Characterizing Salinity and Salinity Matrixes in the Burdekin and Fitzroy Catchments, Queensland, Australia

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Abstract In Australia, salinity is a significant issue plaguing freshwater systems, especially in catchments modified by mining activities. River salinity varies in composition from changes in aquifer lithology, natural salt deposits and salt accumulation due to land altering activities (e.g., mining and agriculture). Complex salinity matrixes arise when different salinity sources and compositions are diluted into freshwater systems. Monitoring waterway salinity and characterizing salinity matrixes is vital to mitigating adverse impacts on agriculture, drinking water supplies and ecosystem health. However, to date, few studies have focused on characterizing salinity in freshwater systems based on source. In this paper, case studies drawn from the Burdekin and Fitzroy catchments, Queensland, are characterized for different salinities associated with mining and natural geogenic mineralization. Salinity coefficients (k_e), a ratio of total dissolved solids (TDS in mg/L) to electrical conductivity (EC in μS/cm), are utilized to identify variations in salinity composition. Long-term water quality data (1964-2023) is retrieved from the Queensland Government's water monitoring program. Findings indicate that mining activities in both catchments have a significant influence on freshwater salinity matrixes, driving lower k_e values (0.561-0.587). A novel method for analyzing long-term k_e data is introduced, utilizing the slope (m) of k_e in cumulative distribution plots. Significant variations in slope in the Fitzroy (m: 9.6, 5.3, 2.3) and in the Burdekin River (m: 8.9, 1.6, 1.0, 0.7) reveal influences on local mineralization and industry, not readily evident when only considering average k_e. This study demonstrates that utilizing known geochemical, EC and TDS relationships and k_e is an effective preliminary method for identifying salinity complexity, composition and source. Salinity in the Fitzroy catchment surpasses aquatic toxicity thresholds (EC50: 2410 µS/cm), revealing significant risks to freshwater aquatic species.

Keywords salinity, salinity characterization, water quality, mining, ecosystem health

INTRODUCTION

Freshwater salinization is an emerging global issue impacting water quality and ecosystem health. Salinity refers to dissolved salts, minerals, or ions in water, with major ions consisting of: sodium (Na^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), potassium (K^+), sulfate (SO_4^{2-}), bicarbonate (HCO_3^-), and chloride (Cl^-). Electrical conductivity (EC) or specific conductance, is the ability of an aqueous substance to conduct an electric current. Total dissolved solid (TDS) or ionic concentration, is the total concentration of salts present within a solution (Hem, 1989). Charged ionic species in solution drives conductance. For example, pure deionized water has very low EC ($< 5 \,\mu S$/cm), containing no salts. Both EC and TDS are quantitative measures of salinity.

The correlation between ionic concentration and specific conductance is well established; as ion concentration increases, conductance increases, thus EC can infer ionic concentration (Hem, 1989). The mathematical relationship between ionic concentration and specific conductance can be described in Eq. (1) as:

$$k_e = TDS/EC \tag{1}$$

Where, k_e is the salinity coefficient, EC is electrical conductivity in µS/cm and TDS is total dissolved solids in mg/L. As EC of a solution increases, TDS increases, resulting in a linear relationship between EC and TDS. This direct relationship applies to both anion and cation components of compounds in a solution. It is common to utilize EC readings and predefined k_e (e.g., U.S. standard of 0.64-0.66) to determine TDS (Hem, 1989). Natural waters however, are not simple solutions, containing both ionic and undissociated species that range widely in amount and proportion (Hem, 1989). Ionic mobility, is the capacity of ions to move through a solution, which transfers charges and enables a conduction of current. Ionic mobility decreases with increasing concentration, owing to interference and interactions among ions (Hem, 1989). Factors such as temperature, solvent, specific ions and high salinity (or ionic concentration) can cause interferences and non-linear behaviour in the EC and TDS relationship, resulting in variable k_e coefficients (Hem, 1989). Therefore, large variations in k_e can convey salinity matrix complexity.

In literature it is well established that k_e is variable in some freshwater systems. However, there is limited data identifying specific k_e associated with local geology and mining (Table 1). The given table identifies a range of k_e values and associations to geogenic and mining influences in literature.

