

Implications of Groundwater Minerals in Dairy Cattle Nutrition

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INTRODUCTION

There is no surprise that dairy cows require lots of water to maintain bodily functions, including the production of milk. The 2001 Dairy NRC called water the most essential nutrient required by cows. Yet, it is one of the least understood inputs we provide for them. Its chemistry is complex, and when coupled with the chemical and biological interactions in the digestive system, it gets even murkier. Until recently, the contribution of minerals from water to the dairy cow's diet has been largely ignored by nutrition models. Though Nutritional Dynamic System (**NDS**) and Agricultural Modeling & Training System (**AMTS**) incorporate water-borne minerals into their models, questions remain about modelling the bioavailability of minerals. The objective of this paper is to establish a starting point for understanding the contribution of water to mineral intake in dairy cows and the potential impacts of that intake on mineral excretion, dietary requirements, and acid-base balance.

INFLUENCE OF WATER SOURCE ON COMPOSITION

The source of water has substantial impact on its quality. Whether a cow's drinking water comes from a well, pond, river, or municipal system; it has picked up solutes along the way. What those solutes are, and in what concentrations they occur, depends on the atmospheric, geologic, and land-use conditions of the regional water cycle. As water evaporates from open water

bodies and soil or transpires from vegetative cover, then condenses and falls back to earth as rain, sleet, hail, or snow; it picks up constituents from the atmosphere. Carbon dioxide, nitrogen oxide, and sulfur dioxide are the most common, and they form weakly acidic solutions ranging from pH 4.3 to 5.6. Upon its return to earth, this acidic solution will either run off the surface to collect in lakes, ponds, and rivers, or it will infiltrate the ground and work its way down to the water table. In either case, the water dissolves minerals, nutrients, or contaminants and takes on characteristics of the soils and bedrock through which it travels. Because of this, a few generalizations will suffice for this discussion of the geologic influence on groundwater sources.

- The concentration of dissolved mineral depends on the type of rock through which water flows, such that: Sedimentary > Metamorphic > Igneous.
- The concentration of dissolved solids generally increases with the depth of the water source: Deep well > Shallow well > Spring; depth being linked to residence time in the groundwater system (Fleeger, 1999).
- Weather events, such as heavy rains or snow melt, can have dramatic effects on water composition if water is drawn from a surface source, from shallow unconsolidated aquifers or from highly porous bedrock such as limestone.

Table 1. Concentrations of minerals (ppm) from 12,162 water samples analyzed by DairyOne Forage Lab and Dairyland Laboratories.

	SO ₄ -S	Cl	Ca	P	Mg	K	Na	Fe
Mean	70.5	183.7	101.5	0.6	34.1	12.29	123.3	0.46
Median	13.0	24.0	57.7	0.1	18.9	3.40	21.2	0.06
90 th percentile	191.0	204.0	183.8	0.5	65.5	15.70	203.4	0.80
Max	3003.0	18760.0	9320.0	124.5	1267.0	707.3	12260.0	40.90

Manure management and application can play a role in water quality via dissolution and carriage of nutrients, minerals, or pathogens into groundwater. Depending on soil type, subsurface structures, and intensity of application, manure constituents can accumulate in the groundwater system locally or be carried miles away, as in the limestone karsts which are prevalent in Pennsylvania.

