+}\) and Na\(^+\) might actually be sourced from a mixture of both marine and weathering salt. However spatial and temporal discrimination between these sources of salt require a higher density of measurements than provided by the database. Therefore subdivision of the Muttama catchment might
be beneficial in isolating areas which discharge predominantly Mg(HCO$_3$)$_2$ salt, and which should be exempt from major revegetation efforts so as to provide reasonable quality water to the creek. This hypothesis is the subject of ongoing work.

The ratio of Cl/HCO$_3$ is probably the best index of the ratio of cyclic to weathering salt since cation ratios such as Na/Mg+Ca might be influenced more by the CEC storage and release characteristics of the soils in the catchment than by hydrology. Acidic soils will minimise HCO$_3^-$ discharge but the acidity is primarily a property of the upper 20 to 50 cm of solum only. The Cl/HCO$_3$ ratio ranged from 0.5 to 2.4, with a mean of 1.36 implying that cyclic (plus geologically stored) salts provided 58% of the salt in the Muttama Creek. There was no correlation of the ratio with flow rate so the relative contribution of basal and event flows cannot be inferred.

The conclusion from this component of our work is that mineral weathering is a major contributor (~42%) to the ionic composition of the Muttama Creek. The Mg$^{2+}$ and HCO$_3^-$ salt is likely to be a “natural” feature of the landscape compared with elevated concentrations of Na$^+$ and Cl$^-$ salts which are blamed on land clearing and European style farming practice. The Mg$^{2+}$ and HCO$_3^-$ are of relatively low concern for human consumption and for irrigation on acidic soils. Scale on pipes and taps is a more easily treatable problem than NaCl salinity. We propose that the downstream impact of salinity will be most effectively managed by minimising the discharge of Na$^+$ and Cl$^-$. These are the ions most likely to concentrate by evaporation and to increase stream salinity. By establishing the temporal and spatial patterns of Na$^+$ and Cl$^-$ discharge within the Muttama subcatchment, as opposed to simply using EC, we aim to obtain the highest possible improvement in water quality while simultaneously
minimising any decrease in water yield from the subcatchment. This will enable us to maximise benefits involved in trade offs between the incomes of land holders and ‘end of valley’ water quality targets required by downstream consumers, for a given level of public and private investment in improved land management (Nordblom et al., 2005).

**General Conclusions and Recommendations for Future Work**

Our first conclusion is that NaCl is often not the dominant salt being discharged to waterways in the mid Murrumbidgee; mineral weathering appears to be contributing a large proportion of the salts. The particular weathering salts encountered are unlikely to ever reach the concentrations which cyclic salt can attain because of the limited solubility of Ca\(^{2+}\) and Mg\(^{2+}\) carbonate.

Our second conclusion is that discharge of Na\(^+\) and Cl\(^-\) is not uniform across the mid Murrumbidgee catchment. At a coarse level we contrasted the Tumut and Goodradigbee Rivers with the Jugiong, Kyeamba and Muttama Creeks. The former two subcatchments have low salt concentrations across their range of flow rates due to the salts being predominantly Ca\(^{2+}\) and Mg\(^{2+}\) bicarbonates. At a finer level, some subcatchments such as the Muttama Creek subcatchment contain a mixture of salts from both marine and weathering origin. On an individual stream basis the correlation between pairs of ions was useful in hypothesizing mechanisms by which different ions might be discharged. Base flow, presumably from the serpentine and ultrabasic volcanics, is the most likely mechanism of Mg(HCO\(_3\))\(_2\) discharge from Muttama
Creek. On the other hand Ca\(^{2+}\), Na\(^+\) and Cl\(^-\) discharge to Muttama Creek were mixed spatially and/or temporally.

Therefore at a finer level we can refine our search for high priority parts of the landscape in at least some subcatchments by measuring ionic composition and tracing Na\(^+\) and Cl\(^-\) rather than simply EC. There will of course be subcatchments where EC alone might give an adequate guide to locating priority areas for treatment e.g. Kyeamba Creek. However there will be subcatchments such as Muttama Creek where we can do better. This better definition of the priority (NaCl leaking) areas for treatment will allow us to leave other parts of that subcatchment to supply runoff and drainage of better quality water. For example, possibly much of the eastern side of the Muttama Creek subcatchment will prove to be providing relatively high quality water, and revegetation to minimise Na\(^+\) and Cl\(^-\) leakage will be best focussed on the western side. Therefore within the Muttama catchment we are formulating Land Management Units (LMU) based on geology, topography and landuse. We hope that we will be able to isolate the LMUs of maximum NaCl leakage. This is also likely to be closer to the scale at which landscape based management actions apply. How successfully the Na\(^+\) and Cl\(^-\) leakage can be treated by land management depends on the relative proportions by which it enters streams by event and basal flows.

Our stated aim is to obtain the maximum reduction in stream salinity with a minimal decrease in flow volume and minimal area of land undergoing changed landuse.

