

# 1 Manganese concentrations in Scottish groundwater

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## 14 Abstract

15 Groundwater is increasingly being used for public and private water supplies in Scotland, but  
16 there is growing evidence that manganese (Mn) concentrations in many groundwater supplies  
17 exceed the national drinking water limit of 0.05 mg l<sup>-1</sup>. This study examines the extent and  
18 magnitude of high Mn concentrations in groundwater in Scotland and investigates the factors  
19 controlling Mn concentrations. A dataset containing 475 high quality groundwater samples  
20 was compiled using new data from *Baseline Scotland* supplemented with additional high  
21 quality data where available. Concentrations ranged up to 1.9 mg l<sup>-1</sup>; median Mn  
22 concentration was 0.013 mg l<sup>-1</sup> with 25<sup>th</sup> and 75<sup>th</sup> percentiles 0.0014 and 0.072 mg l<sup>-1</sup>  
23 respectively. The Scottish drinking water limit (0.05 mg l<sup>-1</sup>) was exceeded for 30% of samples  
24 and the WHO health guideline (0.4 mg l<sup>-1</sup>) by 9% ; concentrations were highest in the  
25 Carboniferous sedimentary aquifer in central Scotland, the Devonian sedimentary aquifer of  
26 Morayshire, and superficial aquifers. Further analysis using 137 samples from the Devonian  
27 aquifers indicated strong redox and pH controls (pH, Eh and dissolved oxygen accounted for  
28 58% of variance in Mn concentrations). In addition, an independent relationship between Fe  
29 and Mn was observed, suggesting that Fe behaviour in groundwater may affect Mn solubility.  
30 Given the redox status and pH of Scottish groundwaters the most likely explanation is  
31 sorption of Mn to Fe oxides, which are released into solution when Fe is reduced.  
32 Since the occurrence of elevated Mn concentrations is widespread in groundwaters from all  
33 aquifer types, consideration should be given to monitoring Mn more widely in both public  
34 and private groundwater supplies in Scotland and by implication elsewhere.

35

36 **Keywords:** groundwater, iron, manganese, redox, Scotland, water supplies

37

38 **1 Introduction**

39

40 The trace metal manganese (Mn) is ubiquitous in the environment; it is a minor component of  
41 most rock types and is also present in soils from weathering and aerial deposition. Mn can  
42 exist in different oxidation states, but the most widely occurring forms in the environment are  
43 soluble Mn (II) when reduced and insoluble Mn (IV) when oxidised. Naturally occurring Mn  
44 is commonly found in drinking water supplies and is essential for human health at low  
45 concentrations (Keen and Zidenberg-Cherr, 1994). The World Health Organization (WHO)  
46 has set a guideline value of 0.4 mg l<sup>-1</sup> (WHO, 2008): nevertheless, most countries have set a  
47 lower limit primarily due to aesthetic and infrastructure problems; e.g. Mn is listed as an  
48 indicator parameter by the EC at a concentration of 0.05 mg l<sup>-1</sup> in drinking water (EC, 1998).

49

50 Excessive Mn concentrations can result in metallic tasting water, staining of clothes, dishes,  
51 and products such as paper or plastics, and reduced water pressure and flow in pipes from  
52 accumulation of Mn oxides (Sly et al., 1990). Although Mn can be removed from water by  
53 treatment (Casale et al., 2002), this is expensive and water supply infrastructure prior to  
54 treatment, such as pipes, pumps and boreholes, may still be adversely affected by build up of  
55 Mn oxides (Sly et al., 1990). Hence if the occurrence of excessive Mn concentrations can be  
56 predicted, it could be avoided when sourcing new water supplies.