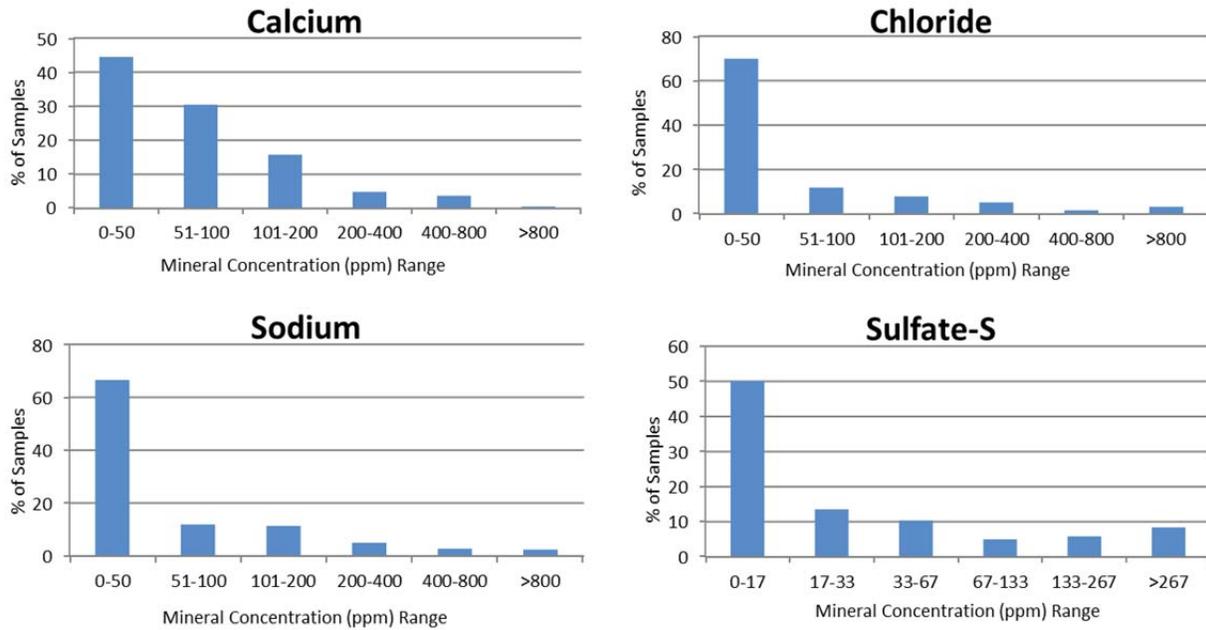
A summary of results from water analyses conducted by DairyOne Forage Lab (Ithaca, N.Y.) and Dairyland Laboratories (Arcadia, Wis.) for the years 2006 – 2013 are in Table 1. The origins of the water samples are unknown, and we should assume that they are not all from dairy water supplies. Trace minerals, other than Fe, were excluded from this summary, as they occurred in trace amounts. For example, Zn, Cu, Mn, and Mo had 90th percentile levels at 0.25, 0.05, 0.37, and 0.01 Laboratories (Arcadia, Wis.) for the years 2006 – 2013 are in Table 1. The origins of the water samples are unknown, and we should assume that they are not all from dairy water supplies. Trace minerals, other

than Fe, were excluded from this summary, as they occurred in trace amounts. For example, Zn, Cu, Mn, and Mo had 90th percentile levels at 0.25, 0.05, 0.37, and 0.01 ppm, respectively, so their contribution to total intake is usually insignificant. Sulfate-S is presented here, but some labs report SO₄. For results reported as SO₄, multiply by 0.333 to get SO₄-S concentrations.

MINERAL INTAKE FROM WATER RELATIVE TO MINERAL REQUIREMENTS

Often, the 100 to 135 L of water consumed daily by a lactating dairy cow provide just a few milligrams to grams of any particular mineral (water intakes calculated for 32 kg milk, 22 kg dry matter intake (**DMI**) and 54 kg milk, 30 kg DMI; respectively). Some sources of water, however, can provide tens to hundreds of grams of mineral. The values above are obviously not distributed normally, but the potential for some water supplies to contribute significantly to mineral intake is also obvious. The distribution of selected minerals from this dataset are in Figure 1.

Figure 1. Distribution of mineral concentrations in 12,162 samples analyzed by DairyOne Forage Lab and DairyLand Laboratories.



Sulfate-S is the mineral of greatest concern, as it has the greatest proportion of samples at the higher values, with 8.4 % of the samples over 267 ppm. At that level, water could be supplying sufficient S to antagonize Cu and Se absorption when combined with a diet that is at or above NRC requirements for S (Ivancic and Weiss, 2001). Extrapolating intake for a lactating cow, consuming 115 L/d of water, results in the following mineral intakes from the water supply alone (Table 2).

Relative to a dairy cow's requirements, many water supplies will make little appreciable impact on total mineral intake through water-borne minerals. However, the Na, Cl, and S intake from water for the average sample in this dataset (Table 2) represents 28, 34, and 39 %, respectively, of the cows' requirement for those minerals. Consequently, the combination of water and dietary minerals could far exceed cows' requirements, and likely justifies altering mineral supplementation of the diet. Some

Table 2. Mineral intake from water (g/d), based on 115 liters of consumed water/day in 12,162 samples analyzed by DairyOne Forage Lab and DairyLand Laboratories.

