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**Isotopes of sulphur, oxygen, strontium and carbon in groundwater
as tracers of mixing and geochemical processes, Murray Basin,
Australia**

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Abstract

Salinisation of groundwater and surface water of the semi-arid Murray Basin is an issue of vital importance to the viability of agriculture in south-east Australia. Furthermore, the understanding of the transport and transfer of water and salts in large sedimentary aquifers is necessary for better management of water resources in the future.

The salinity of groundwater of the regional Murray Group Aquifer increases from 500 mg/l at the south-eastern basin margin, to ~ 23,000 mg/l about 300 km downgradient near the discharge area (River Murray). Addition of saline local recharge and upward leakage from the underlying saline Renmark Group Aquifer are thought to be the most likely causes for the increase in salinity in the Murray Group Aquifer.

The chemical composition and $\delta^{18}\text{O}$ and $\delta^2\text{H}$ of water molecules of the two regional aquifers are not sufficiently different to be used as tracers to identify the locations and extent of mixing. The main aim of this thesis is to assess the usefulness of $\delta^{34}\text{S}$ and $\delta^{18}\text{OSO}_4^{2-}$ of dissolved SO_4^{2-} and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as tracers of inter-aquifer mixing and rock-water interaction between and within the Murray and Renmark Group aquifers in the south-west Murray Basin.

The $\delta^2\text{H}$ and $\delta^{18}\text{O}$ composition of groundwater from both aquifers is depleted in ^2H and ^{18}O relative to sea water, and indicates that groundwaters are derived from rain fall and is not remnant sea water or connate seawater. Major ion distribution in both aquifers indicates that the combination of evapotranspiration of rainfall prior to recharge, carbonate dissolution and cation exchange on clays are major processes determining the current chemical composition of groundwater.

The $\delta^{34}\text{S}$, $\delta^{18}\text{OSO}_4^{2-}$ and $\text{SO}_4^{2-}/\text{Cl}$ ratios suggest that vertical input of sulphate into the Murray Group Aquifer through local recharge is the dominant process relative to the

sulphate derived from groundwater flowing laterally from the basin margin. Further modification of the sulphate concentration in the discharge area near the River Murray occurs due to upward leakage from the Renmark Group Aquifer that has enriched $\delta^{34}\text{S}$ and $\delta^{18}\text{OSO}_4^{2-}$ values due to bacterial sulphate reduction.

The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of groundwater from the south and central part of the Murray Group Aquifer is controlled by dissolution of carbonate as recharge water percolates through the soil zone, and mixes with laterally flowing groundwater. Incongruent dissolution of carbonate minerals in the aquifer is also shown to occur by a model of $^{87}\text{Sr}/^{86}\text{Sr}$ and $\text{Sr}^{2+}/\text{Ca}^{2+}$ ratio variations. This conclusion is further supported by $\delta^{13}\text{C}$ data, which shows that $\delta^{13}\text{C}$ becomes progressively more enriched as the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio evolves towards that of the calcite $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of the aquifer matrix. Sr^{2+} concentrations and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the groundwater in the northern part of the Murray Group Aquifer suggest that the most likely processes influencing groundwater chemistry is mixing with more radiogenic groundwater from the Renmark Group Aquifer through upward leakage. The $^{87}\text{Sr}/^{86}\text{Sr}$ ratios also suggest that in addition to upward leakage, significant amounts of water from the Murray Group Aquifer in the northern part of the study area is derived from local recharge. This is supported by a measurable amount of ^{14}C content in groundwater throughout the study area. The measured ^{14}C content of groundwater in the south and central part of the Murray Group Aquifer was adjusted for the effect of carbonate mineral dissolution and, the adjusted ^{14}C data was used to estimate recharge rates in different parts of the Murray Group Aquifer.