Hence we intend to lower the EC-flow rate curve rather than to simply move up the left arm of the curve (lower flow, higher EC). This study has shown how the use of
simple chemistry can enable an efficient use of public and private resources to combat stream salinisation.

Acknowledgement

We thank Sandy Grant of the DNR Spatial Products and Services Unit, Wagga Wagga, for providing the scale map in Figure 1.

References


Table 1    The solubilities of various salts\textsuperscript{a} (mol/l, \textbf{bold}) and approximate EC (dS/m, \textit{italics}) of the saturated solutions at 25\textdegree C.

<table>
<thead>
<tr>
<th>ions</th>
<th>Cl\textsuperscript{−}</th>
<th>SO\textsubscript{4}\textsuperscript{2−}</th>
<th>HCO\textsubscript{3}\textsuperscript{−}</th>
<th>CO\textsubscript{3}\textsuperscript{2−}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na\textsuperscript{+}</td>
<td>6.11, &gt;200</td>
<td>0.68, 45</td>
<td>0.82, 48</td>
<td>1.34, 63</td>
</tr>
<tr>
<td>K\textsuperscript{+}</td>
<td>4.61, &gt;200</td>
<td>1.38, 93</td>
<td>2.24, 123</td>
<td>16.21, 157</td>
</tr>
<tr>
<td>Ca\textsuperscript{2+}</td>
<td>13.43, 163</td>
<td>\textbf{0.03, 2.4}</td>
<td>\textit{b}</td>
<td>\textbf{0.0003, 0.04}</td>
</tr>
<tr>
<td>Mg\textsuperscript{2+}</td>
<td>11.41, 138</td>
<td>4.32, 55</td>
<td>\textit{b}</td>
<td>\textbf{0.003, 0.60}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} derived from g/l given in the CRC Handbook of Chemistry and Physics, 75\textsuperscript{th} Ed.

\textsuperscript{b} No solid phase.
Table 2. Mean ionic composition and flow (at the time of salt measurement) of streams of the mid Murrumbidgee River catchment. Two stations on the Murrumbidgee River itself are shown in italics.

a. Absolute ion concentrations

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>HCO₃⁻</th>
<th>Cl</th>
<th>SO₄⁻</th>
<th>Flow MI/day</th>
<th>EC dS/m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yass</td>
<td>1.34</td>
<td>3.07</td>
<td>2.84</td>
<td>0.06</td>
<td>3.05</td>
<td>3.09</td>
<td>1.12</td>
<td>127</td>
<td>0.73</td>
</tr>
<tr>
<td>Goodradigbee</td>
<td>0.97</td>
<td>0.28</td>
<td>0.21</td>
<td>0.04</td>
<td>1.17</td>
<td>0.09</td>
<td>0.05</td>
<td>703</td>
<td>0.08</td>
</tr>
<tr>
<td>Jugiong</td>
<td>2.71</td>
<td>4.52</td>
<td>5.40</td>
<td>0.11</td>
<td>4.90</td>
<td>7.01</td>
<td>0.83</td>
<td>501</td>
<td>1.30</td>
</tr>
<tr>
<td>Muttama</td>
<td>2.61</td>
<td>6.44</td>
<td>4.77</td>
<td>0.13</td>
<td>5.82</td>
<td>6.75</td>
<td>1.02</td>
<td>144</td>
<td>1.42</td>
</tr>
<tr>
<td>Tumut</td>
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<td>0.10</td>
<td>0.11</td>
<td>0.02</td>
<td>0.27</td>
<td>0.06</td>
<td>0.03</td>
<td>4388</td>
<td>0.04</td>
</tr>
<tr>
<td>Gundagai</td>
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<td>0.47</td>
<td>0.47</td>
<td>0.03</td>
<td>0.81</td>
<td>0.45</td>
<td>0.11</td>
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<tr>
<td>Tarcutta</td>
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<tr>
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</table>

b. Relative cation and relative anion proportions.

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<thead>
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<th>Na</th>
<th>K</th>
<th>HCO₃⁻</th>
<th>Cl</th>
<th>SO₄⁻</th>
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<tbody>
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<td>42</td>
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<tr>
<td>Goodradigbee</td>
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<td>3</td>
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<td>3</td>
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<tr>
<td>Jugiong</td>
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<tr>
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<td>34</td>
<td>1</td>
<td>43</td>
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<td>8</td>
</tr>
<tr>
<td>Tumut</td>
<td>37</td>
<td>29</td>
<td>30</td>
<td>5</td>
<td>75</td>
<td>16</td>
<td>9</td>
</tr>
<tr>
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<td>34</td>
<td>33</td>
<td>2</td>
<td>59</td>
<td>33</td>
<td>8</td>
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<tr>
<td>Tarcutta</td>
<td>18</td>
<td>33</td>
<td>47</td>
<td>2</td>
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<td>35</td>
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<td>59</td>
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<td>Sea water</td>
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<td>17.7</td>
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c. cation : anion balance (mmol/l)