	SO ₄ -S	Cl	Ca	P	Mg	K	Na	Fe
Mean	25.4	21.1	11.7	<0.1	3.9	1.4	14.2	<0.1
90 th percentile	73.6	23.5	21.1	0.1	7.5	1.8	23.4	0.1

Table 3. Water and diet mineral concentrations, total mineral intake, percent of mineral intake from water and percent of NRC requirements from actual dairies in Texas, Ohio and New Mexico with problematic water supplies.

	Ca	P	Mg	K	S	Na	Cl	Fe
Texas								
Water (ppm)	270.2	0.1	101.7	22.2	422	545.5	855	0.01
Diet (% DM) ¹	0.89	0.41	0.36	1.46	0.21	0.51	0.59	220 ppm
Intake (g)	238	95	95	341	99	183	238	5.1
% from H ₂ O ²	10.9	<0.1	10.3	0.6	41	28.9	34.7	0
% NRC ³	165	120	216	140	213	358	380	1376
Ohio								
Water (ppm)	471	0.1	88.1	14.5	1400	122	100	19.2
Diet (% DM)	0.93	0.4	0.35	1.43	0.2	0.39	0.53	238.7 ppm
Intake (g)	262	94	91	339	175	103	134	7.38
% from H ₂ O	16	<0.1	9	0.3	73	11	7	24
% NRC	176	117	200	136	346	196	209	1914
New Mexico								
Water (ppm)	316	0.1	341	0.1	2330	479	668	0.94
Diet (% DM)	0.9	0.35	0.3	1.35	0.21	0.34	0.42	119 ppm
Intake (g)	251	82	114	317	343	140	183	2.92
% from H ₂ O	16	<0.1	37	<0.1	85	43	45	4
% NRC	172	102	254	128	731	271	288	776

¹ Iron is in ppm rather than %DM.

²% from H₂O is the percentage of the total mineral intake provided by that water supply.

³ % NRC is the percentage of the NRC mineral requirement provided by the combined intake of mineral from water and the diet.

examples of water supplies and diets, the contribution of water to mineral intake, and total mineral intake relative to NRC requirements are in Table 3.

When water intake contributes significant amounts of mineral to a cow's diet, there is an opportunity to adjust the diet to bring total mineral intake in line with daily requirements. For example, at the New Mexico dairy in Table 3, the combined diet and water intake is providing 271 and 288 % of NRC requirements for Na and Cl, respectively. Reducing the dietary salt by two-thirds would bring the total intake of Na and Cl down to about 170 % of requirements. In a survey of California dairies, their diets, water supplies, and mineral excretion in

milk and manure (Castillo, et al. 2013), the authors found that including water minerals increased estimated mineral intake by < 4 % for all minerals except Na and Cl. Including Na and Cl from water increased total Na and Cl intake on average by 9.3 and 6.5 %, respectively. With the exception of Na and Cl, all water values from this study were below the median values shown in Table 1. This is reflective of the igneous geology underlying the Central Valley of California, which contributes relatively little mineral content to water. Adjusting diets to compensate for water minerals will reduce manure excretion of minerals, and may reduce salinization of soils or further accumulation of minerals in groundwater.

If water minerals are excessively high, there is the potential to exceed the maximum tolerable levels (MTL) for minerals ingested by a cow. The MTL for minerals were recently reviewed and updated (NRC, 2005). These updates were based only on dietary mineral intake, but should be considered with regard to the contribution of minerals from water. For Na and S, which are frequently elevated in water and which also have “high” concern levels (NRC, 2005), the MTL was reached in 341 samples for S and 77 for Na in our dataset. These results are based on an assumption that dietary mineral concentrations were fed exactly to NRC, which is rarely the case. We can therefore assume that many more situations would reach MTL when actual dietary and water mineral levels are considered (Table 4). In these cases, water treatment to remove the excessive minerals could be warranted.

MINERAL AVAILABILITY

In order to assess the impact of water-borne minerals on a cow’s daily intake, the availability of minerals derived from a water supply must be considered. Within water, each mineral can exist in its elemental form, as a hydrated ion, or as a complex with another ion or molecule. The forms that

minerals take are referred to as speciation. Dissolved and suspended mineral constituents of water will dissociate and re-associate with other ions to conform to two electrochemical rules:

- 1) the resulting solution be electrically neutral, and
- 2) the solution will be at the lowest possible energy state.

The solutes thus formed represent a wide array of ionic species for each mineral, which will vary depending on the concentrations of the other constituent solutes (Stumm and Morgan, 1996).

