59

2014 ASBC Meeting

Manganese in Beer & Brewing

Jason R. Porter & Charles W. Bamforth

75th ASBC Annual Meeting
June 4–6, 2014
Palmer House, a Hilton Hotel
Chicago, IL

Abstract:

Manganese has been shown to impact the flavor stability of beer by promoting the formation of oxygen radicals, similar to copper and iron, and therefore beer staling. Manganese can be present in beer at higher concentrations than many other heavy metals and has a higher reactivity. These concentrations can be in excess of the levels shown to cause noticeable beer staling. There has been research on its role in flavor stability and yeast nutrition, but not how it enters the system and how process variables may influence the manganese concentration. An overall mass balance of manganese is reported as well as the effects of dry-hopping on manganese concentration.

Grain products used in brewing are lower than hops in their concentration of manganese. However, since their usage quantity is much higher, they influence the final manganese concentration more than do the hops. The amount of manganese and other metals in the dry hopped beer does not seem to be influenced by hop alpha acid content, temperature, or type of hop product. Manganese concentration increases rapidly over the first 3 days of dry hopping. Iron is present at 300-450 ppm in hops, but the dry hopped beer does not display significant amounts. Manganese and zinc are present at 25-50 ppm in hops and release 0.2-0.45mg/L to the beer. While a high dry hopping ratio was used (0.5 oz hops to 1 L beer), a significant number of beers on the market are 0.05-0.25 mg/L.

Objectives:

~ Confirm that manganese promotes staling in beer

~Observe manganese concentrations in common grains, hops, & beers on the market.

~ Create a mass balance of manganese on a 1.5 barrel brewery.

~ Determine if and how much manganese leeches from hops during dry hopping and how it compares to copper, iron, and zinc.

Materials & Methods:

The malt used was from Great Western Malting (Vancouver, WA, USA) or purchased from MoreBeer (Concord, CA, USA). Hop products were from John I Haas (Washington DC, USA) or also from MoreBeer. The sampled beers were purchased from a local market. All samples were collected in 50mL polypropylene centrifuge tubes. All liquid samples were filtered using 0.45µm filters. The samples were then frozen and stored at -20ºC. Analysis was completed at the University of California Agriculture and Natural Resources Analytical Laboratory, Davis, CA. Solid samples were analyzed by a nitric acid/hydrogen peroxide microwave digestion and the determination by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES). Liquid samples were analyzed for soluble and total concentrations. Soluble concentrations were determined by ICP-AES. Total concentration in a liquid was determined by a nitric acid/hydrogen peroxide microwave digestion and then atomic absorption spectrometry (AAS). Reproducibility by the lab is within 8%.

Staling: Two sets of samples of an American Light Lager were spiked with food grade $MnCl_2•4H_2O$ at 0, 0.2, 0.4, 0.6, 0.8, and 1 mg/L. A 0.1M $MnCl_2•4H_2O$ solution and deionized water were used to add 100µL to an opened bottle. The bottle was fobbed and re-crowned. One set of samples went into -2ºC storage for 30 days. The other set was held at 60ºC for 1 day, then -2ºC for 29 days. Samples were ranked on staleness by 8 beer consumers.

Brews: The mass balances were created using the 1.5 barrel University of California, Davis Pilot Brewery. Water treatment salts were from Crosby and Baker (Westport MA, USA). American Ale Yeast 1056 was from Wyeast (Odell, OR, USA). The targets for Brew 1 were 10º Plato Wort, 15 IBUs, and 1.3 Barrel (40 gallons) using American 2-Row malt and Magnum pellets. The targets for Brew 2 were 15º Plato Wort, 40 IBU, and 1.3 Barrels using Am. 2-Row malt, Crystal 60º malt, Columbus pellets, and Citra pellets. Samples were collected and analyzed as stated above.

Dry Hopping: Three hops, Tettnang, Cascade, and Mosaic, were used. For each hop, the following trials were completed: 0.5oz pellets in 1L of degassed American Light Lager @ -2ºC, 0.5oz whole cones in 1L of degassed American Light Lager @ -2ºC, 0.5oz pellets in 1L of degassed American Light Lager @ 20ºC, 0.5oz pellets in 1L of deionized water @ -2ºC. One trial of Isomerized Kettle Extract and Hop Oils, used to direction, was completed in 1L of degassed American Light Lager @ -2ºC. A 50 mL sample was taken from each of the 13 trials after 1, 2, 3, 7, and 14 days.

Acknowledgements:

Thanks to Scott Garden and John I Haas, Inc for providing the hops and hop products for this project. Special thanks to Candace Wallin for her help through the entirety of the project.

Staling & Sample Results:

Figure 1 - Staling Rankings (Least to Greatest)

Ranking	Mn ppm	Trial	Average Rank	Std. Dev.
1	1.0	Cold	2.38	1.87
2	0.0	Cold	3.13	1.83
3	0.4	Cold	3.75	1.56
4	0.6	Cold	4.25	1.39
5	0.2	Cold	5.13	2.09
6	0.8	Cold	5.38	3.43
7	0.0	Hot	7.50	2.60
8	0.4	Hot	8.38	2.39
9	0.2	Hot	8.88	1.76
10	1.0	Hot	9.38	2.69
11	0.6	Hot	9.63	1.80
12	0.8	Hot	10.25	1.79

Figure 2 – Manganese in Select Grains

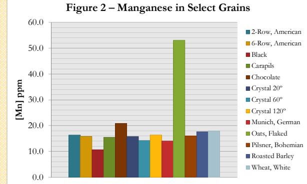


Figure 3 – Manganese in Select Hops

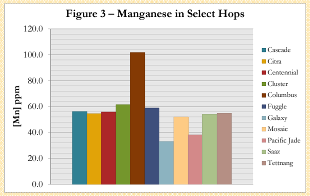
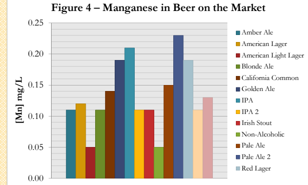


Figure 4 – Manganese in Beer on the Market



~ The staling rankings in Figure 1 show that manganese has an effect on the staling of beer. The beers held at 60ºC for 24 hours were ranked as being significantly staler. For the samples kept at -2ºC, one would expect them to show little signs of staling. This is shown by the random order of manganese concentration and the low range of ranking.

