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**Controls over Carbonate Saturation in Temperate Estuaries:
Insights from Historical Records**

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Increasing atmospheric $p\text{CO}_2$ has a direct impact on dissolved $p\text{CO}_2$ and pH in the surface ocean, which is likely to have far-reaching effects on ecosystems based on the marine organisms that build carbonate structures. However, in estuaries and in the coastal ocean, the greatest impact of atmospheric $p\text{CO}_2$ on carbonate saturation state may be indirect, occurring via its influence over the hydrologic cycle and ocean circulation. We analyzed published historical river flow and carbon system time-series data, combined with new time-series data collected from the same stations, to examine changes in pH, alkalinity, and aragonite saturation in Tomales Bay, northern California since 1987. In addition to strong seasonal variation in surface-water Ω_{arag} due to fluctuations in both pH and alkalinity, a longer-term decline in Ω_{arag} was observed between 1987-1995. Toward the end of the record, Ω_{arag} approached the limit

below which calcifying organisms have difficulty forming shells (<1). This record also shows that most of the decline in Ω_{arag} occurred during an interval of increased terrestrial runoff from 1991-1995. We suggest that in estuaries such as Tomales Bay, Ω_{arag} will be more sensitive to the impacts of salinity variations arising from changing rainfall patterns along the coast than to the direct pH effect from dissolved anthropogenic CO_2 . The effects of precipitation changes are difficult to predict and could include increased input of terrestrially-derived pCO_2 , dilution of alkalinity, and promotion of alkalinity production via sulfate reduction. Local calibrations and core processing are both underway to apply geochemical and faunal proxies in sediment cores for reconstructing salinity, temperature, pH, and carbonate saturation beyond the reach of historical records. We expect these records to provide insights into the geochemical and ecological responses to local human activities within the last 150-200 years.

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