57

58 Furthermore, several studies in different environmental settings have reported significant  
59 associations between exposure to Mn in groundwater-sourced drinking water supplies and  
60 adverse human health effects. For example, Wasserman et al. (2006) identified a significant  
61 negative relationship between well water Mn concentration (0.004-3.91 mg l<sup>-1</sup>) and measures

62 of intellectual function in 142 children of 10 years of age in Bangladesh (notable difference  
63 in intellectual function between  $<0.2 \text{ mg l}^{-1}$  group and  $> 1 \text{ mg l}^{-1}$  group). Mn exposure  
64 associated with drinking water was also significantly positively related with hyperactive  
65 classroom behaviours in a study of 46 children in Québec (Bouchard et al., 2007). In adults,  
66 exposure to elevated Mn concentrations in drinking water has been associated with  
67 manganism, a Parkinson-like disorder. In a study in Greece (Kondakis et al., 1989),  
68 neurological symptoms of chronic Mn poisoning were found to increase with exposure to Mn  
69 from groundwater-sourced water supplies in three populations of adults with similar social  
70 and dietary characteristics (concentrations ranging from  $0.0036$  to  $2.3 \text{ mg l}^{-1}$ , effects were first  
71 noted in a group drinking concentrations  $0.08$  to  $0.25 \text{ mg l}^{-1}$ ). Because of the association  
72 between Mn intake and neurological effects, the WHO current guideline concentration for  
73 Mn in drinking water is  $0.4 \text{ mg l}^{-1}$  (World Health Organization, 2008), although the USA has  
74 a lower health reference level of  $0.3 \text{ mg l}^{-1}$  (USEPA, 2003). In the studies by Wasserman et  
75 al. (2006) and Kondakis et al. (1989) there was evidence of a dose-response relationship  
76 between the severity of neurotoxic effects and exposure to Mn in well water suggesting that  
77 exposure to Mn concentrations *below* the WHO guideline value could still result in adverse  
78 health effects, with children most vulnerable (Ljung and Vahter, 2007). Consequently  
79 Bouchard et al. (2007) recommend that further research is required to establish adequate  
80 guidelines for Mn in drinking water.

81

82 The occurrence and concentration of Mn in groundwater is controlled by many factors, the  
83 main ones being rock geochemistry, water chemistry and microbiological activity. Some rock  
84 types, such as mafic and ultramafic rocks, shale, greywacke and limestone, contain high  
85 concentrations of Mn, which can lead to elevated concentrations in soil and sediment through  
86 weathering processes. Water chemistry, in particular pH, redox potential (Eh), dissolved

87 oxygen (DO), and dissolved organic carbon (DOC), is instrumental in mobilising Mn and  
88 controlling its speciation and concentration in the water environment. Manganese occurs  
89 mainly as the reduced soluble  $Mn^{2+}$  at lower pH and Eh, but is oxidised to form precipitates  
90 in the presence of oxygen and at higher pH (Hem, 1985). Hence in equilibrium conditions  
91 Mn is likely to occur as  $Mn^{2+}$  at pH<7 and at Eh as high as 800 mV. Complexation with  
92 humic substances (e.g. Graham et al., 2002) inhibits Mn oxidation and precipitation, although  
93 complexation with inorganic ligands, such as sulphate or hydrogen carbonate, is suggested to  
94 have only a limited effect on Mn speciation and concentration, apart from at very high ligand  
95 concentrations (Hem, 1972). Micro-organisms can play an important role in Mn mobilisation  
96 in the environment and can both enhance or inhibit concentrations in groundwater. The  
97 effects can be direct, through enzymatic catalysis of Mn oxidation and reduction and specific  
98 binding by cell-associated materials, or indirect, by altering the pH and Eh conditions of the  
99 micro-environment, thereby influencing Mn speciation and concentration (Nealson, 1983).  
100 The impact of microbiological activity on Mn behaviour in water is frequently evident in the  
101 accumulation of oxidised Mn in biofilms on surfaces such as pipes (Sly et al., 1990). The  
102 factors described above frequently interact to determine Mn concentrations in groundwater.  
103 For example, Bourg and Bertin (1994) and Gounot (1994) attributed spatial and temporal  
104 changes in Mn concentrations in two alluvial aquifers in France to different mineralogical  
105 forms of Mn and also to the reduction of solid Mn oxides to the dissolved form in anaerobic  
106 conditions generated by microbial degradation of organic matter.

