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Anion-cation balance in water

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Cross-check for reliability of ion analyses

The ionic composition of inland well water can vary from suitable to toxic to cultured animals. Reliable data on concentrations of major cations (calcium, magnesium, potassium, and sodium) and major anions (bicarbonate, sulfate, and chloride) is therefore important in the management of waters for inland shrimp farming.

Cation concentrations usually are determined by atomic absorption spectroscopy (AA method) or inductively coupled plasma emission spectroscopy (ICP method). Bicarbonate concentration can be calculated from total alkalinity concentration, which is determined by titration with standard acid. Sulfate concentration can be determined by the barium chloride turbidity method, and chloride can be measured by titration with standard mercuric nitrate.

In AA and ICP analyses of saline waters, dissolved salts can cause significant interference, so it is always a good idea to check analyses for reliability.

Testing ion balance can help ensure suitable aquaculture conditions for shrimp and other species.

Anion-cation balance

One useful method for determining the reliability of major ion analyses of freshwater or saline water is measurement of anion-cation balance. This method assumes that major ions comprise most of the total dissolved solids in a water sample, and requires that all major ion concentrations are measured.

The principle of electrical neutrality requires that the equivalent weight of positively charged ions (cations) equal that of the negatively charged ions (anions). Because major ions usually represent most of the dissolved ions in water, equivalent amounts of major cations and anions are typically found. In an accurate analysis, the sum of the milliequivalents of major cations and anions should be nearly equal.

Milliequivalents

The milliequivalent of an ion is determined by dividing its concentration in mg/l by its milliequivalent weight in mg/milliequivalent. Milliequivalent weights for major ions are listed in Table 1.

Boyd, Milliequivalent weights of major ions. Table 1

Anions	Anions	Cations	Cations
Bicarbonate	61 mg/meq	Calcium	20.04 mg/meq
Sulfate	48 mg/meq	Magnesium	12.16 mg/meq
Chloride	35.45 mg/meq	Potassium	39.1 mg/meq
		Sodium	23 mg/meq

Table 1. Milliequivalent weights of major ions.

Balance calculation

The anion-cation balance calculation can be illustrated with data on the average concentrations of ions in water from a saline aquifer in Alabama, USA as follows: calcium, 86 mg/l; magnesium, 21 mg/l; potassium, 7.7 mg/l; sodium, 1,392 mg/l; sulfate, 2.0 mg/l; chloride, 2,274 mg/l; total alkalinity, 105 mg/l.

First, convert total alkalinity to bicarbonate by the following equation:

Bicarbonate (mg/l) = Total Alkalinity in mg/l as $CaCO_3$ x 1.22

Bicarbonate (mg/l) = 105 x 1.22 = 128 mg/l

The balance calculations are shown in Table 2. Close agreement between the milliequivalents of anions and cations indicates the concentrations of major ions in the sample were analyzed accurately.

Boyd, Anion-cation balance example, Table 2

Anions	Anions
Bicarbonate: 128 mg/l ÷ 61 meq/mg = 2.10 meq/l	Calcium: 250 mg/ ÷ 20.04 mg/meq = 12.48 meq/l
Sulfate: 2.0 mg/l ÷ 48 meq/mg = 0.04 meq/l	Magnesium: 22 mg/l ÷ 12.16 mg/meq = 1.81 meq/l
Chloride: 2,274 mg/l ÷ 35.45 meq/mg = 64.15 meq/l	Potassium: 14 mg/l ÷ 39.1 mg/meq = 0.36 meq/l
	Sodium: 820 mg/l ÷ 23 mg/meq = 35.65 meq/l
Total = 46.24 meq/l	Total = 50.30 meq/l

Table 2. Anion-cation balance example.

Another example

Consider another example from a recently published paper on inland shrimp farming. The concentrations of major ions were reported as follows: calcium, 250 mg/l; magnesium, 22 mg/l; potassium, 14 mg/l; sodium, 820 mg/l; bicarbonate, 248 mg/l; sulfate, 690 mg/l; chloride, 985 mg/l. The anion-cation balance calculation (Table 3) reveals a greater difference between total anions and total cations than the first example. The average difference in milliequivalents of anions and cations can be estimated as follows:

$$\text{Average Difference (\%)} = \frac{|\Sigma \text{Anions} - \Sigma \text{Cations}|}{(\Sigma \text{Anions} + \Sigma \text{Cations})/2} \times 100$$

$$\text{Average Difference} = \frac{|46.24 - 50.30|}{(46.24 - 50.30)/2} \times 100 = \frac{4.06}{48.27} \times 100 = 8.41\%$$

If the average difference exceeds 15 percent, one should have serious reservations about the accuracy of the analysis.

Boyd, Anion-cation balance example, Table 3

Anions	Anions
Bicarbonate: 248 mg/l ÷ 61 meq/mg = 4.07 meq/l	Calcium: 250 mg/ ÷ 20.04 mg/meq = 12.48 meq/l
Sulfate: 690 mg/l ÷ 48 meq/mg = 14.38 meq/l	Magnesium: 22 mg/l ÷ 12.16 mg/meq = 1.81 meq/l
Chloride: 985 mg/l ÷ 35.45 meq/mg = 27.79 meq/l	Potassium: 14 mg/l ÷ 39.1 mg/meq = 0.36 meq/l
	Sodium: 820 mg/l ÷ 23 mg/meq = 35.65 meq/l
Total = 46.24 meq/l	Total = 50.30 meq/l

Table 3. Anion-cation balance example.

Checking accuracy

Another way of checking the accuracy of ion analyses is to determine if the sum of major ions is roughly equal to total dissolved solids. This procedure is suitable in freshwater or waters with 1 to 2 ppt salinity. However, at greater salinities, water of hydration is retained by the salt residue resulting from evaporation of the sample for total dissolved solids analysis. This leads to erroneously high values for total dissolved solids in saline water samples.

Conclusion

Reliable data on major cation and anion concentrations in waters is an important consideration for inland shrimp farming. The anion-cation balance method presented here to determine the reliability of major ion analyses of fresh- or saline water assumes that major ions comprise most of the total dissolved solids in a water sample, and requires that all major ion concentrations be measured.

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