Table 1 k_e value ranges in literature

k_e Ranges	Description	Reference
0.64 - 0.66	US Geological Survey Standard Coefficient at 25°C	Hem (1989)
0.59 - 0.72	Australian surface waters (EC range 50 - 1000 µS/cm)	McNeil & Cox (2000)
0.54 - 0.96	Natural waters	Parker (2001)
0.90 - ≥ 1.00	Natural waters influenced by dolerite or schist	Parker (2001)
0.24 - 1.34	South Africa Mine Waters (EC range of 70 -16000 µS/cm)	Hubert & Wolkersdorfer (2015)

Complex salinity matrixes of multiple contaminants arise when different salinity sources (i.e., mine water and industrial effluent) are diluted into freshwater systems (Kaushal et al., 2021). These irregular salinity compositions are of varying ionic strength, pH, redox, and temperature (e.g., mine pit water discharge can increase water temperatures by 3.9℃); collectively influencing adsorption, contaminant mobilization and ecotoxicity risk (Wright et al., 2017). High salinity (>1000 µS/cm) can impact freshwater aquatic species reproduction and cause death (Mann et al., 2014).

OBJECTIVE

This study's objective is to demonstrate the application of k_e as a preliminary method to identify and characterize complex salinity matrixes in highly altered freshwater environments. This paper aims to investigate salinity matrixes in the Burdekin and Fitzroy catchment by (1) identifying k_e values associated with mining (Fig. 1, Table 2), and (2) k_e cumulative distribution plots (Fig. 2) to distinguish long-term influences of local geogenic mineralization and industry. This study further examines the impact of salinity composition on ecosystem health, by comparing salinity data to aquatic toxicity thresholds for 6 freshwater species (Fig. 3) (Mann et al., 2014).

METHODOLOGY

The Burdekin (~130,000 km^2) and Fitzroy (~142,000 km^2) catchments have extensive gold (Charters Towers, Ravenswood, and Mt. Morgan) and coal mining (Collinsville, and Callide), sugarcane farming, grazing, and hydrological alterations (Burdekin Falls Dam: 1,860,000 ML and Fitzroy River Dam: 480,000 ML) (Fig. 1). These subtropical river systems are two of the largest coastal river inputs to the Great Barrier Reef (GBR), a world heritage listed site. The Burdekin and Fitzroy catchments were chosen as case studies due to their established mining developments and the potential impact upon protected ecosystems.

In this study, water quality data is retrieved from the Queensland Government's Water Monitoring Information Portal (WMIP). The WMIP database provides long-term water quality measurements (1964 – 2023) for both TDS and EC (Queensland Government, 2023). A total of 21 gauging stations were chosen; 10 sites in the Fitzroy and 11 in the Burdekin River (Fig. 1). Site selection focused on gauging stations downstream from mining developments. Sites located in tributaries, without anthropogenic activity were utilized as a comparison to natural geogenic inputs.
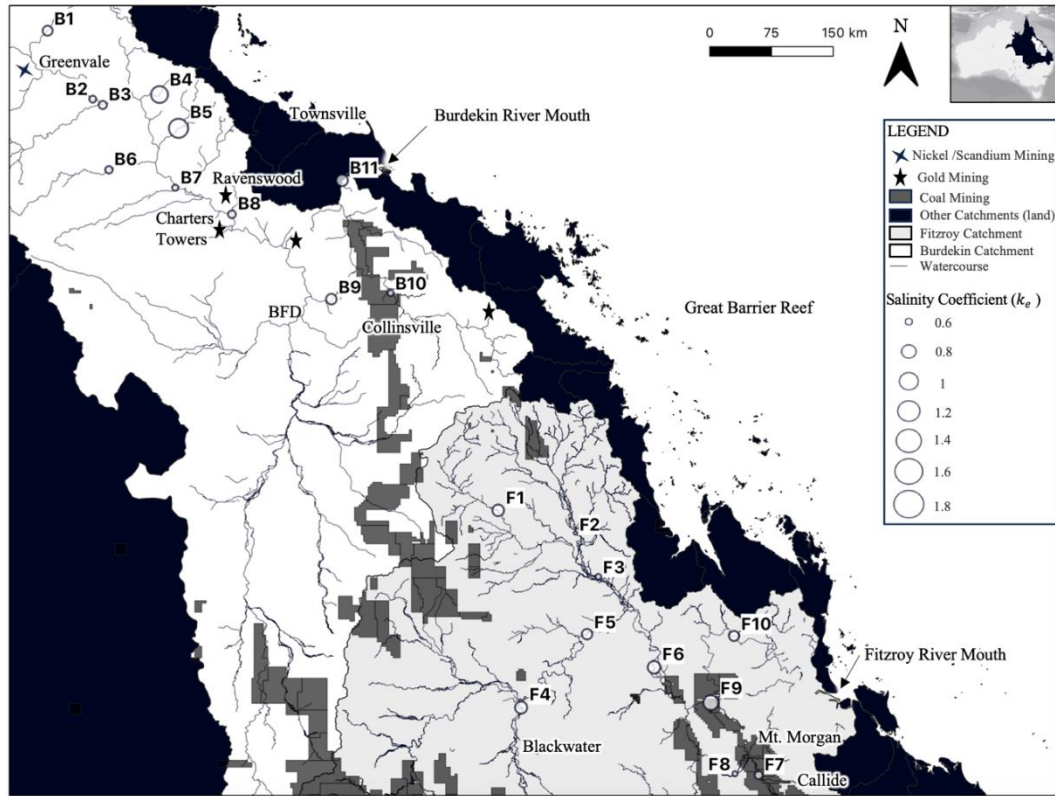
Fig. 1 Fitzroy and Burdekin catchments with electrical conductivity at gauging station sites

