HEY! WHAT'S THAT IN MY DRINK? NEW CONSIDERATIONS ON DRINKING WATER QUALITY FOR DAIRY CATTLE

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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 the Nutritional Dynamic System (NDS) and Agricultural Modeling & Training System (AMTS) incorporate water-borne minerals into their models, the intricacies of mineral availability remain unclear. 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 and 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.

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 - 2011 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 SO_4 . For results reported as SO_4 , multiply by 0.333 to get SO_4 -S concentrations.

Table 1. Concentrations of minerals (ppm) from 6460 water samples analyzed by DairyOne Forage Lab and Dairyland Laboratories.

	SO ₄ -S	CI	Ca	Р	Mg	K	Na	Fe
Mean	61.5	232.0	112.2	0.3	35.3	11.9	145.1	0.4
Median	13.0	24.0	59.1	0.1	17.5	3.9	24.5	0.05
90 th percentile	152.3	210.4	202.1	0.6	67.2	16.4	215.0	0.8
Max	1795.0	18760	9844	38.2	1267	472.4	10620	40.9

MINERAL INTAKE FROM WATER RELATIVE TO MINERAL REQUIREMENTS

Often, the 100 to 135 liters 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 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 concentrations for selected minerals from this dataset is in Figure 1.

Sulfate-S is the mineral of greatest concern, as it has the greatest proportion of samples at the higher values, and almost 8% of the samples are 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 liters of water per day, results in the following mineral intakes from the water supply alone (Table 2).

Figure 1. Distribution of mineral concentrations in 6460 water samples analyzed by DairyOne Forage Lab and DairyLand Laboratories.

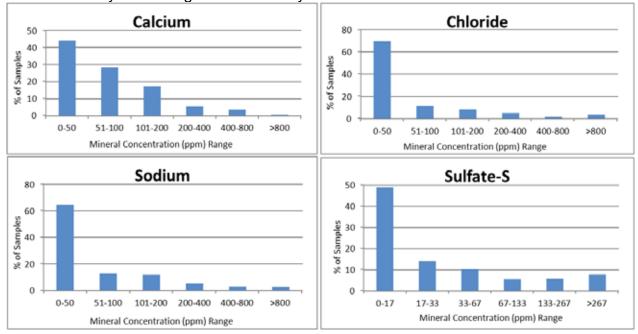


Table 2. Mineral intake from water (g/d), based on 115 liters of consumed water/day in 6460 water samples analyzed by DairyOne Forage Lab and DairyLand Laboratories.

	SO ₄ -S	CI	Ca	Р	Mg	K	Na	Fe
Mean	23.7	26.7	12.9	<0.1	4.1	1.4	16.7	<0.1
90 th percentile	69.0	24.2	23.2	0.1	7.7	1.9	24.7	0.1

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 (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.

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

Argentina, Ohio and New Mexico with problematic water supplies.

	Ca	Р	Mg	K	S	Na	CI	Fe	Zn	Cu
<u>Argentina</u>										
Water (ppm)	87.7	0.15	79.9	50.7	978.1	2442	1652	0.05	0.02	0.01
Diet (%DM)	0.4	0.38	0.29	1.72	0.24	0.11	0.09	313	47	12
Intake (g)	90	76	67	349	159	301	207	6.27	0.94	0.24
% from H ₂ O ^a	11	<0.1	14	2	70	92	91	<0.1	0.2	0.4
% NRC ^b	72	111	176	166	399	683	382	1959	90	109
OH										
Water (ppm)	471	0.1	88.1	14.5	1400	122	100	19.2	2.0	0
Diet (% DM)	0.93	0.4	0.35	1.43	0.2	0.39	0.53	238.7	95.2	19.2
Intake (g)	262	94	91	339	175	103	134	7.38	2.43	0.45
% from H ₂ O	16	<0.1	9	0.3	73	11	7	24	7	0
% NRC	176	117	200	136	346	196	209	1914	196	173
NM										
Water (ppm)	316	0.1	341	0.1	2330	479	668	0.94	0	0
Diet (%DM)	0.9	0.35	0.3	1.35	0.21	0.34	0.42	119	85	14
Intake (g)	251	82	114	317	343	140	183	2.92	2.00	0.33
% from H ₂ O	16	<0.1	37	<0.1	85	43	45	4	0	0
% NRC	172	102	254	128	731	271	288	776	163	127

^a % from H₂O is the percentage of the total mineral intake provided by that water supply ^b % NRC is the percentage of the NRC mineral requirement provided by the combined intake of mineral from water and the diet.