107

108 There is increasing evidence (Robins, 2002; MacDonald and Ó Dochartaigh, 2005) that Mn is  
109 often present in Scottish groundwaters at concentrations in excess of the Scottish drinking  
110 water supply limit of  $0.05 \text{ mg l}^{-1}$  (as defined by the Water Supply (Water Quality) (Scotland)  
111 Act 2001) and may be in excess of the WHO guideline value of  $0.4 \text{ mg l}^{-1}$ . In Scotland

112 groundwater is the main source of water for an estimated 30,000 private water supplies and  
113 approximately 7% of public water supplies and is also a major contributor to environmental  
114 flows, through baseflow to rivers and streams (MacDonald et al., 2005). Concerns related to  
115 excessive Mn concentrations are greatest for private water supplies, which are generally  
116 groundwater based, but are not subject to such stringent testing as public water supplies so  
117 that elevated concentrations could go unnoticed.

118 The aims of this current research are to assess the concentrations of Mn in Scottish  
119 groundwaters, compare between different aquifer types, and examine controls on elevated  
120 concentrations in groundwater.

121

## 122 **2 Methods**

123

124 The first step in the research was to compile a quality-controlled dataset of Mn concentrations  
125 and other physicochemical parameters in Scottish groundwaters. Since 2005 considerably  
126 more data on Scottish groundwater have become available through the Baseline Scotland  
127 project, jointly funded by the British Geological Survey (BGS) and Scottish Environment  
128 Protection Agency (SEPA), which is systematically sampling and analysing groundwater  
129 from the main hydrogeological units across Scotland (BGS, 2010). Groundwater chemistry  
130 data from the Baseline database assembled prior to 2008 for 190 sites in eastern and southern  
131 Scotland were used. Collected samples were passed through a 0.45  $\mu\text{m}$  filter and acidified to  
132 1% v/v with Aristar grade concentrated nitric acid in the field. Samples were analysed by  
133 ICP-MS at BGS laboratories in the UK and a commercial laboratory in Canada.

134

135 Groundwater chemistry data for Scotland collected prior to 2005 in other BGS projects and  
136 by other organizations were compiled and reviewed by MacDonald and Ó Dochartaigh

137 (2005). These datasets had been subject to quality assurance, such as removing samples from  
138 highly contaminated sites and samples in which the balance between cations and anions  
139 differed by >10%, and were included in the Mn dataset after further quality control. The  
140 criteria for including samples in the Mn dataset were a limit of detection <0.003 mg Mn l<sup>-1</sup>  
141 and use of the same sample preparation procedure as the Baseline samples (i.e. filtration and  
142 acidification in the field). The final step in compiling the dataset was to select one set of  
143 chemistry data for the *c.*100 sites which had duplicate samples in order to minimise data bias  
144 to a particular location or geology type. Where a site had been sampled by more than one  
145 organization, following the practice in other studies (Shand et al., 2007) data with better  
146 detection limits and a more comprehensive suite of analysis were preferred. Mn  
147 concentrations reported as less than a detection limit (only data below 0.003 mg l<sup>-1</sup>) were  
148 given a numerical value of half the detection limit for statistical analysis.

149 The final dataset contained data for Mn in groundwater from 475 sites across Scotland  
150 (Figure 1). Data were divided into nine geological categories, based on the principal  
151 geological units from which samples were taken (Figure 2). Categories were chosen to enable  
152 comparison with previous work on characterising Scottish aquifers (MacDonald and Ó  
153 Dochartaigh, 2005) and to contain sufficient numbers of samples for analysis to determine the  
154 effect of geology on Mn concentrations. Relationships between Mn and a number of other  
155 physicochemical parameters measured in the same samples (where available) which are  
156 likely to influence Mn concentrations (Eh, pH, DO, DOC, specific electrical conductance  
157 (SEC), HCO<sub>3</sub>, NO<sub>3</sub>-N, Fe, Ca, Mg) were examined using scatter plots and multiple linear  
158 regression to assess the effect of water chemistry on Mn concentrations. Mn and Fe  
159 concentrations were log<sub>10</sub>-transformed for the regression analyses, conducted in Minitab v.15,  
160 in order to normalise the data distributions. P values were used to test significance at 95%  
161 probability.