RESULTS AND DISCUSSION

Table 2 provides mean TDS, EC, and k_e in the Burdekin and Fitzroy Rivers. In both catchments, river waters in proximity to mining areas (nickel [Ni], scandium [Sc], gold [Au] and coal) are correlated to lower k_e values (0.561 - 0.587) (Table 2). Sites B2 and B3 positioned near Greenvale (Ni and Sc), have a k_e range of 0.576 to 0.587. Charters Towers and Ravenswood (Au), B7 and B8, have a k_e range of 0.571 to 0.583. Sites in proximity or downstream of coal mining operations (F2, F3, F7, F8 and B10) have a k_e between 0.561 and 0.584. B10 is downstream of the decommissioned Collinsville coal power station (operated from 1967-2018) and the mean k_e of 0.570 likely captures previous inputs. Henderson et al. (2022), linked lead isotopes ($^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$) to coal fly ash signatures in Burdekin waterways, further validating the influence of the coal power station. F9, is located at a junction of tributaries downstream of coal and gold mining and likely captures a complex salinity composition from multiple sources, driving a higher k_e of 0.685.

Sites outside of mining operations in the Burdekin (B1, B9 and B11) and the Fitzroy (F1, F4, F5, F6 and F10) have notably different k_e (Burdekin: 0.607-0.628 and Fitzroy: 0.608-0.643), reflecting reduced ionic complexity and a stronger association to k_e standard (0.64-0.66). B4, B5, and B6 are located in areas of minimal anthropogenic activity but have high and low k_e ranges (B4: 0.725, B5: 0.777, B6: 0.580). Exposed pegmatites and granites are prominent at B4 and B5, likely contributing to high silica content in the water column. Eroded basalts at B6 increase Mg-Ca-NaHCO₃, impacting local water chemistries. High k_e ratios are driven by the prominence of weakly

ionized cations and anions; from pesticides, organic compounds, dissolved gases, and neutral salts (calcium carbonate, silicates, and boron) (Day and Nightingale, 1984; Hubert and Wolkersdorfer, 2015). Alternatively, low k_e are reflective of waters high in free acid, alkalinity, $NaHCO_3$ and NaCl. (Hills et al., 2022; Hubert and Wolkersdorfer, 2015). These geochemical trends align with our findings of low k_e associated with mining and basalt mineralization and high k_e driven by dissolved silica from local geology.

Table 2 Mean total dissolved solids (TDS), electrical conductivity (EC), and salinity factor (k_e) in the Burdekin and Fitzroy catchments