If water minerals are excessively high, there is 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 168 samples for S and 65 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.

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	CI	Fe	Cu	Mn
Water	1786	861	2023	430	2044	3336	104	6	428
			% Dr	y Mattei				ppm -	
Diet	0.67	0.2	1.06	0.2	0.22	0.28	17	11	13
MTL ^a	1.5	0.6	2	0.4	1.17	1.83	500	40	2000
Concern Level ^b	Med	Low	Med	High	High	High	Med	High	Low

^a Maximum Tolerable levels are for cattle on a dry matter basis. Numerous factors affect MTLs, including bioavailability of mineral, duration of exposure and animal factors. ^b Concern levels consider both the ability of the animal to clear the dose and the severity of the animal response.

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 with 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 & Morgan, 1996).

Using the hydrogeochemical model PHREEQC (Parkhurst & Appelo, 1999) the speciation of minerals in a water sample can be calculated. As an example: as the level of sulfate increases, everything else 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 change (Figure 3).

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 Ksp, the solubility product, and is the molar concentration at which that mineral species reaches saturation and becomes insoluble (Stumm & Morgan, 1996). The larger the Ksp, 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 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.

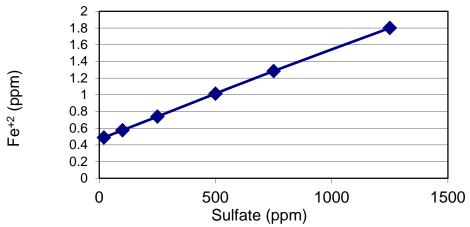


Figure 3. Concentration of select ion species in a water sample of low (120 ppm) or high (1200 ppm) sulfate and all other mineral constituents held constant.

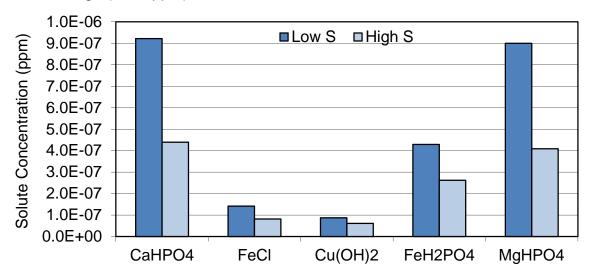


Table 5. Ion species of calcium and iron, their concentration and solubility in a representative water sample.

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
CaHPO₄	9.22 x 10 ⁻⁷	1.0 x 10 ⁻⁷
CaH2PO ₄ ⁺	7.49 x 10 ⁻⁸	4.68 x 10 ⁻⁶
CaPO ₄	2.36 x 10 ⁻⁸	2.07 x 10 ⁻³²
CaOH⁺	7.97 x 10 ⁻¹⁰	4.62 x 10 ⁻⁶
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

THE STRONG ION DIFFERENCE

One cause of speciation behavior is the requirement that aqueous solutions maintain electrical neutrality. The 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 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).

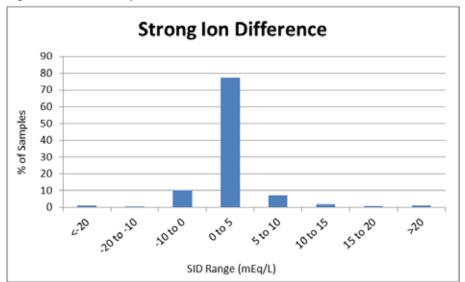
Most research on the effects of individual water constituents, namely minerals, on dairy cows has yielded unremarkable results (Digesti and Weeth, 1976; Challis, et al., 1987). Consequently, many have concluded that water-borne minerals have little if any effect on dairy cows even at elevated levels. Given our previous discussion of the complex interactions of ion species and their relative solubility in an aqueous solution, i.e. rumen fluid, 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. Apper-Bossard and co-workers (2006) provided diets with DCAD values of 0, 15 or 30 mEq/100g DM (Na+K-Cl-S) to lactating cows consuming either high or low starch diets and observed linear effects of DCAD on dry matter intake and fat-corrected milk yield only in the high starch group. Roche and co-workers (2005), drenched grazing cows twice per day to achieve DCAD levels of 23 to 88 mEq/100 g DM (Na+K-Cl-S). There was a linear effect of DCAD on fat corrected milk yield. 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 VFAs 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 cation and anions is water or feed.