162

163 **3 Results**

164

165 3.1 Analysis of the complete dataset of Mn concentrations in Scottish groundwaters

166 Mn concentrations in Scottish groundwaters are log-normally distributed, with the lower end  
167 of the distribution affected by samples with concentrations below the limits of detection  
168 (Figure 3). The median Mn concentration was  $0.013 \text{ mg l}^{-1}$ , but there was a wide variation in  
169 Mn concentrations and 25<sup>th</sup> and 75<sup>th</sup> percentiles were  $0.0014 \text{ mg l}^{-1}$  and  $0.072 \text{ mg l}^{-1}$ ,  
170 respectively. The Scottish limit for Mn in drinking water of  $0.05 \text{ mg l}^{-1}$  was exceeded in 30%  
171 of samples; the WHO health guideline (WHO, 2008) of  $0.4 \text{ mg l}^{-1}$  was exceeded in 9%, and  
172 the USEPA limit (USEPA, 2003) of  $0.3 \text{ mg l}^{-1}$  exceeded in 12%.

173

174 Similar distributions of Mn concentrations in groundwater used for drinking water have been  
175 reported elsewhere. In Sweden, the median Mn concentration in 12,000 sampled wells was  
176  $0.06 \text{ mg l}^{-1}$  and around 20% of wells exceeded the Swedish recommended guideline value for  
177 private wells of  $0.3 \text{ mg l}^{-1}$  (Ljung and Vahter, 2007). In a survey of 2160 private wells in the  
178 USA used for household drinking water (DeSimone, 2008), 5% of those tested had Mn  
179 concentrations greater than the health reference level ( $0.4 \text{ mg l}^{-1}$ ) and 21% had concentrations  
180 in excess of the USEPA Secondary Maximum Contaminant Level set for aesthetic quality  
181 and other non-health reasons ( $0.05 \text{ mg l}^{-1}$ ). In a survey of total Mn (i.e. not filtered) from  
182 10,000 groundwater sources in New Zealand, Daughney (2003) found that 39% exceeded  
183  $0.05 \text{ mg l}^{-1}$  and 15% exceeded the New Zealand health guideline of  $0.5 \text{ mg l}^{-1}$ .

184

185 Figure 1 shows the spatial distribution of groundwater Mn concentrations and Figure 2 the  
186 bedrock aquifer units in Scotland. Mn concentrations in groundwater varied widely across

187 Scotland and also locally. Many groundwater samples from Moray, Aberdeenshire, the  
188 Central Belt and Dumfries and Galloway contained excessive Mn concentrations. In contrast,  
189 generally low Mn concentrations occurred in groundwater samples from the Strathmore area  
190 and much of southern Scotland. Mn concentrations also varied within and between rock types  
191 from which groundwater samples were taken (Figure 4). The Scottish drinking water limit  
192 was exceeded by some groundwater samples from all geological categories and lay within the  
193 interquartile range (25<sup>th</sup>-75<sup>th</sup> percentiles, the lower and upper limits of the boxes in Figure 4)  
194 in the Superficial, Permian/Triassic/Jurassic and most notably in the Carboniferous and  
195 Northern Devonian categories. Mn concentrations in groundwater samples varied by at least  
196 three orders of magnitude within each geological category emphasising that it is not possible  
197 to predict from rock type alone whether groundwater might have elevated Mn.

198 Multiple linear regression of 10 other physicochemical parameters with Mn concentration for  
199 the 119 samples for which all these data were available showed that Mn was significantly  
200 inversely related to pH, Eh and DO and significantly positively related to Fe (Table 1).  
201 Together these parameters explained 50% of the variance in Mn concentrations. When  
202  $\log_{10}\text{Fe}$  was not included, 42% of the variance was explained and the strength of the  
203 relationship with pH and Eh increased. Since Mn and Fe are often closely related in natural  
204 waters (Collins and Buol, 1970; Hem, 1985; DeSimone, 2008), the controls on Fe  
205 concentrations in Scottish groundwaters were investigated by repeating the multiple  
206 regressions with Fe as the dependent variable (Table 1). Although  $\log_{10}\text{Mn}$  concentrations  
207 were significantly related to  $\log_{10}\text{Fe}$ , when this predictor was excluded, the parameters  
208 significantly related to Fe were Eh (negatively), DOC and SEC (positively), suggesting that  
209 Mn and Fe concentrations in groundwater are affected by rather different physicochemical  
210 conditions.