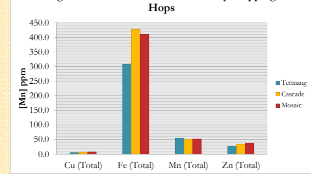
~The hot sample with no manganese added was ranked lowest of all the heated ones, showing that while it showed some staling, it wasn't as stale as the samples with manganese.

~ The 0.2 mg/L heated sample was ranked closely with those with higher concentrations of Mn, showing that even that amount was significant in respect of staling. Looking at the beers in Figure 4, one can see how many of these beers might have sufficient manganese to promote staling.

~Figures 2 & 3 show that hops are much richer in manganese than is grain, but due to the usage weight difference, grain has the most influence. The only grain to stand out is flaked oats.

Dry Hopping Results:

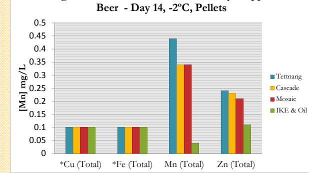
Figure 5 - Metal Concentration in Dry-Hopping Hops



*Minimum values for detection are 0.1 mg/L for Cu, Fe, & Zn. Mn minimum detection is 0.02 mg/L. In all dry hopping samples, Cu & Fe were below detection levels.

Figure 5 shows that there are high amounts of Fe in hops while Figure 6 shows that negligible amounts leech into the beer. They also show that while the Mn concentration is low compared to Fe, a significant amount is leeched into the beer.

Figure 6 - Metal Concentration in Dry Hopped Beer - Day 14, -2ºC, Pellets



Figures 7, 8, & 9 show that temperature and alpha acid content do not affect manganese leeching. Alcohol may affect leeching rates as the Mn from dry hopping of water control remained significantly lower. It can also be seen that leeching slows drastically after the first 3 days.

Figure 7 - Manganese from Tettnang (4.7%AA) Dry Hopping

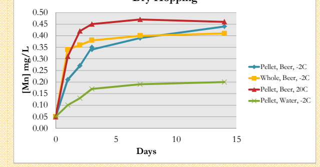
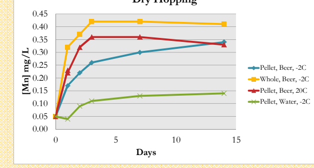
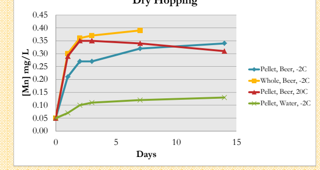


Figure 8 - Manganese from Cascade (6.7%AA) Dry Hopping



This experiment was performed with a high dry hopping rate of 0.5 oz/L. In comparison to the beers' [Mn] in Figure 4, this shows that significant amounts of manganese can be delivered through dry hopping.

Figure 9 - Manganese from Mosaic (12.8%AA) Dry Hopping



Mass Balance Results:

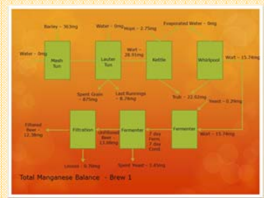


Figure 10 – Mass Balance of Brew 1

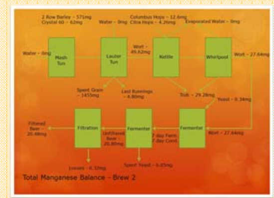


Figure 11 – Mass Balance of Brew 2

~Figures 10 & 11 show that manganese in the final beer is influenced by the amount of malt. While the hops are higher in manganese than the grain, much less total manganese is added to the system.

~ A majority of the manganese and other metals leave with the spent grain. The spent grains consistently measured higher in all metal concentrations. It is unclear why.

~The concentrations of manganese in the final product were 0.11mg/L for brew 1 and 0.16mg/L for brew 2. These fall within the range of concentrations found in the beers on the market (Figure 4).

Conclusions:

~ There is not a correlation between hop alpha acid content and the concentration of manganese within the hop materials. The range of manganese in hops is 30-100ppm and is likely influenced by the soils that they are grown in.

~ Grain products used in brewing are lower in manganese, but due to their much higher usage, they influence the final manganese concentration more than the hops.

~ During dry hopping, temperature and alpha acid content do not seem to affect the leeching of manganese or other metals into the beer. Whole cones and pellets leech at similar concentrations. There may be an effect of alcohol on the leeching.

~ While iron is present at 300-450 ppm in hops, the dry hopped beer does not have significant amounts (<0.10 mg/L) of iron. Manganese and zinc are present in much smaller amounts in the hops, but leech significant amounts of 0.2-0.45mg/L to the beer as beers on the market are 0.05-0.25 mg/L.

~ Manganese content rapidly increases throughout the first 3 days of dry hopping then plateaus.

Dept. of Food Science and Technology, University of California, Davis
jrport@ucdavis.edu & cwbamforth@ucdavis.edu