From the water dataset (Table 1), SID values average 1.14 mEq/L with a median of 0.96 mEq/L and a 90th percentile value of 5.32 mEq/L. However, the wide range in SID values, from -232 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 the efficiency of fermentation in the rumen, 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.

Figure 4. Distribution of SID values in 6460 water samples analyzed by DairyOne Forage Lab and DairyLand Laboratories.



For a complete 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 DM basis, and added to the calculated DCAD. This was done for the example farms in Table 3 (Table 6). The examples are from problematic farms, but would not be uncommon in areas with water of either high Na, CI 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 prefresh 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.

CONCLUSION

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 water quality for their cows. In 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.

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 Argentina, OH and NM.

Dairy	Cow Status	SID ^a	DCAD ^a	TICAD ^a
Location		(mEq/L)	(mEq/100g DMI)	(mEq/100g DMI)
Argentina	Lactating	26.0	32.8	47.6
Ohio	Lactating	-44.9	30.8	15.0
New Mexico	Lactating	-78.5	29.9	-12.4

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

REFERENCES

- Apper-Bossard, E., J.L. Peyraud, P. Faverdin and F. Meschy. 2006. Changing dietary cation-anion difference for dairy cows fed with two contrasting levels of concentrate in diets. J. Dairy Sci. 89:749.
- Castillo, A.R., N. St-Pierre, N. Silva-del-Río, and W.P. Weiss. 2013. Mineral concentrations in diets, water, and milk and their value in estimating on-farm excretion of manure minerals in lactating dairy cows. J. of Dairy Sci. 96(5):3388-3398.
- Challis, D.J., J.S. Zeinstra and M.J. Anderson. 1987. Some effects of water quality on the performance of high yielding cows in an arid climate. Vet. Rec. 120:12.
- Constable, P.D. 2003. Hyperchloremic acidosis: The classic example of strong ion acidosis. Anesth. Analg. 96:919.
- Digesti, R. D. and H. J. Weeth. 1976. A defensible maximum for inorganic sulfate in drinking water of cattle. J. Anim. Sci. 42:1498-1502
- Durand, M. and S. Komisarczuk. 1988. Influence of major minerals on rumen microbiota. J. Nutr., 118:249.
- Fleeger, G.M., 1999. The geology of Pennsylvania's groundwater (3rd ed.): Pennsylvania Geological Survey, 4th ser., Educational Series 3, 34 p.
- Goff, J.P. 2006. Mineral disorders of the transition period: origin and control. Proceedings of the World Buiatrics Congress. Nice, France.
- Ivancic, J. and W.P. Weiss. 2001. Effect of dietary sulfur and selenium concentrations on selenium balance of lactating Holstein cows. J. Dairy Sci. 84:225.
- Lock, A.L., T.R. Overton, K.J. Harvatine, J. Giesey, and D.E. Bauman. 2006. Milk fat depression: impact of dietary components and their interaction during rumen fermentation. Proceedings of the Cornell Nutrition Conference for Feed Manufacturers. Syracuse, NY.
- Miller, J.K., E. Brezezinska-Slebodzinska, and F.C. Madsen. 1993. Oxidative stress, antioxidants and animal function. J. Dairy Sci. 76:2812.

- National Research Council. 2001. Nutrient Requirements of Dairy Cattle. Natl. Acad. Sci., Washington, DC.
- National Research Council. 2005. Mineral Tolerance of Animals. 2nd rev. ed. Natl. Acad. Sci., Washington, DC.
- Parkhurst, D.L., and Appelo, C.A.J., 1999, User's guide to PHREEQC. U.S. Geological Survey Water- Resources Investigations Report 99-4259, 312 p.
- Roche, J.R., S. Petch and J.K. Kay. 2005. Manipulating the dietary cation-anion difference via drenching to early-lactation dairy cows grazing pasture. J. Dairy Sci. 88:264.
- Spears, J.W. 2003. Trace mineral bioavailability. J. Nutr. 133:1506S
- Stewart, P.A. 1983. How to understand acid-base: a quantitative acid-base primer for biology and medicine. Elsevier North Holland, Inc. New York, NY. 186 p.
- Stumm, W., and J.J. Morgan. 1996. Aquatic chemistry: chemical equilibria and rates in natural waters. 3rd ed. John Wiley & Sons, Inc. New York, NY. 1022 p.