Author reply to Discussion by W. R. Knocke and J. E. Tobiason, 2014, 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

Barry Chiswell, Geoff Hamilton, John Terry, David Dixon and Lindsay Sly

Barry Chiswell (corresponding author)
Entox (The National Research Centre for Environmental Toxicology),
University of Queensland,
39 Kessels Road, Coopers Plains, Qld, 4108,
Australia
E-mail: *chiswell1936@gmail.com*

Geoff Hamilton
GHCE Consultant Engineers,
PO Box 810, Mudgeeraba, Qld, 4213,
Australia

John Terry
Consultant,
Pine Ridge Road, Coombabah, Qld, 4216,
Australia

David Dixon
Department of Chemical and Biomolecular Engineering,
University of Melbourne, Vic, 3010,
Australia

Lindsay Sly
School of Chemistry and Molecular Biosciences,
University of Queensland, Qld, 4072,
Australia

We wish to thank Knocke & Tobiason (2014) for their interest in our paper (Hamilton *et al.* 2013) and their help in raising the profile of what we all believe is an important topic – the removal of manganese species from drinking water supplies. The complexity of the issue stems from the fact that manganese can exist in a variety of oxidation states and may be present in soluble, colloidal and particulate forms depending on both pH and Eh. The traditional methods of removal necessarily involve significant changes to both pH and Eh and therefore it is not surprising that there is healthy debate about the mechanism of removal.

To add to the difficult nature of the system, we contend that despite the progress made in analytical techniques there are still uncertainties in:

1. The way we try to fractionate manganese species before analysis using standard filters. Any colloidal manganese oxides will readily pass through these filters and are not accounted for in conventional assays.
2. The spectroscopic techniques we use to determine the nature of the species still fail to differentiate between the possible oxidation states, particularly Mn(III) species.

As a consequence, we believe it is unrealistic to suggest there is just one mechanism for removal across the range of conditions encountered in the real world of water treatment and it is our experience that reliance on the sole 'greensand' or autocatalysis theory has failed to provide the process parameters needed to design and operate all water treatment

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plants across a range of different and variable raw water supplies and operational protocols. This was the driving force for our pilot plant study which we designed to be as close as possible to the full scale treatment plant and on this scale we again found that the surface catalysis approach did not explain our results.

Under the range of conditions we employed to simulate what happened in the plant, we observed a dark deposit that collected on top of the filter bed that simply did not fit the current theory and suggested the existence of another means of removal – oxidation in the aqueous phase followed by physical entrapment on the filter. We suggest that manganese oxides are formed and do attach to the filter media but in association with the flocs and particulates already in existence ahead of the filter, not as a result of surface catalysis on the filter. In our view the accompanying headloss is a result of these flocs and particulates (in association with the Mn oxides) being entrapped on the top of the filter bed.

In conclusion, we believe that there are remaining deficiencies in the traditional analytical methods for manganese in all its forms which are compounded by the wide range of both pH and Eh conditions experienced during treatment with different oxidants and further complicated by the presence of other surfaces such as the flocs generated by adding coagulants. As a result, we suggest that there are several possible mechanisms involved at full scale plant level including the surface catalysis model that has been so extensively studied by Knocke *et al.* but also including a physical entrapment approach that better approximates what we have seen occur in both pilot and full scale plant operation. The relative importance of these mechanisms is undoubtedly a subject for continued discussion and debate, but we are confident that our observations and data are accurate.

REFERENCES

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