Station [a]	Site	N[b]	Description	TDS (mg/L)[c]	EC (µS/cm)[c]	k_e [c]
120123A	B1	24	Burdekin: Valley of Lagoons	295 ± 81.8	487 ± 134	0.607 ± 0.016
120107B	B2	31	Burdekin: Blue Range (Ni, Sc)	258 ± 72.2	448 ± 121	0.576 ± 0.022
120110A	B3	151	Burdekin: Blue Range (Ni, Sc)	229 ± 83.5	394 ± 150	0.587 ± 0.033
120120A	B4	36	Burdekin: Mt. Bradley	42 ± 9.6	60 ± 15	0.725 ± 0.236
120112A	B5	35	Burdekin: Star R.	82 ± 58	117 ± 102	0.777 ± 0.354
120106B	B6	71	Burdekin: Basalt R.	400 ± 156	690 ± 263	0.580 ± 0.029
120122A	B7	30	Burdekin: Charters Towers (Au)	222 ± 80.1	394 ± 152	0.571 ± 0.030
120002C	B8	187	Burdekin: Ravenswood (Au)	174 ± 58.3	301 ± 108	0.583 ± 0.038
120015A	B9	92	Burdekin Falls Dam	108 ± 33.6	179 ± 64.5	0.615 ± 0.044
120205A	B10	56	Burdekin: Bowen R. (Coal)	144 ± 64.2	253 ± 110	0.570 ± 0.076
120006B	B11	201	Burdekin: Home Hill	130 ± 53.0	222 ± 94.4	0.628 ± 0.547
130410A	F1	47	Fitzroy: Upper Isaac	182 ± 141	313 ± 259	0.629 ± 0.181
130404A	F2	130	Fitzroy: Connors (Coal)	195 ± 73.0	352 ± 140	0.561 ± 0.056
130401A	F3	138	Fitzroy: Lower Isaac (Coal)	187 ± 67.0	335 ± 129	0.568 ± 0.057
130504B	F4	47	Fitzroy: Blackwater	140 ± 76.0	228 ± 145	0.637 ± 0.054
130106A	F5	86	Fitzroy: Mackenzie	128 ± 46.0	213 ± 89.0	0.613 ± 0.079
130105B	F6	14	Fitzroy: Mackenzie	107 ± 32.0	171 ± 62.0	0.643 ± 0.052
130327A	F7	82	Fitzroy: Callide (Coal)	228 ± 143	399 ± 262	0.584 ± 0.037
130306B	F8	123	Fitzroy: Callide (Coal)	955 ± 1299	1684 ± 2243	0.565 ± 0.035
130003B	F9	106	Fitzroy: (Coal, Au)	242 ± 190	370 ± 337	0.685 ± 0.146
130005A	F10	223	Fitzroy: Rockhampton	164 ± 111	284 ± 204	0.608 ± 0.072

Source: a WMPI Database retrieved 2023, b. number of samples between 1964-2023, and c mean± standard deviation

Figure 2 shows the cumulative distribution of k_e in the Burdekin and Fitzroy Rivers between 1964 and 2023. In freshwater environments, the proportions and quantity of dissolved salts naturally fluctuate over time (Walton, 1989). In Fig. 2, differences in k_e slope offers an additional approach to identify geogenic mineralization and industry influences on river chemistries. Fig. 2A demonstrates three types of salinity matrixes which correspond to shifts in k_e , slope (m) (m: 9.6, 5.3, 2.3). Fitzroy is heavily impacted by mining activity, with sites F2, F3, F7, and F8 aligning with slope m: 9.6.
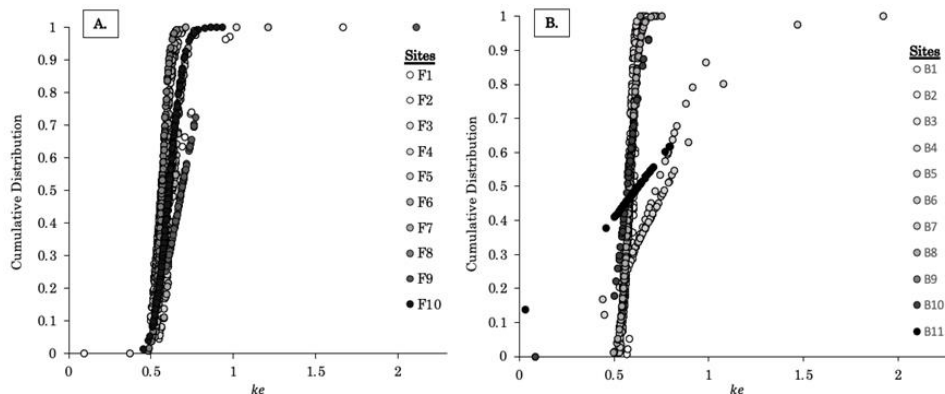

Fig. 2 Cumulative distribution of k_e values for the Fitzroy (A) and Burdekin Rivers (B)

Sites not impacted by mining (F1, F4, F5, F6, F10) fall under slope m: 5.3. As previously identified, F9 is located at a junction of multiple tributaries downstream from coal and gold mining sites. F9 has the largest k_e variation (m: 2.3) within the Fitzroy catchment, reflecting the ionic complexity from multiple salinity sources. Fig 2B indicates four distinct k_e slopes (m: 8.9, 1.6, 1.0, 0.7) in the Burdekin River. B1, B2, B3, B6, B7, B8, and B10 align with m: 8.9 (k_e : 0.70-0.607). B4 (m: 1.6) and B5 (m: 1.0), have a significantly larger variation of k_e, indicating geogenic influences previously established by mean k_e (B4: 0.725, B5: 0.777).

