Title

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NOTE

Manganese in brewing raw materials, disposition during the brewing process and impact on the flavor instability of beer[1]

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Running heads

Porter, J.R., and Bamforth, C.W. Manganese and flavor instability of beer

ABSTRACT

Like iron and copper, manganese promotes the staling of beer, by converting ground state oxygen to reactive oxygen species. Manganese was detected in beers at levels that are likely to impact the aging of beer. Manganese originates in the grist materials but is present at even higher levels in hops. Although there is substantially more iron in those hops than manganese, the delivery into beer of these ions is much greater for manganese. Leaching of manganese into beer is much higher than in the equivalent quantity of deionized water. This study suggests that further study is warranted into the adverse impact of dry hopping on the flavor stability of beers.

Keywords: Beer, hops, manganese, staling

Minimizing the deterioration in flavor once beer has been packaged and is in the marketplace remains one of the major technological challenges facing brewers (2). The issue is immensely complex and involves a wide range of chemical changes that can occur in the finished beer and also during brewing (11).

One fundamental aspect of many of the relevant chemical reactions is oxidation and it has long been recognized that it is essential to package beer with the lowest possible oxygen content. However it is also acknowledged that the oxygen molecule *per se* is not especially reactive, and it is necessary to convert ground state oxygen into so-called “reactive oxygen species” (ROS), which are much more damaging. The contribution that ROS makes to de-stabilizing beer flavor was first reported by Bamforth and Parsons (3) and has been extensively explored since (1). ROS are generated in a series of reactions involving transition metal ions (5) and the deleterious impact on beer of notably iron and copper has been amply documented (3, 6, 11, 12).

Zufall (12) drew attention to the possible role that manganese may have in the context of oxidation. The role of manganese in promoting the production of reactive oxygen species has been reported (4,7)

In this paper we confirm that manganese elevates staling in beer, we have compared manganese levels in a range of beers and we have identified the contribution of different raw materials and processes to the level of manganese surviving into beer.

EXPERIMENTAL

Evaluation of staling

Bottles of a commercial light beer were spiked with food grade manganese chloride to final concentrations in the beer of 0, 0.2, 0.4, 0.6, 0.8, and 1 mg/L. Bottles were fobbed and re-crowned. One set of samples was placed into storage at -2°C for 35 days. The other set was held at 60°C for 1 day, then at -2°C for 34 days. Eight tasters were asked to sort the 12 beers in order from least stale (ranked as 'one') to most stale (ranked 'twelve').

Materials

The 2 row malt used for brewing was from Great Western Malting (Vancouver, WA, USA). The malt samples analyzed for manganese and Crystal 60° for Brew 2 were purchased from MoreBeer (Concord, CA, USA). The hop samples analyzed were purchased from Williams Brewing (San Leandro, CA, USA). Magnum, Columbus and Citra hop pellets for brewing were from MoreBeer. Tettnang, Cascade, Mosaic, and other hop products for the Dry Hopping trials were from John I Haas (Yakima, WA, USA). Water Treatment Salts (15% Calcium) were from Crosby and Baker (Westport MA, USA). American Ale 1056 yeast was from Wyeast Labs (Odell, OR, USA). Filter pads (Cellupore grade 19455D) were from Gusmer Enterprises (Fresno, CA, USA). Commercial beers were purchased from a local market.

Analysis of manganese

All liquid samples (50 mL) were collected in polypropylene conical centrifuge tubes (Corning Life Sciences DL No. 352070). All liquid samples were filtered using 0.45µm Nitrocellulose filters (Millipore HAWP4700) and 25mL polypropylene disposable syringes. The samples were stored frozen at -20°C. Analysis was completed at the University of California Agriculture and Natural Resources Analytical Laboratory, Davis, CA (http://anlab.ucdavis.edu). Solid samples were dried so that analysis was done on 100% dry basis. They were then analyzed by a nitric acid/hydrogen peroxide microwave digestion (9) followed by Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES; 8) . The minimum detectable limit for iron, manganese and zinc was 1.0 ppm and was 0.5ppm for copper. Liquid samples were analyzed for soluble and total concentrations of the metal ions. Soluble concentrations were determined by ICP-AES according to U.S. EPA Method 200.7 (10). Total concentration in a liquid was determined by a nitric acid/hydrogen peroxide microwave digestion and then by atomic absorption spectrometry (AAS) (8). For liquid determinations, the minimum detectable concentrations were 0.1 mg/L copper, iron and zinc and 0.02 mg/L for manganese. Reproducibility by the lab for all 3 determination procedures was within 8%.

