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Export of excess Cl by river systems indicates long-term changes to groundwater-surface water interaction

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Understanding whether catchments are in chemical mass balance is important in understand long-term groundwater-surface water interactions. The mass balance of a conservative solute such as Cl in a catchment is:

P*Cl(P) = SW*Cl(SW) + GW*Cl(GW) + dST*Cl(ST)

where P, SW, and GW, are net precipitation, surface water outflows, and groundwater outflows and dST accounts for changes to water held in storage, primarily in the groundwater system. Cl() is the concentration of Cl in the various water components. Precipitation and river discharges are commonly well constrained and in many regions there are also rainfall, groundwater, and surface water geochemistry data. Groundwater fluxes and changes to water in storage are less well known meaning that it is difficult to perform accurate solute balances. However, if the flux of a conservative solute out of a catchment via the river system is larger than the input from rainfall (i.e. if SW*Cl(SW) > P*Cl(P)), the catchment is a net exporter of solutes. In turn this implies a change to the amount of water stored in the catchment and/or a change in chemistry of water in storage.

We apply this technique to several regional-scale catchments (areas up to 15,000 km2) from Victoria, southeast Australia. Cl/Br ratios indicate that the Cl in groundwater and surface water in this region is derived from evapotranspiration of rainfall. Rivers from several catchments in Victoria are saline (Cl >500 mg/L) due mainly to groundwater inflows. Cl concentrations and EC values are well correlated allowing a long-term (up to 25 years) continual record of Cl fluxes to be estimated from sub-daily river discharge and EC data. Many of the rivers export significantly higher volumes of Cl than is delivered via rainfall (up to 1800%). Two scenarios may explain this chemical imbalance. Firstly, saline marshes and lakes developed on young (<1 Ma) basaltic lava plains have gradually drained as blocked river systems re-established. Evapotranspiration and repeated recharge-discharge cycles within these lakes and wetlands produced shallow groundwater with high Cl concentrations that is currently being exported via the re-established river systems. Secondly, in many catchments land-clearing over the last 200 years has resulted in lower evapotranspiration rates and increased recharge. The increased recharge has resulted in a rise of regional water tables and increased baseflow to the rivers. As a consequence, Cl from the groundwater that has relatively long residence time is now being exported. In both cases, the catchments are adjusting to a new hydrological balance and the Cl mass balance indicates that the present patterns of groundwater-surface water interaction are transitory. Both scenarios involve a decrease in evapotranspiration in the catchments that results in groundwater salinities decreasing. Thus, over time, the Cl concentrations in these rivers will decrease as fresher groundwater increasingly forms the baseflow to the rivers and the catchments will tend toward chemical balance; the timescale of change however may be several ka.