Using the hydrogeochemical model PHREEQC (Parkhurst and Appelo, 1999), the speciation of minerals in a water sample can be calculated. As an example: as the level of sulfate increases, and all other mineral constituents being constant, the concentration of free iron (Fe^{+2}) increases, with a concomitant decrease in the other iron species (Figure 2). Similarly, as sulfate concentration increases, the concentrations of non-sulfur containing ion species in water also decrease (Figure 3).

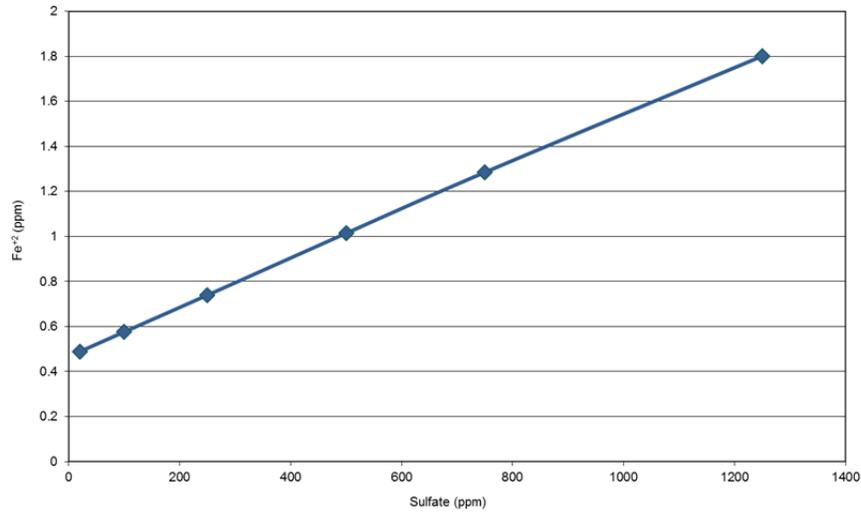
Table 4. Water mineral concentration (ppm) needed to reach maximum tolerable level (MTL, from NRC 2005) when added to a diet formulated to meet 100 % of NRC requirements for a cow producing 45Kg of milk and consuming 120 L of water.

	Ca	Mg	K	S	Na	Cl	Fe	Cu	Mn
Water, ppm	1786	861	2023	430	2044	3336	104	6	428
	----- % Dry Matter -----					----- ppm -----			
Diet	0.67	0.2	1.06	0.2	0.22	0.28	17	11	13
MTL ¹	1.5	0.6	2	0.4	1.17	1.83	500	40	2000
Concern Level ²	Med	Low	Med	High	High	High	Med	High	Low

¹ Maximum Tolerable Levels are for cattle on a dry matter basis. Numerous factors affect MTL, including bioavailability of mineral, duration of exposure, and animal factors.

² Concern levels consider both the ability of the animal to clear the dose and the severity of the animal response.

Figure 2. Concentration of Fe^{+2} in a water sample containing 3 ppm total Fe, varying amounts of sulfate and all other constituents being held constant.¹

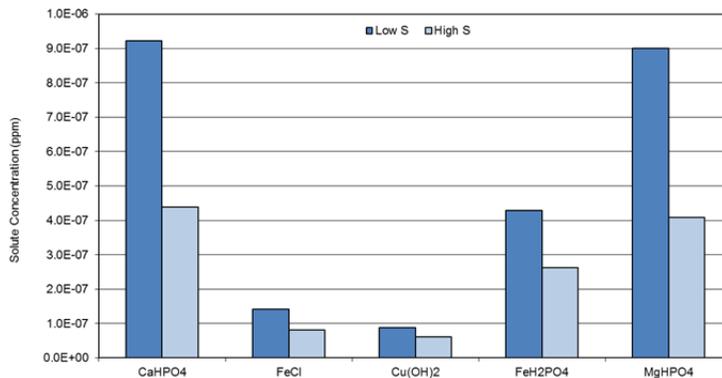


¹ Concentrations calculated using PHREEQC (Parkhurst and Appelo, 1999).

To gain a more complete understanding of the bioavailability of minerals, we must also consider the solubility of each of these ion species. The relative solubility of a species will influence the availability in the digestive tract and the extent to which it is absorbed. Table 5 has speciation and solubility parameters for Ca and Fe in a representative water sample. Solubility is expressed as K_{sp} , the solubility product, and is the molar concentration at which that mineral species reaches saturation and

becomes insoluble (Stumm and Morgan, 1996). The larger the K_{sp} , the greater the solubility. The ultimate form, concentration, and availability of ingested minerals within the rumen and/or intestine are highly dependent on these interactions, whether the minerals come from water or the diet. Simply knowing the concentration of a mineral in water or feed tells us little of its speciation or solubility, and therefore little about its availability or potential for toxicity (NRC, 2005).