Mass Balance Brews

Brew 1. The first brew was a pale ale with a target of 10° Plato, 15 IBU and a brew length of 151 L. The ingredients used were: 22.7kg malt, 36.8g Magnum Pellets (12.3% alpha) plus 31.2g Magnum Pellets (13.8% alpha), 90.9L Deionized water, 121.2 g of Water Treatment Salts and Wyeast 1056 American Ale yeast. The malted barley was milled in a 2-roll mill directly prior to mashing in at 44°C for 5 minutes. The temperature of the mash was raised at 2°C per minute until the mash was at 68°C, where it was held for 45 minutes. The temperature of the mash was again raised at 2°C per minute up to 80°C and held for 10 minutes. During the entire mashing procedure, the tun was agitated at 70RPM. The mash was transferred to the lauter tun and vorlaufed for 10 minutes before transferring to the brew kettle at 4L/min. Sparge water was at 76°C. The rakes were not employed. Once 151L had been collected, lautering was terminated and the kettle was brought to a boil. The Magnum pellets were added to the kettle at the start of a 45 minute boil. The wort was transferred to the whirlpool for a 10 minute stand. Afterwards, the wort was cooled to 18°C via a water chilled counter-flow plate heat exchanger (PHE) and glycol chilled PHE in series. Medical grade compressed air was introduced to the wort after the glycol PHE as wort headed to the fermenter. Yeast was pitched at $1x10^6$ cells/mL per °P and fermentation was at 20°C. The total residence time for fermentation and warm maturation was 14 days before applying chilling to -2°C and removal of yeast from the cone. After 48h the beer was filtered using filter pads.

Brew 2. The second brew was identical to the first brew except the beer was a pale ale with a target of 15° Plato, 45 IBU. The ingredients used were: 35.5kg malt, 4.5kg Crystal 60° Malt, 134.4g Columbus Pellets (15.0% alpha), 85g Citra Pellets (13.9% alpha). The Citra pellets were added during a 15min whirlpool stand.

Dry Hopping Trials

Three hops, Tettnang (4.7% alpha), Cascade (6.7% alpha) and Mosaic (12.8% alpha), were used for the dry hopping trials. For each hop, several incubations were completed: (a) 14.2g pellets in 1L of de-gassed American Light Lager held at -2°C; (b) 14.2g cones in 1L of degassed American Light Lager held at -2°C; (c) 14.2g pellets in 1L of degassed American Light Lager held at 20°C; (d) 14.2g pellets in 1L of deionized water held at -2°C. The samples were prepared by adding 1L of light lager and the hop product to a 6L Erlenmeyer flask. The hop addition caused rapid decarbonation which was aided by shaking the flask. Care was taken to make sure there were no losses due to overflow. The samples were then transferred to 1L Erlenmeyer flasks, stoppered and stored. Sampling was after 1, 2, 3, 7, and 14 days.

RESULTS AND DISCUSSION

The impact of manganese on aged character in beer

The panel of tasters was not specifically trained as part of this study to detect aged character however they were experienced tasters familiar with the characteristics of oxidized products. As Figure 1 shows, there was considerable variance in the rankings that emerged, however clearly the beers that had not been force aged were distinguished from those that had been heated. This was the case irrespective of whether manganese had been added. However the mean rating for the beer devoid of added manganese indicated less perceived aged character compared to those to which manganese had been added. There is an indication that the degree of staling is generally increased as the manganese level is raised, especially at the elevated storage temperature.

Levels of manganese in commercial beers

The level of manganese present in fifteen commercial beers ranged from 0.05 to 0.23ppm (Table 1). This is at the lower end of the range of manganese levels tested above, but may be sufficient in some of the beers to be of concern as a causative agent in staling.

Levels of manganese in grist materials

The thirteen grist materials surveyed do not vary tremendously in their levels of manganese, with the exception of flaked oats, which display a substantially higher content of manganese (Table 2).

