Appendix 4: Detailed Methods

Example of a Mass Balance Calculation

Table 1 shows an example mass balance and how data is interpreted. In the example, upstream was good quality with pH 7, negative net acidity, and low concentrations of metals. Downstream was poor quality with pH 3, positive net acidity, and up to 5 mg/L of metals. Two discharges were sampled. Discharge 1 was an alkaline Fe discharge with high concentrations of Fe and low concentrations of Al. Discharge 2 was acidic discharge with high concentrations of Al.

Loadings were calculated and Upstream, Discharge 1, and Discharge 2 loadings summed. The percentage of pollution was calculated as the summed loadings divided by the downstream loadings. Only certain parameters are conserved (i.e. not removed in a stream) and should be used to calculate mass balances. For example, SO_4 does not precipitate in a stream so all SO4 into a stream should be measurable downstream. Mn and flow are also typically conserved. Conversely, Fe can precipitate in a stream so some Fe that enters a stream will likely precipitate and stay in the stream as iron oxide and will not be measurable downstream. Al is also typically not conserved because it can precipitate in a stream.

Approximately 85% of the downstream flow, net acidity, Mn, and SO_4 are accounted for by the upstream locations. This is a good result and suggests that the two discharges are responsible for a most of the pollution gained by the stream. Accounting for greater than 100% of Fe and Al suggests that Fe and Al precipitate in the stream.

Unaccounted for loadings and flow were calculated by subtracting the summed loading/flow by the downstream loading/flow. Estimated concentrations were calculated using the loading equation above. Calculated concentrations of the unaccounted water suggest it is more similar to Discharge 1 based on SO_4.

While mass balances are useful to qualifying a well constrained stream segment, it should be considered a semi-quantitative method for long stream segments and/or high flows. Unpolluted streams, which are usually not sampled, are a critical part of mass balances as they add alkalinity (negative net acidity) and may add SO_4.

Table 1. Example mass balance. ppd = lb/day. Net acidity and alkalinity units are mg/L $CaCO_3$.
% Accounted = sum(upstream loading+discharge loadings)/downstream loadings
Unaccounted loading = downstream loading – sum(upstream loading+discharge loadings)
Unaccounted concentration = ppd/gpm/0.012

Location	**Flow**	**pH**	**Net acidity**	**Alkalinity**	**Fe**	**Al**	**Mn**	**SO_4**	**Net acidity**	**Fe**	**Al**	**Mn**	**SO_4**
	gpm		**mg/L**						**ppd**				
Upstream	100	7.0	-41	50	1.0	1.0	1.0	100	-49	1	1	1	120
Downstream	200	3.0	86	0	5.0	3.0	5.0	250	207	12	7	12	601
Discharge 1	60	6.0	149	20	80.0	1.0	10.0	300	107	58	1	7	216
Discharge 2	15	3.0	636	0	5.0	100.0	10.0	950	115	1	18	2	171
Sum	175								173	60	20	10	508
% Accounted	88%								84%	498%	277%	85%	85%
Unaccounted	25		112		-159	-42	6	310	34	-48	-13	2	93

Measured vs Calculated Acidity Values

Figure 2 shows that measured and calculated net acidity concentrations are similar. However, measured acidity concentrations were generally 7 mg/L higher than calculated net acidity concentrations. This difference is important for samples with low concentrations of net acidity. In this study, the majority of locations with near neutral net acidity were a few instream and tributary locations in Penn Run. These near neutral net acidity concentrations should be interpreted with caution.

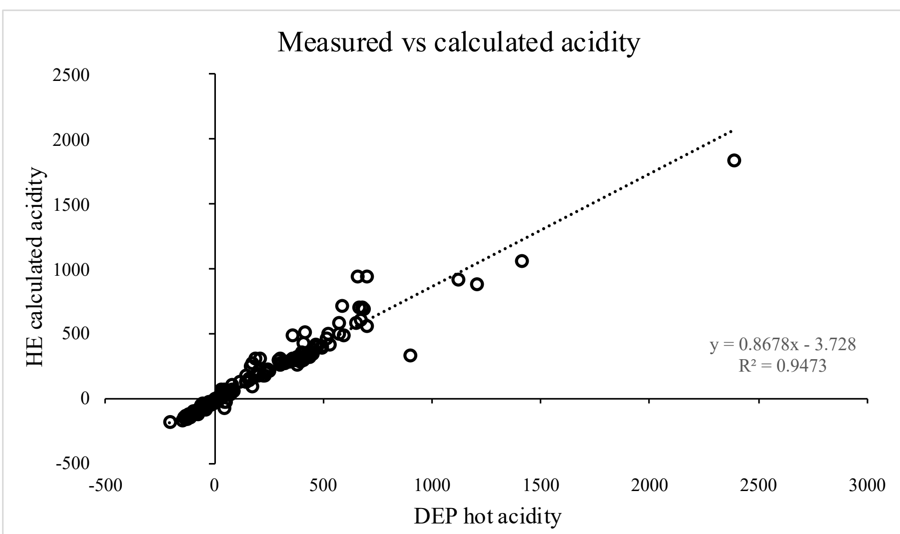

Figure 1: Comparison of hot acidity measured in the lab to Hedin's calculated acidity values.