

DISCOVERING DIFFERENCES IN IRON AND MANGANESE BEHAVIOUR IN SERVICE RESERVOIRS

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Abstract

Service reservoirs (SRs) are crucial components in drinking water distribution systems (DWDSs). In the UK, regulatory monitoring is conducted infrequently at SR outlets and for disinfectant residual and bacteriological indicators only, providing limited information on SR performance and its effect on drinking water quality. In this research, long term monitoring at the inlet and outlet of multiple SRs across the UK for various water quality parameters, and analysis of accumulated material collected from SRs during maintenance activities, provided valuable information on iron and manganese behaviour in these assets. Results showed that a lower proportion of iron appears to be retained within SRs in comparison to manganese. These findings challenge the understanding of how water quality risks posed by iron and manganese (e.g., discolouration) manifest in SRs and this knowledge can be used to help inform a targeted approach specific to SRs for the proactive management of those risks.

Keywords

Service, Reservoirs, Distribution, Water, Quality, Iron, Manganese, Monitoring, Deposits, Discolouration.

1 INTRODUCTION

Service reservoirs (SRs) are treated water storage tanks, used to balance water supply and maintain diurnal demand in drinking water distribution systems (DWDSs), making them crucial and integral components of the system. Despite their importance, there is a limited understanding surrounding SR performance and its effect on drinking water quality, in comparison to other stages of the DWDS, such as water treatment works (WTW) and pipes [1]. A key reason for this gap is the current UK regulatory SR monitoring programme, which although considered good practice in comparison to other countries where there is no regulatory requirement for routine sampling at SRs at all, is fundamentally limited [2]. For instance, there is no regulatory requirement to monitor water quality at SR inlets, making it impossible to track water quality changes with travel through these assets, or to attribute any observed changes in water quality directly to the SR [2,3]. Additionally, disinfectant residual and bacteriological indicators are the only regulated parameters monitored at SR outlets, unlike other key indicator water quality parameters (e.g., metals, turbidity, pH, and conductivity), which are regulated at other stages of the DWDS [4]. The lack of inlet sampling and monitoring for a greater range of water quality parameters substantially limits the amount of information that could be obtained on SR performance and on water chemistry and microbiology within SRs, making it difficult to proactively manage these assets [2,5].

All inorganic compounds in the DWDS influence water quality but much of the research focus has been on regulated metals, primarily iron and manganese. Both metals are found in every DWDS, but concentrations vary based on source water type, the efficacy of treatment, and system materials [5]. Upon contact with oxygen or disinfectant, both metals may be oxidised to their soluble states, facilitating accumulation as particulate matter in the DWDS; both have been shown to be the most common metals found in DWDS accumulated material [6,7,8]. Material



accumulation occurs throughout DWDSs, especially in low flow zones like SRs where the low velocities in these assets allow material entering storage to settle on interior surfaces [5,9]. The remobilisation of iron and manganese containing material (triggered by changes to normal operating flow regimes) can cause discolouration events, which makes the water appear unattractive and can lead to customer complaints and penalties for water utilities [6,10]. Controlling the accumulation of material in DWDSs and mitigating discolouration is therefore important and water utilities take measures to remove network material through procedures like flushing pipes and cleaning SRs [5,11], typically as a reactive measure [10]. It is only from thorough understanding of entire system processes and mechanisms that lead to discolouration events that water utilities will be able to foresee such incidents and proactively reduce risks [10]. Such comprehensive understanding is not currently possible as, despite the risks associated with the presence of iron and manganese and the knowledge that material accumulation is a continuous process in SRs, metals are not monitored at this stage of the DWDS, nor is SR accumulated material collected and analysed for its inorganic constituents.

This paper reports results from an extensive water quality monitoring programme conducted at the inlet and outlet of multiple SRs from four UK water utilities, and analysis of accumulated material collected from SRs during maintenance activities, on the behaviour of iron and manganese in these critical assets in comparison to the rest of the DWDS. Results provide a first-time insight into the differences in the accumulation and remobilisation behaviour of these metals in SRs, challenging current literature on the composition of DWDS accumulated material and adding to the understanding of discolouration risk posed by iron and manganese at this stage of the network.

2 METHODS

Field site selection

Field study sites were selected from each of the four different UK water utilities (termed A, B, C and D) who were part of a larger study on assessing SR performance and its effect on drinking water quality. SR site selection requirements included: (1) having a consistent source water and treatment; (2) being completely post treatment; (3) either having a pre-existing accessible inlet and outlet sampling line and tap or having the scope for installation; (4) having separate inlet and outlet pipes; and (5) having scope to carry out downstream/upstream sampling in the surrounding DWDS.