Levels of manganese in hops

By contrast with most of the grist materials, hops contain relatively substantial levels of manganese (Table 3). Whilst the quantities of hops employed for bittering purposes even in the highest IBU beers is substantially less than the amount of malts and adjuncts used, the question is begged about the impact of dry hopping on the delivery of manganese into beer (see later). We are unable on the basis of this study to identify the reason for the high Mn levels in hops and whether it is a possible function of fungicides applied to the hops.

Mass balance of manganese through brewing and fermentation

The majority of the manganese introduced from the grist and the kettle hops is lost with spent grains, trub and yeast (Figs 2 and 3). The higher manganese levels introduced in the second brew are reflected in higher manganese in the final beer.

The impact of dry hopping on manganese levels in beer

There is vastly more iron in pelleted hops than manganese, zinc and copper (Fig 4). However analysis of beers dry hopped with these hops (as pellets) reveals that there is proportionately more leaching of manganese (and to a lesser extent zinc and copper) than iron into beers (Fig 5). Levels of manganese, copper and iron are at levels shown in this paper for manganese and elsewhere (3) for iron and copper to be of the order of magnitude that can cause staling via ROS formation.

More manganese is leached from hops into beer than into water (Figs 6a, b). Whether the hops are in the form of whole cones or pellets does not seem to have a major impact and neither does the temperature at which the beer is held. The levels of manganese extracted in this experiment are substantially in excess of those registered in the commercial beers tested.

In conclusion, the data in this Note suggest that more attention should be paid to manganese as a possible promoter of stale character in beer and to the flavor deterioration of products, especially those that are dry hopped.

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Table 1 – Manganese in Commercial Beers

Beer	ABV%	Mn Total (mg/L)
American Light Lager	4.2	0.05
Non-Alcoholic	0.5	0.05
Sorghum Ale	4.0	0.11
California Common	4.9	0.14
Wheat Ale	4.6	0.13
Pale Ale*	5.0	0.15

Blonde Ale	4.0	0.11
Pale Ale 2*	4.8	0.23
Irish Stout	4.2	0.16
Red Lager	4.9	0.19
Amber Ale	5.2	0.11
Imperial IPA*	8.5	0.21
Golden Ale	5.5	0.19
Pilsner	5.0	0.12
IPA*	7.2	0.11
*** - Dry Hopped Beer**		

Beers were purchased at a local supermarket in October 2013

Table 2 – Manganese in 2013 Crop Year Grain Samples (100% Dry Basis)

Malts	Mn (ppm)
2-Row, American	15.2,15.8
6-Row, American	15.9
Black	10.7
Carapils	15.5
Chocolate	20.9
Crystal 20°	15.8
Crystal 60°	14.3
Crystal 120°	16.4
Munich, German	14.1
Oats, Flaked	53.1
Pilsner, Bohemian	16.1,16.2
Roasted Barley	17.7
Wheat, White	18.0

Table 3 – Manganese in 2013 Crop YearHop Samples (100% Dry Basis)

Hops	% Alpha Acid	Mn (ppm)
Cascade	6.7	56.3
Citra	13.9	54.5
Centennial	9	55.9
Cluster	6.5	61.6
Columbus	15	101.9
Fuggle	4.98	59.0
Galaxy	14.3	33.1
Mosaic	12.8	52.0
Pacific Jade	15	38.2
Saaz	2.9	54.2, 54.2
Tettnang	4.7	54.9

Fig 1 The impact of manganese on stale character in beer. Beers dosed with different levels of manganese were aged at either -2ºC or 60ºC for 1 day (prior to holding at -2ºC) and then the 12 samples were ranked in order of displayed aged character (1= least stale and 12= most stale)