211



### 212 3.2 Analysis of data for the Devonian sedimentary aquifer

213 Multiple regression analyses of the complete dataset helped to identify overall  
214 physicochemical influences on Mn and Fe concentrations in groundwater across a range of  
215 rock types, but the patterns observed may also be affected by variation in rock geochemistry,  
216 which may account for some of the unexplained variance. However, whole rock  
217 geochemistry data are not widely available for groundwater sampling sites in Scotland, so  
218 further analysis including rock geochemistry is not currently possible. Therefore, in order to  
219 assess in more detail the physicochemical controls on Mn concentrations in groundwater,  
220 data for one aquifer type (Devonian sedimentary rocks) were further interpreted, to minimise  
221 large variations in manganese rock geochemistry (BGS, 2009). Devonian aquifers are  
222 widespread in Scotland and provide a valuable groundwater resource (Graham et al., 2009).  
223 Samples were available for Devonian aquifers in three geographical locations: Northern  
224 Devonian (north of Aberdeen), Strathmore Devonian (between Aberdeen and the Firth of  
225 Tay) and Southern Devonian (south of the Firth of Tay).

226  
227 For the Devonian dataset, multiple linear regression analyses to predict Mn and Fe  
228 concentrations with different numbers of predictors (Table 2) showed broadly similar  
229 relationships as for the total dataset. The same physicochemical parameters (pH, Eh and DO)  
230 were significantly related to Mn concentrations but for the Devonian samples there was no  
231 observable independent relationship with Fe. These three parameters alone explained 58% of  
232 the variance (compared with only 42% of the variance for the total dataset explained by pH,  
233 Eh, DO and an additional 6 parameters (Table 1)). Eh was the strongest independent  
234 predictor (see Table 2 and Figure 5) followed by pH and DO. Iron concentrations in the  
235 Devonian groundwater samples were again significantly related to Eh and DOC as in the  
236 complete dataset but there was no significant relationship of Fe with Mn or SEC (Table 2).

237

238 **4 Discussion**

239

240 The analysis of groundwater chemistry data has shown that undesirable Mn concentrations  
241 are a problem in Scotland's groundwater, with the Scottish drinking water limit being  
242 exceeded at 30% of the 475 sites sampled, and the WHO health guideline limit being  
243 exceeded at 9% of the sites. Mn concentrations were significantly negatively correlated to the  
244 redox and pH conditions of the water. Excessive Mn concentrations occurred particularly in  
245 groundwater from the Northern Devonian, Carboniferous and Superficial geological  
246 categories, although high concentrations were measured in samples from all geological  
247 categories.

248

249 4.1 Geology as a control on Mn concentrations

250 The variation in groundwater Mn concentrations between and within different geological  
251 categories may be caused both by differences in the concentration and nature of Mn present  
252 in the aquifer rocks and also the physicochemical conditions within the aquifer. There are  
253 insufficient rock chemistry data to be able to test this hypothesis robustly; however, the broad  
254 data distribution suggests that the water chemistry conditions are more significant than Mn  
255 mineralogy. There is considerably more variability in Mn concentrations within aquifer types  
256 than between them (Figure 4) and this variability is largely explained by redox and pH  
257 conditions.