Figure 3. Concentration of select ion species in a water sample of low (120 ppm) or high (1200 ppm) sulfate and all other mineral constituents held constant.¹



¹ Concentrations calculated using PHREEQC (Parkhurst and Appelo, 1999).

Table 5. Ion species of calcium and iron, their concentration and solubility in a representative water sample.¹

Ion Species	Species Concentration (M)	Solubility K _{sp} (M)
Ca ⁺⁺	6.01 x 10 ⁻⁴	2.5 x 10 ⁻¹
CaSO ₄	7.17 x 10 ⁻⁵	7.1 x 10 ⁻⁵
CaHPO ₄	9.22 x 10 ⁻⁷	1.0 x 10 ⁻⁷
CaH ₂ PO ₄ ⁺	7.49 x 10 ⁻⁸	4.68 x 10 ⁻⁶
CaPO ₄ ⁻	2.36 x 10 ⁻⁸	2.07 x 10 ⁻³²
Fe ⁺⁺	5.95 x 10 ⁻¹³	2.0 x 10 ⁻¹
FeOH ⁺	3.82 x 10 ⁻¹³	1.46 x 10 ⁻²⁵
FeSO ₄	6.56 x 10 ⁻¹⁴	4.30 x 10 ⁻²⁷
FeHPO ₄ ⁺	5.83 x 10 ⁻¹⁵	3.39 x 10 ⁻²⁹

¹ Concentrations calculated using PHREEQC (Parkhurst and Appelo, 1999).

THE STRONG ION DIFFERENCE

One cause of speciation behavior is the requirement that aqueous solutions maintain electrical neutrality. A primary means by which water achieves electrical neutrality is instantaneous dissociation and association of the water molecule itself such that the H⁺ and OH⁻ ions are available to associate with unpaired ions of the opposite charge. The ions that exert the largest effect are those which dissociate completely in water, with dissociation constants > 10⁻⁴ Eq/L, and are known as the strong ions; Na⁺, K⁺, Mg⁺⁺, Ca⁺⁺, Cl⁻, PO₄⁻, and SO₄⁻ (Stewart, 1983). In that seminal publication, the principles of the strong ion difference (**SID**), a version of which we know as the dietary cation anion difference or **DCAD** (Goff, 2006), are outlined. We now appreciate that the acid-base status of an animal is largely driven by these strong ions (Constable, 2003).

Most research on the effects of individual water constituents, namely minerals, on dairy cows has yielded unremarkable results (Digesti and Weeth, 1976; Challis et al., 1987). Consequently, many have concluded that water-borne minerals have little if any effect on dairy cows even at elevated levels. Given the

previous discussion of the complex interactions of ion species and their relative solubility in an aqueous solution, i.e. rumen fluid or digesta, it is not surprising that naturally occurring minerals in drinking water sources rarely lead to acute toxicoses. Rather, elevated mineral levels tend to result in more subtle, chronic conditions of poor performance or increased health problems (NRC, 2005). These effects may be mediated through alteration of rumen function (Durand and Komisarczuk, 1988), antagonisms amongst the minerals (Spears, 2003), oxidative stress (Miller et al., 1993) or altered acid-base balance (i.e., DCAD).

A meta-analysis of DCAD effects in dairy cattle (Hu and Murphy, 2004) suggests that a DCAD between 34 to 40 mEq/100g DM (Na+K-Cl) is optimal for milk production and dry matter intake. Multiple studies have documented linear effects of DCAD on dry matter intake and fat-corrected milk yield (Apper-Bossard et al., 2006 and Roche et al., 2005). Interestingly, both studies measured increases in *cis*-9, *trans*-11 conjugated linoleic acid with the high DCAD diets, suggestive of altered rumen fermentation patterns (Lock et al., 2006).