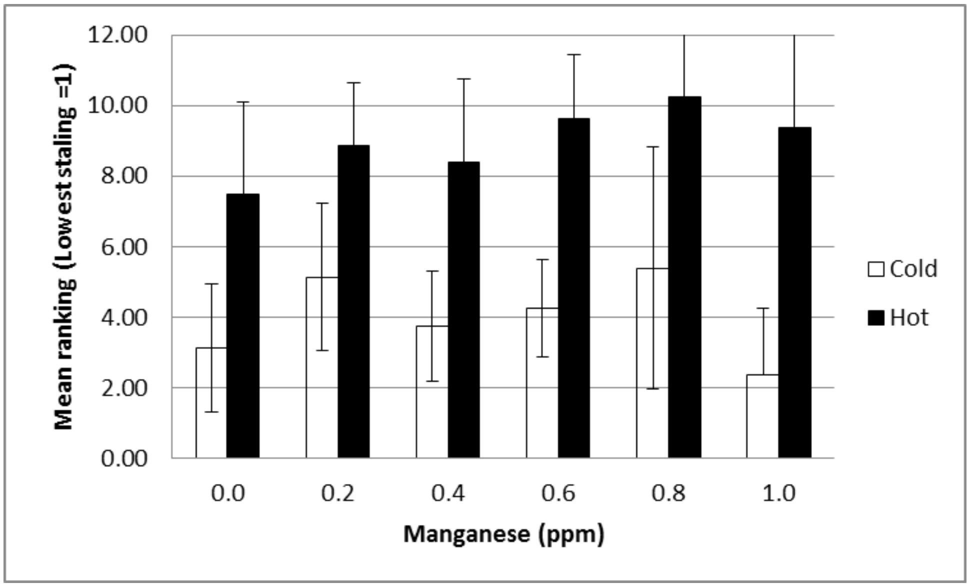


Fig 2. Mass balance for manganese, Brew 1.