258

259 4.2 pH and redox conditions as controls on Mn concentrations

260 The significant influence of pH and redox conditions on Mn concentrations in Scottish  
261 groundwaters was further investigated by plotting the Mn concentrations measured in

262 Scottish groundwaters on a predominance diagram (Figure 6). This diagram illustrates that  
263  $Mn^{2+}$  can be mobilised over a large range of Eh and pH values. All of the Scottish data above  
264 detection limit plot within the  $Mn^{2+}$  area of the predominance diagram as would be expected.  
265 However, some samples have low Mn concentrations even in conditions where  $Mn^{2+}$  can be  
266 mobilised, indicating that redox and pH conditions do not totally explain manganese  
267 distributions in groundwater.

268 The predominance diagrams for Mn suggest a stronger influence of pH on Mn mobilisation  
269 than Eh, since there is a greater gradient of  $Mn^{2+}$  concentration change in relation to pH than  
270 Eh. However, this pattern is not apparent in either the total dataset or the Devonian subset,  
271 where Eh was a much stronger predictor of  $Mn^{2+}$  concentrations than pH (Table 1 and  
272 Figure 5). This discrepancy may exist because at the near neutral pH of most Scottish  
273 groundwater,  $Mn^{2+}$  concentrations may be influenced by other factors such as complexation  
274 with bicarbonate and sulphate ions if they are present at high concentration (Hem, 1972) or  
275 interaction with Fe (Collins and Buol, 1970).

276

#### 277 4.3 Fe as a control on Mn concentrations

278 Multiple linear regression analysis of the complete dataset showed that the water chemistry  
279 parameter most strongly related (along with dissolved oxygen) to Mn concentrations in  
280 Scottish groundwaters was Fe. However, the relationship between Mn and Fe concentrations  
281 is not linear (Figure 7). The scatterplot of concentrations of the two elements showed that  
282 high Fe concentrations only occur with high Mn concentrations, but high Mn concentrations  
283 occur across the range of Fe concentrations. The regression analyses for predicting Mn and  
284 Fe separately using the complete dataset provided further evidence that the two elements do  
285 not behave in exactly the same way in Scottish groundwaters, since Mn concentrations were  
286 significantly related to Eh, DO and pH, and Fe to DOC and SEC in addition to Eh. The

287 significant relationship of both Mn and Fe with Eh suggests that interaction between the two  
288 elements in groundwater is mediated by Eh.

289

290 There is a close relationship between Mn and Fe oxidation and reduction in natural waters  
291 beyond the common redox conditions required for mobilisation (Marshall, 1979; Lind et al.  
292 1987; Thamdrup 2000). Since  $Mn^{2+}$  has a high affinity for ferric oxides, the precipitation of  
293 Fe oxides at lower Eh than Mn may lead to the removal of Mn by occlusion and sorption to  
294 precipitated Fe (Morgan and Stumm, 1965; Collins and Buol, 1970). Therefore, in solutions  
295 containing both Mn and Fe, such as Scottish groundwaters, which are not strongly reducing  
296 and are circumneutral,  $Mn^{2+}$  concentrations may be lower than expected at a particular Eh.  
297 Conversely, when Fe oxides are reduced,  $Mn^{2+}$  is released. Along with the occurrence of pH  
298 and Eh conditions which result in both Mn and Fe mobilisation, this process may also explain  
299 why high Fe concentrations often occur with high Mn concentrations in Scottish  
300 groundwater. An additional complication is that  $Fe^{2+}$  is more likely to adsorb or form  
301 complexes with DOC than Mn, resulting in higher  $Fe^{2+}$  concentrations occurring than  
302 expected at a particular Eh (Hem, 1972).

303

#### 304 4.4 Implications for groundwater monitoring

305 The research results have particular implications for monitoring of private water supplies in  
306 Scotland, which are often groundwater based. Water quality standards for private supplies in  
307 Scotland are derived from EC regulation, and monitoring and protection is carried out by  
308 local authorities. The level of monitoring depends on whether a private water supply is  
309 classified as Type A (providing 10 m<sup>3</sup> or more per day, supplying 50 or more people, or used  
310 for commercial or public activity) or Type B supplies (all others) (Astron, 2006). Chemical  
311 parameters are tested for in both types of supply, but Type A supplies are subject to more

312 regular and stringent testing and enforcement of water quality regulations than Type B, which  
313 are only monitored on a discretionary basis (Donnelley, 2008). Therefore, Mn may not be  
314 tested and high concentrations can go undetected.