Water quality monitoring programme

As inlet monitoring at SRs is not a regulatory requirement for water utilities in the UK, there were no available functioning inlet sampling points at the four project SRs. To enable investigation of SR performance using incoming and outgoing water quality, inlet sample lines and taps were either installed or recommissioned in accordance with UK Water Supply Regulation 8 and made from materials complying with BS 6920 [12,13]. A water quality monitoring programme was then undertaken at both the inlet and outlet of project SRs for a range of water quality parameters including total iron and manganese, conducted on a weekly basis across 2018-2020. All samples were collected and analysed in accordance with standard procedures for regulatory compliance monitoring ISO/IEC 17025, ISO/IEC 17024, and the Drinking Water Testing Specification, accredited by the United Kingdom Accreditation Service [14,15].

Water quality monitoring results presented in this paper are for SR D4; an underground, rectangular, twin-compartment, 9.1 ML reinforced concrete (with a brick compartment-dividing wall) SR with an average retention time of 28 hours. It is fed by a 0.22 km ductile iron cement-lined trunk main directly from the WTW. Treated water is reservoir abstracted with free chlorine



as the secondary disinfectant and further UV dosing at the inlet of the SR. Table 1 below presents summary site information for D4 and other studied SRs discussed in this paper.

Collection and analysis of SR accumulated material samples

SR accumulated material was collected from five SRs (B6, C7, C8, C9, and D4; note, D4 was also monitored for water quality as described above) during scheduled structural inspections and cleans. The criteria for site selection was to collect material from a variety of different SRs with respect to geometry, retention time, distance from WTW, and secondary disinfectant type (see Table 1 below for summary site details). As no standardised existing procedure was found, material was collected using a protocol developed in this research, built on experience from SR cleaning operations and based upon elements of existing literature on material collection from SRs for microbiological analysis and material collected as loose deposits from raw waterbodies [16,17,18]. Sampling guidelines stipulated that material needed to be collected in a way that represented the entire floor area of the SR. This included, where feasible, collection from each corner, the middle, and around any other features such as inlet and outlet pipes. All samples were collected immediately after the SRs were drained and before any further work or cleaning had commenced, except in one case where cleaning was inadvertently started prior to collection of one sample (C7 SR - middle of compartment 2). Samples were collected using sterile plastic spatulas, kept in sterile plastic sample bottles, and refrigerated as soon as possible using cooler boxes and fridges. Material was then analysed for its organic and inorganic composition in a set of two experiments, one investigating the effect of material resuspension on the surrounding water quality (material from SRs B6 and D4) and the other on the influence of sampling location within SRs on material composition (material from SRs C7, C8, and C9).

For the resuspension experiment, different masses of dry material were placed into deionised water at concentrations of 60 mg/l (low), 120 mg/l (medium), and 240 mg/l (high). The bottles were placed on a shaker table and shaken for a period of 48 hours. The table was stopped, and samples collected at 2 and 48 hours. The shaking process was done to recreate the effect of immediate resuspension of material for the 2-hour samples (e.g., following a sudden event like a pipe burst) and prolonged resuspension for the 48-hour samples (e.g., from a more permanent change in hydraulic operation of a SR). 6 of the 18 samples were removed from the table entirely at the 24-hour mark and left to settle for an additional 24 hours, after which a sample for analysis was taken. The purpose of removing the samples from the shaker table was to observe whether the re-settling of material begins to reverse any potential effects that resuspension might have on the surrounding water quality.

Samples were analysed for a range of metals and elements, focussing on those often found in DWDSs including aluminium, arsenic, cadmium, chromium, cobalt, copper, iron, lead, magnesium, manganese, nickel, potassium, uranium, and zinc. The analysis was done using an Agilent 7900 ICP-MS with Ultra High Matrix Introduction following manufacturers' guidelines [19]. One sample, 'C7 SR - middle of compartment 2', required a five-factor dilution (using deionised water) as the total organic carbon content of the sample was over 20 mg/l and could have interfered with the ICP-MS.