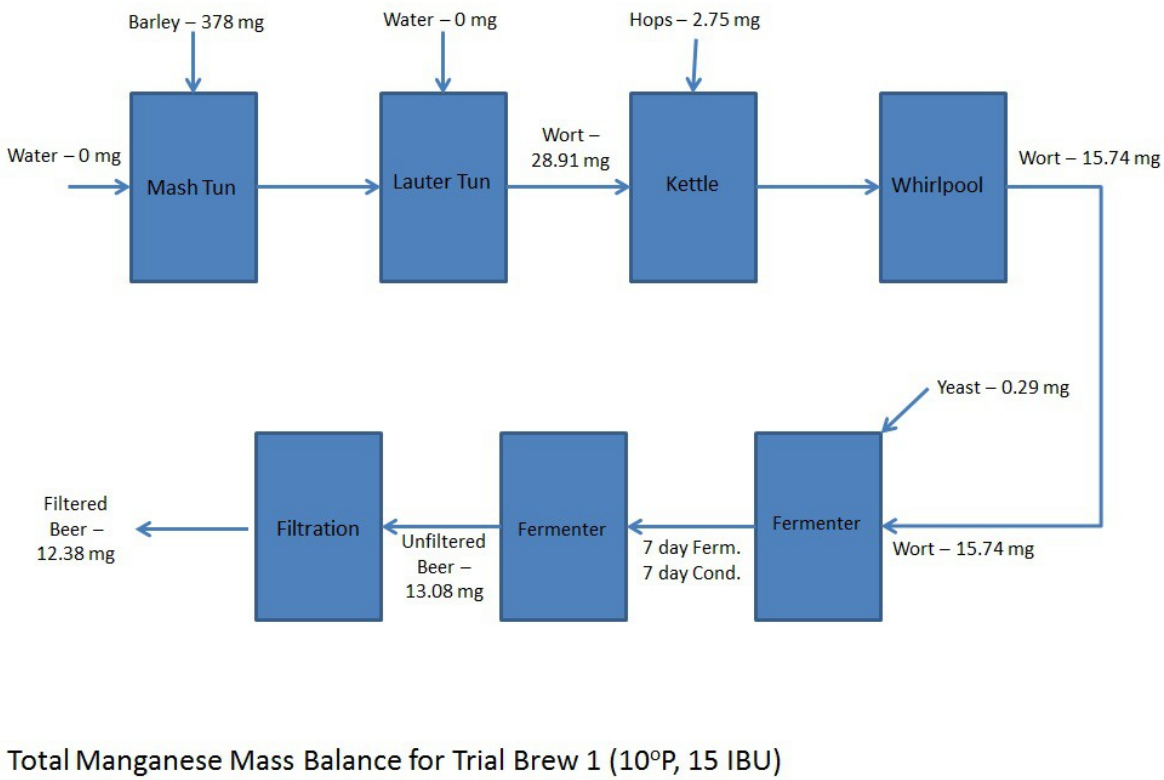
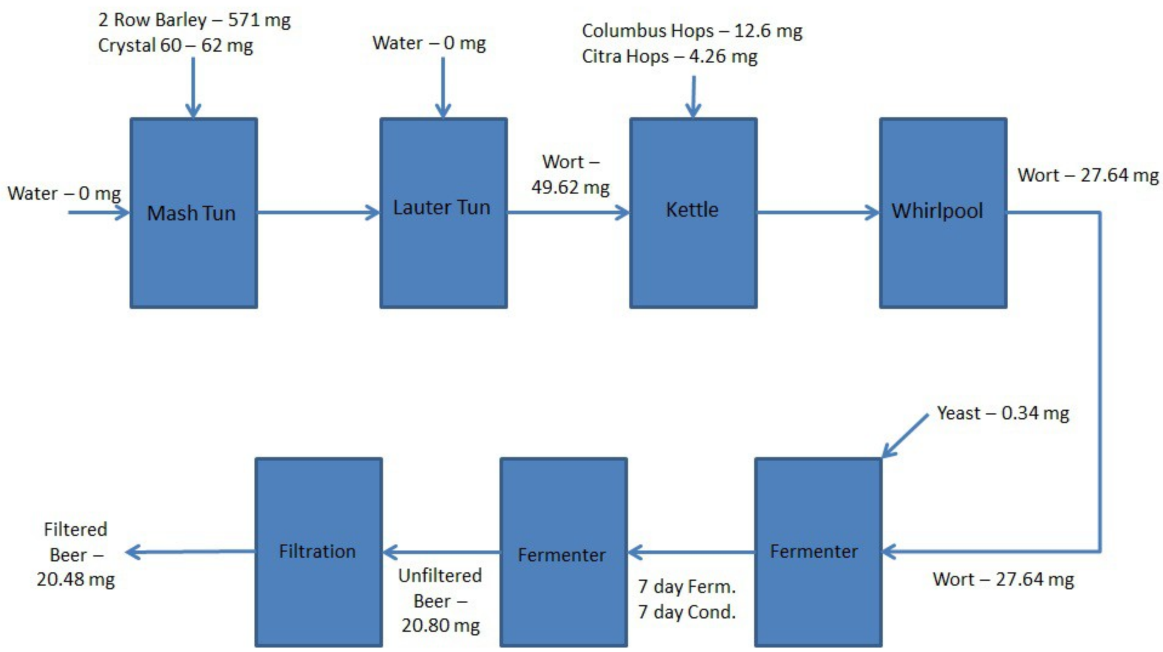