B11 is also distinctive (m: 0.7) and although not previously apparent by its mean k_e (0.628), the cumulative distribution curve demonstrates B11 has a complex ionic composition. Located in the estuary B11 variations are likely driven by pesticide run-off from nearby sugarcane farming and the sugar mill industry established at Home Hill (Henderson et al., 2022).

Figure 3 compares both acute and chronic EC50 (effective concentration; where 50% of the toxicity response is observed) toxicity thresholds to salinity levels in the Burdekin and Fitzroy Rivers. Mann et al. (2014) dosed test species in solutions representative of coal mine water to generate freshwater toxicity limits identified in Fig. 3. The majority (95%) of Burdekin and Fitzroy sites have salinity levels well below aquatic toxicity limits (Fig. 3). F8 (k_e : 0.565) however, has high salinity levels (EC maximum: 11,500 µS/cm); four out of five test species surpassed the ecotoxicity limit, indicating the high toxicity response of aquatic species at this location. These results align with Chapman and Simpson (2005) findings, a study which outlined issues of acid mine drainage and heavy metal toxicity (aluminum and copper) from mine water at Mt. Morgan (EC 12,900 µS/cm; pH 2.7).
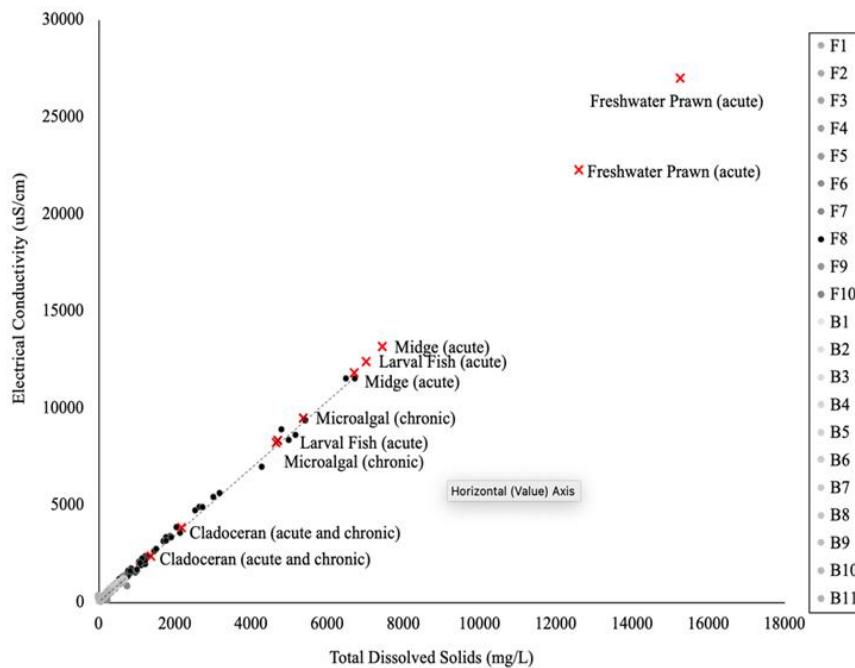
Fig. 3 Aquatic ecotoxicity data retrieved from Mann et al. (2014). Electrical conductivity versus total dissolved solids for the Burdekin and Fitzroy Rivers

CONCLUSION

In highly altered freshwater environments, river salinity reflects a blend of ionic compositions from diverse anthropogenic and natural sources. The Fitzroy and Burdekin River waters are heavily influenced by mining activities, which are characterized by lower k_e (0.561-0.587). An innovative approach utilizing the slope (m) in k_e cumulative distribution plots reveal distinct differences in k_e slope (m: 9.6, 5.3, 2.) in Fitzroy and in the Burdekin River (m :8.9, 1.6, 1.0, 0.7). This slope-based analysis offers an additional approach to examine salinity distribution structure in freshwater systems

and provides additional insights, not readily evident when only considering mean k_e (B11 m: 0.7, k_e: 0.628). High salinity values at F8 exceed Mann et al.'s (2014) EC50 aquatic species limit (minimum 2410 µS/cm), demonstrating high risks to ecosystem health from coal and gold mining at this location.

ACKNOWLEDGEMENTS

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