Service reservoir name	Geometry and Material	Volume (ML)	Height (m)	Average retention time (hours)	Inlet pipe (direct upstream main) length, diameter (inches), and material	Source water	Secondary and on-site disinfectant (where applicable)
D4	Underground Rectangular Twin compartment Reinforced concrete with a brick dividing wall	9.1	5.4	28.1	Length: 0.223 km 23.6" DI cement lined	Surface (reservoir) Soft water	Secondary: Chlorine On site: Ultraviolet irradiation (dosed at the inlet)
B6	Underground Rectangular Twin compartment Reinforced concrete	9.4	4.8	NA	Length: ~52 km 22.1" HPPE down to 17.7" DI	Surface (river and reservoir) Slightly hard water	Secondary: Chlorine
C7	Underground Twin compartment Rectangular Reinforced concrete	5.2	6.7	63.5	Length: 0.51 km 15.7" DI	Surface (reservoir) Soft water	Secondary: Chlorine
C8	Underground Twin compartment Rectangular Reinforced concrete	0.8	4.8	82.4	Length: 1.1 km 12" SI	Surface (reservoir) Soft water	Secondary: Chloramine
C9	Underground (part exposed) One compartment Circular Concrete	0.4	3.3	71.6	Length: primary main from WTW 11.5 km, but immediate main tapping off this is 0.02 km 9" primary main and 6" immediate main, both AC	Surface (reservoir) Soft water	Secondary: Chloramine

Table 1. – Summary information fo	or characteristics of project SRs
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3 RESULTS

Total iron and manganese in bulk water pre and post SR clean

D4 SR was inspected and cleaned during the water quality monitoring programme conducted in this project. A variety of water quality parameters were monitored pre, during, and post clean, enabling the investigation on the efficacy of SR maintenance on asset performance. Figures 1 and 2 show the water quality monitoring results for SR D4 over 4 time periods: (1) prior to the clean; (2) when the first compartment was taken out of service, so the entire flow was travelling through a single, uncleaned compartment; (3) when the second compartment was taken out of service, so the entire flow was travelling through a single, cleaned compartment; and (4) after both compartments had been cleaned. When looking at discrete sampling data for total iron and manganese, results show that iron concentration does not change significantly at the SR outlet



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pre, during, or after the clean, suggesting that the clean did not affect SR performance with respect to iron levels (Figure 1). Results for manganese sampling show that pre clean manganese levels were slightly higher at the SR outlet in comparison to SR inlet and that upon the commencement of the clean, and post clean, manganese levels became lower at the SR outlet in comparison to SR inlet, irrespective of the concentration of incoming manganese (Figure 2). Based on these results, it appears that cleaning the D4 SR improved its performance in terms of it removing, instead of contributing manganese, into the water supply. With a reduction of manganese entering the downstream network, it can be proposed that this reduces the rate of accumulation on pipe surfaces and thus alleviates future mobilisation and hence reduces discolouration risk posed by this metal.





Figure 1. Discrete total iron concentrations (mg/l) at the D4 SR across four time periods; pre SR clean, with one compartment out of service, post one compartment clean, and post the entire SR clean. In the fourth time period, all SR inlet values (n = 25) were below the minimum detection limit of 0.011 mg/l and are represented here as limit of detection/2 (0.0055 mg/l).



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Figure 2. Discrete total manganese concentrations (mg/l) at the D4 SR across four time periods; pre SR clean, with one compartment out of service, post one compartment clean, and post the entire SR clean.



Composition of metals in SR accumulated material

Figure 3 provides the results of the resuspension experiments for D4 and B6 SR material samples. Results are shown for the different concentrations of material (low 60 mg/l, medium 120 mg/l, and high 240 mg/l) and different times in resuspension (2 hours, 48 hours, and settled). Total aluminium was also present in all D4 and B6 SR samples but is not presented in Figure 3; values ranged from 0.0038-0.0526 mg/l in samples from D4 SR and 0.0024-0.0053 mg/l in samples from B6 SR.

Figure 4 presents the dominant metals identified in the accumulated material collected from C7, C8, and C9 SRs. Results from sample 'C7 SR - middle of compartment 2' were much higher than in material samples from other SRs. This was also the only sample where arsenic (0.0010 mg/l), lead (0.0007 mg/l), and uranium (0.0001 mg/l) were identified.





Figure 3. Total metals (mg/l) in resuspension analysis of material collected from D4 and B6 SRs.





Figure 4. Total metals (mg/l) in material samples collected from different locations within C7, C8, and C9 SRs.