Fig 3. Mass balance for manganese, Brew 2.



Total Manganese Mass Balance for Trial Brew #2 (15^{o}P, 45 IBU)

Fig 4. Levels of ions in three hop varieties

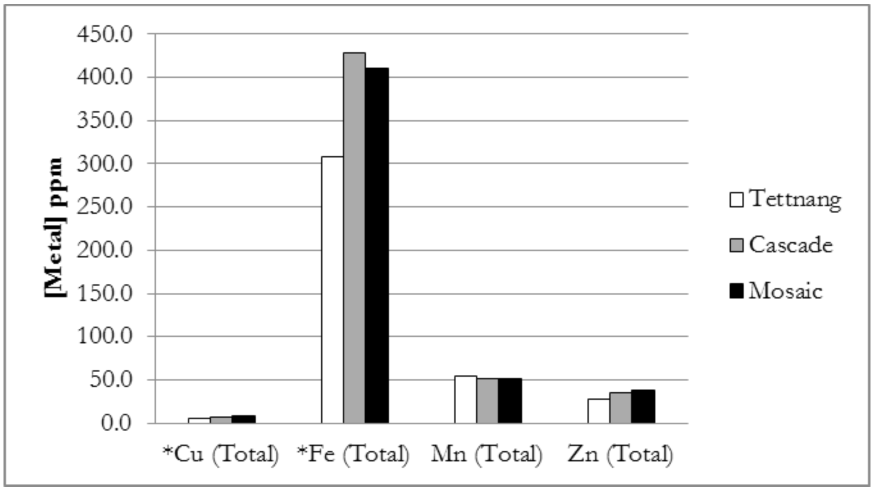


Fig 5. Levels of ions extracted into beer from hops

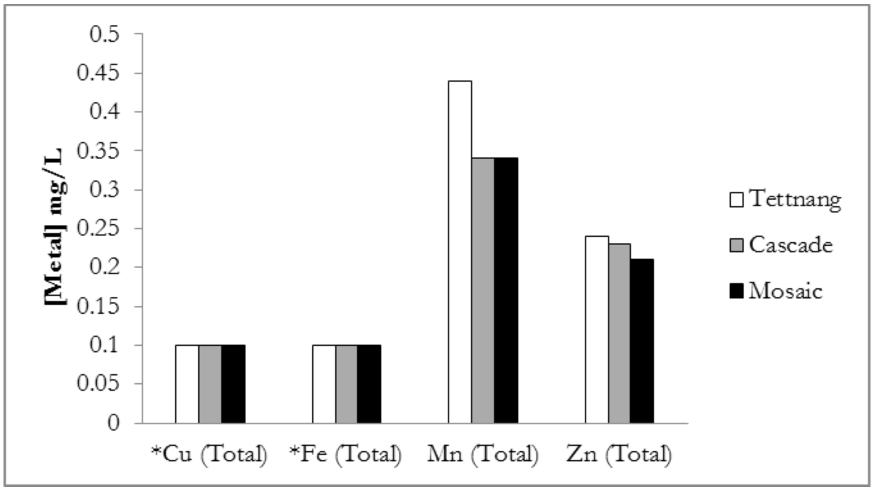


Fig 6a. Extraction of manganese from Mosaic (12.8% alpha) during dry hopping

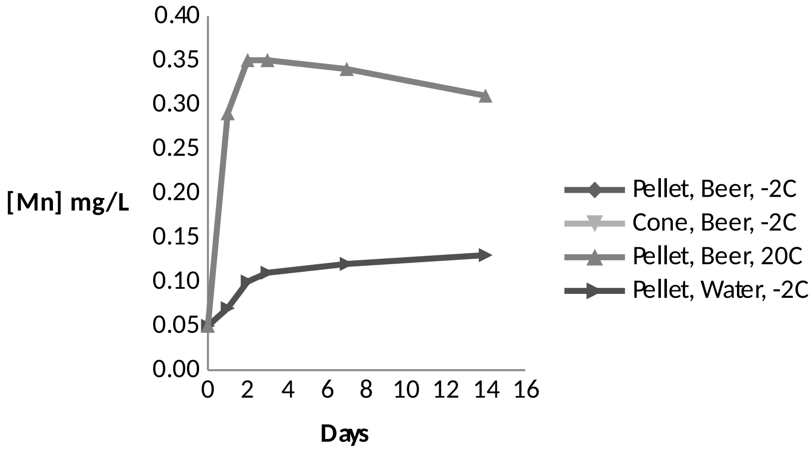
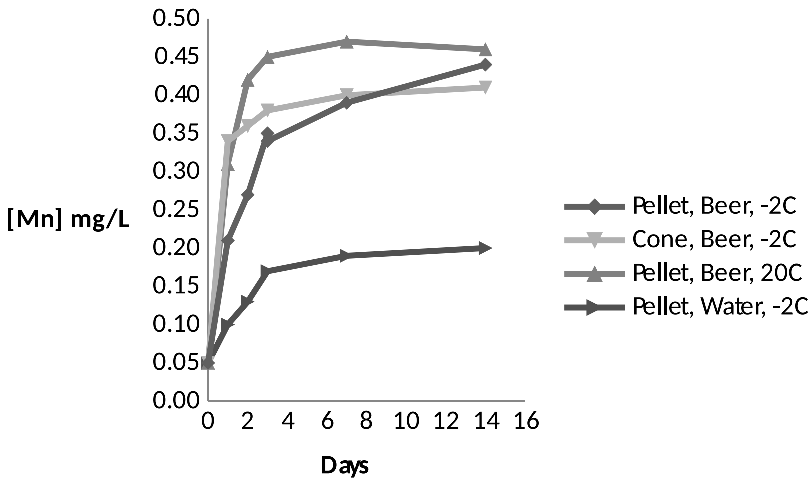


Fig 6b. Extraction of manganese from Tettnang (4.7% alpha) during dry hopping



[Mn] mg/L
0.50
0.45
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
2
4
6
8
10
12
14
16
Days
Pellet, Beer, -2C
Cone, Beer, -2C
Pellet, Beer, 20C
Pellet, Water, -2C