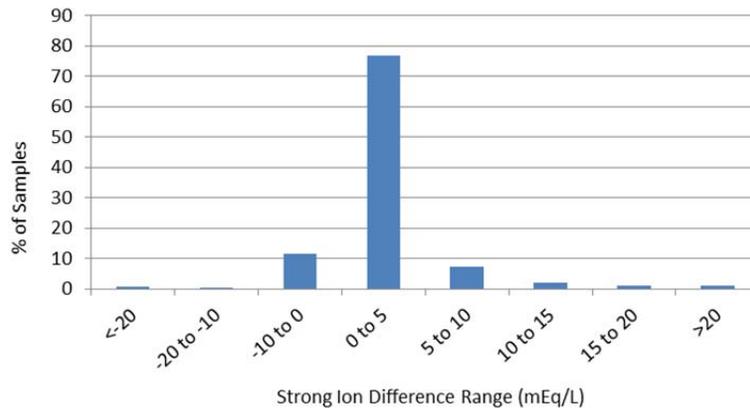
When water with a negative SID is introduced to the rumen of a dairy cow consuming large quantities of fermentable carbohydrates, with the concomitant production of the anionic VFA and lactate, it may be sufficient to alter the fermentation of the rumen negatively. Recent work (Constable, personal communication) suggests that the beneficial effects of higher DCAD diets is due to an improved rumen fermentation environment. Rumen function is influenced by the SID (a.k.a. DCAD) whether the source of strong cations and anions is water or feed.

From the water dataset (Table 1), SID values average 1.17 mEq/L with a median of 0.94 mEq/L and a 90th percentile value of 5.32 mEq/L. However, the wide range in SID values, from -313 mEq/L up to 406 mEq/L (Figure 4) is notable. Considering the extent of variation in SID of water supplies, and the potential impact on fermentation in the rumen and acid-base status, we believe it is warranted to evaluate water samples not only for the individual mineral constituents which may pose a problem, but also for SID.

For a comprehensive understanding of the impact the total strong ion intake has on

the acid-base status of the cow, the calculation of the SID for water and DCAD for the diet need to be integrated. One approach is the calculation of a Total Intake Cation Anion Difference (**TICAD**) which includes the intake of strong ions from water, adjusted to a mEq/100 g DMI basis, and added to the calculated DCAD. This was done for some example dairy situations (Table 6). The examples are from problematic farms, but would not be uncommon in areas with water of either high Na, Cl, or S content. The water supply may, by virtue of its SID, be thwarting our efforts to get lactating cows into an optimal positive DCAD range, and pre-fresh cows into an optimal negative DCAD range. The New Mexico dairy, for example, has a DCAD near the optimal range for dry matter intake and milk production; but the water, by virtue of its strongly anionic SID, is pulling the cows down to a negative TICAD. Conversely, the New York dairy has a positive SID water supply, which may require additional dietary anionic supplements to achieve acidification of the pre-fresh cows and prevention of hypocalcemia.

Figure 4. Distribution of SID values¹ in 12,162 samples analyzed by DairyOne Forage Lab and DairyLand Laboratories.



¹ SID of water calculated as $(Na+K+.15Ca+.15Mg)-(Cl+.2S+.3P)$

Table 6. Strong Ion Difference (SID) in water, Dietary Cation Anion Difference (DCAD) and Total Intake Cation Anion Difference (TICAD) calculated from water analyses and diets of specific dairy herds in New York, Ohio and New Mexico.

Dairy Location	Cow Status	SID ¹ (mEq/L)	DCAD ¹ (mEq/100g DMI)	TICAD ¹ (mEq/100g DMI)
New York	Prefresh	25.8	0.8	9.28
Ohio	Lactating	-44.9	30.8	15.0
New Mexico	Lactating	-78.5	29.9	-12.4

¹ SID, DCAD and TICAD calculated with the WaterForCows[®] model, accessed at www.waterforcows.com

CONCLUSIONS

The typical water supply for dairy cows does not contain enough mineral to warrant much attention. However, average values for a locale cannot be assumed to represent a particular water source. Consequently, every dairy should test their supply to get an accurate assessment of the mineral content of the water for their cows. For those cases in which the water supplies high levels of particular minerals, opportunities exist to adjust the diet, water supply, or both, to bring total mineral intake down to reasonable levels. This would bring mineral intake in line with the cows' requirements while reducing mineral excretion in manure and accumulation in soil. Additionally, greater consideration needs to be given to water for its provision of strong ions to the dairy cow. In either highly positive or highly negative SID water supplies, the potential to perturb rumen function or acid-base balance of the cow is very real.

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model is made available from a licensing agreement with Vi-COR, Inc.

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