Discussion of *Filtration and manganese removal* by Geoff Hamilton, Barry Chiswell, John Terry, David Dixon and Lindsay Sly, 2013 *Journal of Water Supply: Research and Technology—AQUA* 62 (7), 417–425, doi:10.2166/aqua.2013.093

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We wish at the outset to acknowledge the efforts of Hamilton *et al.* (2013) in publishing their research findings related to soluble manganese (Mn) removal during filtration processes. We believe that soluble Mn removal via $MnO_x(s)$-coated filter media is a key component of successful Mn control in many water treatment facilities, and that too little research work has been published on the subject to date. However, after careful review of the publication by Hamilton *et al.*, we feel the need to bring forward this discussion to highlight several concerns about the research work that was reported by the authors.

First, we wish to correct a few misconceptions presented in the paper regarding our own work. In the Introduction section the authors claim that 'most of Knocke *et al.*'s work was carried out with lower pH water (typically in the range 5–6.5) …' and later, 'We (Hamilton *et al.*) have also used treated waters with pH values in the range of 6.8–7.4 … values somewhat higher than those present in Knocke's work.' In fact, the pH range associated with most of our work (including three publications specifically cited by the authors) cover a wide range of solution pH conditions, and with no specific focus on lower pH waters (relevant information is found in Table 1). In reality we

have substantial research experience in the specific pH range of interest in the Hamilton *et al.* (2013) study; further, we believe we have a very solid understanding of the means by which soluble Mn removal is accomplished in filtration systems wherein $MnO_x(s)$ surfaces are present on the filter media.

Hamilton *et al.* (2013) reach the following key conclusions as a result of their literature review and experimental studies:

(1) The role of chlorine in the pH range of study (6.8–7.4) is to promote extremely rapid oxidation of soluble Mn in the feedwater prior to its contact with the filter media. This conclusion was based partially on the observation that Mn removal was essentially unchanged whether 2 or 39 minutes of contact was provided between the chlorine and soluble Mn prior to filtration.

(2) Such rapid oxidation is the result of high pH micro-environments that occur specifically when sodium hypochlorite is added to the water being treated.

(3) The role of the filter media in Mn removal is in facilitating the capture of particulate and/or colloidal $MnO_x(s)$ solids formed by this rapid oxidation of soluble Mn by

Table 1 | Range of pH conditions evaluated by Knocke and co-workers regarding Mn removal on $MnO_x(s)$-coated filter media

Publication citation	Reported pH range of study
Knocke et al. (1988)	pH 6.0–9.0
Knocke et al. (1991)	pH 5.5–8.5
Coffey & Knocke (1990)	pH 6.0–7.5
Hargette & Knocke (2001)	pH 6.0–7.3
Islam et al. (2010)	pH 6.3–7.8
Knocke et al. (2010)	pH 6.2–7.9

the chlorine. This specific conclusion appears to be heavily based upon two observations:

(a) The presence of an accumulated dark layer in the very top of the filter media over time.

(b) The accumulation of significant amounts of head loss across the pilot filter media, observed to be in proportion to the observed Mn removal.

We question the conclusion reached by the authors that Mn removal in these filtration systems is due primarily to pre-filter oxidation of the Mn and subsequent capture of the particulate or colloidal $MnO_x(s)$ solids. First, the literature contains multiple references (Knocke et al. 1990; Hao et al. 1991; Allard et al. 2013) which report that the oxidation of soluble Mn by free chlorine is very slow even at pH 8.0, let alone at the pH conditions employed by the authors in this study (pH 6.8–7.4). These literature sources reported contact times of multiple hours being necessary to initiate significant Mn oxidation even at pH 8; as such, it is questionable that substantial Mn oxidation would occur via chlorine addition in the time periods (2 or 39 minutes) available in the author's studies. Hamilton et al. (2013) do not present any results for measurements of the forms of Mn present after chlorine addition; such measurements are needed to document the extent of conversion of soluble Mn to particulate or colloidal $MnO_x(s)$ solids. Furthermore, the authors suggest that sodium hypochlorite dosing produces specific microenvironment conditions of elevated pH to promote the hypothesized rapid Mn oxidation. However, the vast majority of the literature studies cited in Table 1 of this discussion also employed sodium hypochlorite dosing as the source of free chlorine for pre-filter application. Evidence of significant direct solution oxidation of soluble Mn prior to the filter was not observed in any of the cited studies.