Results from Figures 3 and 4 show that aluminium was the most dominant metal, present in 100% of the samples, followed by manganese in 90%, copper in 73%, zinc in 40%, and iron in just 13% of the samples. The results also demonstrate that the accumulated material is not homogenous, with variation in results from different locations and from different subsamples within a single material sample. For example, different metals were detected in the different subsample concentrations prepared from the same larger material sample in the resuspension experiments (Figure 3). An exception was the sample collected from the middle of compartment 2 in C7 SR, an outlier sample where iron was present at levels that breached UK prescribed concentration value (PCV) in drinking water, set at 0.2 mg/l. Manganese concentration in the sample also breached UK PCV at 50 times the set value of 0.05 mg/l. This was also the only material sample that contained arsenic, uranium, and lead. Although not confirmed, it is suspected that this sample was exposed to a biocide solution, used as part of the cleaning process of SRs, prior to collection. This solution is used to strip biofilm and other accumulated materials off concrete and metal structures and in SRs is sprayed onto walls and internal structures [20]. It is likely that this particular sample was impacted by the removal of a large area of biofilms and the resulting effluent ending up in the collected sample, which could explain these large concentrations and the detectable presence of arsenic, uranium, and lead. These results suggest that some of the metals and elements that enter SRs may accumulate in small concentrations in biofilms and are not present in their loose, particulate forms in accumulated material, e.g., iron.

4 **DISCUSSION**

The aim of this research was to investigate how SRs affect drinking water quality as water travels through these essential assets. From the analysis of SR accumulated material, it was observed that iron was absent in the majority (87%) of collected material samples (Figures 3 and 4). This finding contradicts much of the current literature, which finds that iron is the predominant metal in the DWDS, both in bulk water and in accumulated material, but draws primarily on samples from pipes for these conclusions [6,7,8]. Results from the D4 SR clean showed that iron does not appear



to remain within the SR in comparison to manganese, given that cleaning D4 SR made no difference to outlet iron levels but did for manganese (Figures 1 and 2). The lack of iron accumulation in D4 SR aligns with the results from the analysis of the collected material sample from this SR, which contained no iron in 89% of the subsamples while manganese was present in the majority (89%) (Figure 3).

Another example where SRs appear to be contributing manganese into the downstream network, but not iron, comes from higher manganese levels observed at SR outlets during the pandemic. In the UK, water utilities started using SR outlets as alternative sampling points to customer taps for regulatory monitoring for metals (44% samples taken at surrogate locations in England in 2020) [4]. This SR sampling resulted in fewer sample failures for iron, but more sample failures for manganese.

All of these results suggest that there are differences in how water quality parameters behave in SRs as compared to pipes. The work from this study suggests that iron potentially settles and remobilises more in pipes than SRs, and manganese settles and remobilises more in SRs than pipes. A similar observation highlighting different environments and consumption rates between pipes and SRs was made by Pick et al. (2021) [21], who found that the concentration of assimilable organic carbon decayed through pipes but increased slightly with travel through SRs. In pipes, both manganese and iron are known to accumulate in cohesive layers on pipe walls, assimilated into biofilms [22]. Potentially, the same thing is happening to iron in SRs, where small amounts are likely accumulating in biofilms on SR walls and internal structures over time, but not large amounts as loose deposits. The metals composition in the sample 'C7 SR - middle of compartment 2' that was likely exposed to biofilm-sloughing biocide, where not only was iron (and other metals) present, but concentrations also breached PCV (Figure 4) gives an indication of this iron accumulation at the SR wall. Internal corrosion of iron-based materials such as steel ladders within the SRs, was also observed to be taking place and may be contributing larger amounts of particulate iron to localised areas.

The findings in this study on iron and manganese behaviour in SRs are preliminary and highlight the need for further research into SR material accumulation and water quality changes at this stage of the network, for proactive management of associated risks.

Another valuable outcome of this research came from monitoring SR performance pre and post clean, which made it possible to, for the first time, measure and evaluate the effectiveness of SR maintenance on asset performance in terms of water quality and which demonstrated that the removal of material from SRs can reduce discolouration risk.

The above observations would not have been possible to make without the inclusion of inlet monitoring or monitoring parameters other than disinfectant residual and bacteriological indicators at SRs, or the collection and analysis of SR accumulated material. This highlights the importance and value of a more inclusive monitoring programme at this currently overlooked stage of the network.

5 CONCLUSIONS

- Inlet and outlet water quality monitoring at SRs indicates a difference in the behaviour of iron and manganese in that manganese appears to remain within the SR more than iron.
- Analysis of SR accumulated material shows high accumulation of manganese, but generally not iron in SRs.
- Conducting both inlet and outlet monitoring at SRs and for water quality parameters other than those stipulated by regulation enables the ability to assess SR performance and evidence the effectiveness of asset maintenance.



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