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# Sodium and chloride levels in rainfall, mist, streamwater and groundwater at the Plynlimon catchments, mid-Wales: inferences on hydrological and chemical controls

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Abstract. Variations in sodium and chloride in atmospheric inputs (rainfall and mist), stream runoff and groundwater stores are documented for the upper Severn River (Afon Hafren and Afon Hore catchments), Plynlimon, mid-Wales. The results show five salient features.

1. Sodium and chloride concentrations are highly variable and highly correlated in rainfall and mist. The sodium-chloride relationship in rainfall has a slope close to the sodium/chloride ratio in sea-water, and an intercept that is not significantly different from zero. This indicates that sea-salt is the dominant source of both sodium and chloride in rainfall, which would be expected given the maritime nature of the metrology. For mist, there is also a straight line with near-zero intercept, but with a slightly higher gradient than the sea-salt ratio, presumably due to small additional sodium inputs from other sources.
2. There is an approximate input-output balance for both sodium and chloride, with the exception of one groundwater well, in which high chemical weathering results in an anomalous high Na/Cl ratio. Thus, atmospheric deposition is the dominant source of both sodium and chloride in groundwater and streamflow.
3. The fluctuations in sodium and chloride concentrations in the streams and groundwaters are strongly damped compared to those in the rain and the mist, reflecting the storage and mixing of waters in the subsurface.
4. On all timescales, from weeks to years, sodium fluctuations are more strongly damped than chloride fluctuations in streamflow. The additional damping of sodium is consistent with ion exchange buffering of sodium in the catchment soils.
5. Sodium and chloride concentrations are linearly correlated in the streams and groundwaters, but the slope is almost universally less than the sea-salt ratio and there is a non-zero intercept. The Na/Cl ratio in streamflow and groundwater is higher than the sea-salt ratio when salinity is low and lower than the sea-salt ratio when salinity is high. This pattern of behaviour is again consistent with ion exchange buffering of sodium in the catchment soils.

The core features of this study are two fold. Firstly, sodium and chloride concentrations are highly damped within the streams and groundwaters relative to the atmospheric input. Secondly, streamflow sodium and chloride respond in similar ways across the catchments, except for the added cation exchange damping of the sodium signal. These findings are remarkable given the heterogeneous nature of the catchments and the complexity of the chemical time series signals in the streams.

Keywords: Sodium; chloride; rainfall; mist; stream water; groundwater; Plynlimon; Hafren; Hore; Tanllwyth; moorland; Sitka spruce; forest; cation exchange; fractal

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