<table>
<thead>
<tr>
<th>Location</th>
<th>$\Sigma$ cations (M$^+$)</th>
<th>$\Sigma$ anions (A$^-$)</th>
<th>$\Delta$ (M$^+$-A$^-$)</th>
<th>$% \Delta/\Sigma$ (M$^+$+A$^-$)</th>
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</thead>
<tbody>
<tr>
<td>Yass</td>
<td>7.30</td>
<td>7.26</td>
<td>0.04</td>
<td>0.3</td>
</tr>
<tr>
<td>Goodradigbee</td>
<td>1.49</td>
<td>1.31</td>
<td>0.19</td>
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<tr>
<td>Jugiong</td>
<td>12.74</td>
<td>12.73</td>
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<td>Muttama</td>
<td>13.95</td>
<td>13.59</td>
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<tr>
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<td>0.36</td>
<td>0.36</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Gundagai</td>
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<tr>
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<td>0.3</td>
</tr>
<tr>
<td>Wagga Wagga</td>
<td>1.44</td>
<td>1.39</td>
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<td>1.8</td>
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</table>
Table 3   Correlation matrix for the mean ionic composition of the nine stream waters in the mid Murrumbidgee River catchment.

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>HCO\textsubscript{3}</th>
<th>Cl</th>
<th>SO\textsubscript{4}</th>
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<tr>
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<td></td>
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<tr>
<td>Mg</td>
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<td>K</td>
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<td>0.937</td>
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<tr>
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<td>0.960</td>
<td>0.985</td>
<td>0.891</td>
<td>0.973</td>
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<tr>
<td>SO\textsubscript{4}</td>
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<td>0.889</td>
<td>0.821</td>
<td>0.831</td>
<td>0.840</td>
<td>1</td>
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</table>
Table 4  Correlation matrix for the ionic composition of water amongst individual water sampling times in the Muttama Creek subcatchment.

<table>
<thead>
<tr>
<th>r</th>
<th>pH</th>
<th>Ca</th>
<th>Mg</th>
<th>Na</th>
<th>K</th>
<th>HCO₃</th>
<th>Cl</th>
<th>SO₄</th>
<th>EC</th>
<th>Flow</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td>Ca</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Na</td>
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<tr>
<td>K</td>
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<td></td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>HCO₃</td>
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<td>0.767</td>
<td>0.989</td>
<td>0.663</td>
<td>0.105</td>
<td>1</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>0.712</td>
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<td>0.976</td>
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<td>0.744</td>
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<tr>
<td>SO₄</td>
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<td>0.764</td>
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<td>0.433</td>
<td>0.732</td>
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<td>EC</td>
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<td>0.934</td>
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<td>0.902</td>
<td>0.953</td>
<td>0.872</td>
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</tr>
<tr>
<td>Flow</td>
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<td>-0.53</td>
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<td>-0.55</td>
<td>-0.43</td>
<td>-0.65</td>
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</tr>
</tbody>
</table>
Captions to figures

Figure 1  Mid Murrumbidgee River catchment: essential features and scaled map.

Figure 2  EC (dS/m) as a function of flow rate (ML/day) for two contrasting streams; one Cl (●) and one HCO₃ (○) dominated.

Figure 3  Ternary plots of the major cations and anions. Mean values are given for Goodradigbee River (○), Jugiong Creek (■), Muttama Creek (□), Yass River (●), Tarcutta Creek (▼), Kyeamba Creek (▲), Tumut River (▲), and the Murrumbidgee River at Gundagai (△) and Wagga Wagga (♦). Seawater (◇) is also shown.

Figure 4  Weathering versus cyclic salt in the mid Murrumbidgee Catchment. (Go = Goodradigbee, Tu = Tumut, Ta = Tarcutta, Y = Yass, K = Kyeamba, M = Muttama, J = Jugiong, W = Wagga Wagga, G = Gundagai). The horizontal dotted line represents the average Na/Cl ratio of 0.86 in sea water. Points above this line indicate addition of Na from mineral weathering. The vertical dotted line represents the average Cl concentration in rainwater for the region. Points to the right of this line indicate evaporative concentration of Cl.

Figure 5  Strongest associations between cations and anions for Muttama Creek:

(a) Cl and Na  Na = 0.673(0.024)Cl  n = 43  r² = 0.952
(b) Cl and Ca  Ca = 0.410(0.018)Cl  n = 43  r² = 0.928
(c) HCO₃ and Mg  Mg = 1.033(0.025)HCO₃  n = 43  r² = 0.977
Saturation with respect to MgCO$_3$ at 0.00035 atm CO$_2$, and assumed to be 0.6 g MgCO$_3$/l, is shown as an open circle. The dotted line represents the isoline.
Rain Cl$^{-}$ (0.04 mM)

Sea water

Cl (mM)

Na / Cl (M)