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A case for geochemical control of concentration–discharge relationships

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Stream water solute concentrations often decrease with increasing discharge. This phenomenon is generally attributed to dilution of baseflow or "old" water by "new" water with lower solute concentrations (e.g., Johnson et al., 1969; Christophersen et al., 1982). In these mixing models, concentrations are lower in new water because short contact time or small contact area (i.e., overland flow or preferential flow paths) limit opportunities for chemical interaction. In catchment-scale sprinkler experiments, we have found that solute concentrations in runoff decrease with increasing discharge even when the rainfall being applied has higher solute concentrations than baseflow. Mixing models would predict rainfall with such a high solute load to increase runoff solute concentrations, opposite to the behavior we observed. Our experiments demonstrate that storm runoff undergoes significant chemical interaction with the soil and/or bedrock at our study site. This process may also be important in other catchments.

Our experiments were conducted on a small (860 m^2) catchment near Coos Bay, Oregon, U.S.A. The steep (43–45°), unchanneled valley or hollow (Dietrich et al., 1986) in the Coast Range of Oregon is the site of a comprehensive study of hydrology and runoff chemistry (Anderson et al., 1990; Montgomery et al., 1990; Torres et al., 1990). We have conducted sprinkling experiments applying rain of known chemistry and we have monitored several natural rain storms. Organic-rich, low-bulk-density colluvium, ranging from 0.1 to ~2 m thick, mantles gently dipping Eocene graywacke sandstone. Deep drilling revealed a weathered exfoliation zone over fresh, tight bedrock. This zone varies from ~7 m thick at the ridge top to ~1 m down slope. During sprinkling experiments water samples were collected every 4 hr at weirs in the ephemeral channel draining the catchment.

Solute concentrations and pH in the runoff decrease similarly with increasing flow in both natural rainstorms and sprinkler experiments (Table 1). These decreases occur whether the input water is natural rain with low solute concentrations, or sprinkler water with high solute concentrations. In fact, the concentrations of many species, most notably nitrate, were higher at a given discharge during natural rainstorms than during the sprinkler experiments. In other words, for a given discharge, runoff carried a higher solute load during a natural rainstorm, than during a sprinkler experiment. There is probably a biological explanation for the differences in nitrate export during the natural

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TABLE 1

Typical solute concentrations (in mg l^{-1}) at baseflow (~10 ml s^{-1}) and at a high flow of 160 ml s^{-1}

Species	Natural rainstorms			Sprinkling experiments		
	precipitation	baseflow	high flow	precipitation	baseflow	high flow
pH	5.4	6.9	6.5	7.6	6.9	6.5
Ca^{2+}	0.1	5.0	4.3	6.0	3.8	3.0
Mg^{2+}	0.1	1.6	1.4	1.7	1.1	0.9
Na^{+}	0.9	5.4	4.7	5.3	5.4	4.2
K^{+}	0	0.6	0.6	0.7	0.5	0.4
Si	0	6.8	5.7	5.4	6.5	5.5
Alkalinity (as HCO_3^-)	n.m.	15	n.m.	28	20	10
Cl^{-}	1.8	3.0	2.8	4.3	2.5	2.5
SO_4^{2-}	0.4	2.8	2.4	3.0	3.1	3.0
NO_3^-	0.2	18	17	2.6	4.0	3.0

n.m. = not measured.

storms in January and the sprinkler experiments conducted in May, but the point remains that these concentration–discharge relationships cannot be explained by a purely physical mechanism. The decrease in solute concentrations in runoff at high flow during our sprinkler experiments requires chemical interaction of the storm runoff with the soils and bedrock in the catchment.

Several lines of evidence indicate that the runoff during our sprinkler experiments is "new" water, rather than a curiously dilute "old" water being pushed through the catchment. The total amount of water applied in each experiment was approximately equivalent to a conservative estimate of the stored water in the catchment. During the experiments the basin reached hydrologic steady state, meaning the discharge equaled the input rate. This steady condition was maintained for 3–4 days, during which time the runoff chemistry too was remarkably steady. We did not observe the temporal trend in concentrations one might expect if old water of one composition were gradually being displaced by new water of a different composition. Instead, the runoff chemistry mirrors the discharge at the weirs: concentrations fall as discharge goes up, are steady at steady discharge, and rise as discharge declines, and at all times, the concentrations of most species are lower in the runoff than in the sprinkler-applied rainfall.

These observations beg the question: What causes the observed concentration–discharge behavior? Clearly, the decline of concentrations in runoff during the sprinkling experiments requires chemical interaction of rainwater with the catchment. All rain that falls on this catchment infiltrates through the vadose zone, and this may be where chemical interaction occurs. The vadose zone is by definition a place where macropores are not filled, and is therefore a place of intimate soil and water contact. We suggest that the colluvial soil in our study catchment buffers water toward a particular chemistry, less concentrated than our sprinkler water and more concentrated than rainwater. The concentration–discharge behavior then may be explained in terms of: (1) the proportion of water flow through saturated soil vs. weathered bedrock; and (2) the operation of preferential flow paths. We can demonstrate that while most of the water in the catchment is transmitted through the exfoliation zone in the bedrock, a saturation layer develops at the base of the colluvium and thickens with increasing discharge (Montgomery, 1991). Runoff chemistry variations with discharge may in part reflect the degree of reconditioning exerted by the soil in this saturation layer. We also have evidence of preferential flow, presumably fracture flow or macropore flow. Rapid transmittal of water through these features may limit chemical interaction and contribute to the discharge dependence of runoff concentrations. It cannot be over-emphasized however, that our sprinkler experiment results require chemical interaction of storm runoff within the catchment in addition to these physical processes.

At our study catchment we see decreases in major cation concentrations, pH, and alkalinity with increasing discharge during both natural rain events and sprinkling experiments using water with solute concentrations higher than baseflow compositions. The vadose zone, where intimate soil contact occurs during infiltration, may be where these widely differing input chemistries are buffered. The dependence of the runoff chemistry on discharge could stem from some combination of three effects. Preferential flow (accelerated transport through macropores and fractures) and different flow paths (transport through the soil vs. shallow exfoliation zone) are two physical controls. The third effect, and one that appears to play a significant role in this small catchment, is the apparent chemical buffering of water by the soil it passes through.

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