**Figure 1:**(a) Location map with elevation, weather station, flow recorder and synoptic sampling locations, (b) Bedrock geology classification and synoptic sampling locations and (c) Soil classification and groundwater logger locations across the Bruntland Burn.

**Figure 2:** (a) Precipitation and discharge and (b) Groundwater level at location PG2 during sampling period. Groundwater levels are measured as depth below soil surface. Missing data have been interpolated from available data using rates of water table fluctuation from the same logger (black dashed lines). Blue (wet) and red (dry) dashed lines indicate different wetness states of the catchment.

**Figure 3:** Piper diagrams of major ion samples for the different sub-catchments: (a) HW1, (b) HW2, (c) HW3 and (d) MS. Lower ternary diagrams show major cation (left) and anion (right) composition as relative abundance in % based on charge equivalents. Upper diamond in each diagram is a composite plot, aggregating both cation and anions. Colours represent different sampling dates.

**Figure 4:** Spatial distribution of alkalinity concentrations for (a) April, (b) June, (c) August and (d) September 2013.

**Figure 5:** Spatial distribution of base cation concentrations for (a) April and (b) September 2013.

**Figure 6:** Spatial distribution of anion concentrations for (a) April and (b) September 2013.

**Figure 7:** Isotopic composition in relation to global meteoric waterline (δD=8\*δ18O+10) and local meteoric waterline (δD=7.5\*δ18O+4.0) for (a) HW1, (b) HW2, (c) HW3 and (d) MS.

**Figure 8:** PCA of hydrochemical (Cl-, NO3-, SO42-, NO2-, Br-, Na+, NH4+, K+, Mg2+, Ca2+) and isotopic (2H, 18O) parameters as biplot for (a) April and (b) September 2013. The first two principal components are displayed on the primary axes, explaining 69% of the total variance. The investigated sampling locations are printed as numbers (see Figure 1a).

**Figure 9:** Conceptual scheme showing the origin of major ions along a hillslope transect in the Bruntland Burn during wet (a) and dry (b) conditions. Red arrows indicate hydrological processes affecting mass transport into the stream.