The authors noted a darkening of the upper layers of the filter media over time which is an expected outcome resulting from uptake of soluble Mn(II) and subsequent oxidation at the media surface. Essentially all of the studies cited in Table 1 of this discussion have reported on such a phenomenon occurring, and most have in fact quantified the presence of the $MnO_x(s)$ coating on the filter media under different Mn loading, chlorine level, and applied water pH conditions. Hargette & Knocke (2001) studied the accumulation of $MnO_x(s)$ coatings on filter media over a 9-month loading period, demonstrating how such coatings build over time and are partially dislodged during backwash. In the Hargette and Knocke study the pilot-scale columns were loaded with 0.3 mg/L soluble Mn on a continuous basis over the 9-month period. The authors reported no evidence of particulate or colloidal $MnO_x(s)$ formation in the filter-applied water for studies conducted at pH 6.0 and pH 7.3. Hamilton et al. (2013) could have readily tested their hypothesis by exposing waters containing soluble Mn to sodium hypochlorite and then passing those treated solutions through standard 0.45 μm filters or perhaps an ultrafilter to ascertain the formation of $MnO_x(s)$, but no such tests were reported. We believe their hypothesis of significant $MnO_x(s)$ formation in the pre-filter water to be unsubstantiated by the experimental resulted they have reported.

The authors noted the development of head loss across their filters during the study and attributed this to the formation of $MnO_x(s)$ and its subsequent capture in the filters. However, we question this interpretation of the experimental results. The authors report that the source of water to their experimental studies was effluent from the full-scale clarifier, which would obviously contain suspended matter (the authors report the turbidity of this filter-applied water to be between 0.4 and 2 NTU). Further, in evaluating Figure 1 from their paper (detailing the pilot plant setup) and the associated text it is unclear if the authors had a suitable control experiment in place to clearly differentiate head loss in their pilot columns due to $MnO_x(s)$ formation and accumulation versus head loss due to the suspended matter in the clarifier effluent water used in their studies. In comparison, Hargette & Knocke (2001) did not observe significant head loss accumulation across their pilot-scale columns receiving 0.3 mg/L soluble Mn and filter-applied sodium hypochlorite even when operated for

several days (typically 4-day cycles). Their filters were back-washed to study the release of particulate $MnO_x(s)$ from the filter media and not based upon any evidence of head loss accumulation.

In conclusion, we the discussers do not believe the conclusions reached by Hamilton *et al.* in this paper can be justified based upon the data presented. We believe the bulk of the published literature supports the concept that soluble Mn removal in these filtration systems (with free chlorine applied to the filter media) is predominantly by sorptive uptake of the Mn onto the $MnO_x(s)$ coatings on the media surface, with subsequent surface catalyzed oxidation of that sorbed Mn on the $MnO_x(s)$ surface. We believe that the possibilities of a small amount of Mn oxidation occurring within microenvironments of extremely elevated pH (as proposed by the authors to result from sodium hypochlorite addition) is plausible. However, our experience over many years of working with full-scale water utilities is that colloidal $MnO_x(s)$ that is formed just prior to filtration (e.g. within an ozonation step) is often not effectively captured on filter media, most likely due to the extremely negative surface charge associated with $MnO_x(s)$ in the pH range normally used in water treatment practice; the particulate $MnO_x(s)$ will not be destabilized and effectively deposited unless additional coagulant is added subsequent to formation but prior to the media filtration. We believe that any pre-filter $MnO_x(s)$ formation that may occur is a very minor contributor to the overall soluble Mn removal which is observed in media filtration systems; rather, sorptive uptake of Mn and subsequent catalytic oxidation on the $MnO_x(s)$ surface in the presence of free chlorine is the primary removal mechanism.

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