315

316 Another major issue is sampling protocol. Samples collected for routine monitoring carried  
317 out by the regulatory bodies are often not filtered or acidified in the field, giving unreliable  
318 Mn data. In creating the dataset used for this Scottish study, a comparison was undertaken  
319 between samples collected with good and poor protocol for 40 locations. For samples with  
320 poor field protocol Mn concentrations were consistently underestimated by more than an  
321 order of magnitude. In addition, for a reliable measure of exposure to Mn for public health  
322 reasons, samples would need to be taken throughout the year to capture natural variations.

323 The range of Mn concentrations encountered in each geological unit also has implications for  
324 groundwater monitoring. Manganese concentrations in excess of the Scottish limit of 0.05  
325 mg l<sup>-1</sup> and the WHO health guideline value of 0.4 mg l<sup>-1</sup> were found in each aquifer unit, and  
326 there was more variability within each unit than between them. Therefore, developing hazard  
327 maps identifying areas of potential elevated Mn concentrations from geology alone are  
328 unlikely to be effective. Monitoring therefore needs to be widespread.

329

330 Based on the discussion above, more widespread testing of Scottish private water supplies  
331 using appropriate sampling protocols is required to give greater confidence in the Mn  
332 concentrations in private water supplies in Scotland. These recommendations have relevance  
333 elsewhere. Although studies in other countries have reported elevated Mn concentrations in  
334 groundwater-sourced drinking water supplies, monitoring of drinking water supplies for Mn  
335 is not routine.

336

## 337 **5 Conclusion**

338

339 This research developed a quality-controlled dataset of groundwater Mn concentrations  
340 across Scotland for 475 sites, which forms the basis of the analysis in this paper, and can  
341 serve as a resource for future research into Mn occurrence in Scottish groundwaters. Analysis  
342 of this dataset showed that elevated Mn concentrations ( $> 0.05 \text{ mg l}^{-1}$ ) occurred in 30% of the  
343 Scottish groundwater sites sampled, particularly in Superficial, Carboniferous, and Northern  
344 Devonian aquifers; and 9% of sites had concentrations above the WHO health drinking water  
345 limit ( $0.4 \text{ mg l}^{-1}$ ). The principal controls on Mn concentrations in groundwater in Scotland are  
346 redox conditions and pH, with some influence of Fe behaviour. Redox conditions exercise  
347 the strongest control. The scale of the problem of excessive Mn concentrations in  
348 groundwater across all aquifer types highlights the need for wider sampling for Mn in private  
349 water supplies in Scotland, and by implication, worldwide.

350

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- 444

445 **Table 1** P values for multiple linear regression analysis of Scottish dataset for  $\log_{10}\text{Mn}$  and  
 446  $\log_{10}\text{Fe}$  vs. selected physicochemical parameters. The sign in parentheses after each P  
 447 value indicates whether the predictor was positively (+) or negatively (-) related. P  
 448 numbers in bold indicate significance at 95% probability.  
 449

	<i>Predicting <math>\log_{10}\text{Mn}</math></i>		<i>Predicting <math>\log_{10}\text{Fe}</math></i>	
	<i>Incl. Fe</i>	<i>Excl. Fe</i>	<i>Incl. Mn</i>	<i>Excl. Mn</i>
pH	<b>0.001</b> (-)	< <b>0.001</b> (-)	0.855 (+)	0.146 (+)
Eh	<b>0.022</b> (-)	< <b>0.001</b> (-)	<b>0.001</b> (-)	< <b>0.001</b> (-)
DO	< <b>0.001</b> (-)	< <b>0.001</b> (-)	0.152 (+)	0.220 (+)
SEC	0.638 (+)	0.169 (+)	0.066 (+)	<b>0.011</b> (+)
DOC	0.187 (+)	0.060 (+)	0.105 (+)	< <b>0.001</b> (+)
HCO <sub>3</sub>	0.852 (+)	0.518 (+)	0.452 (+)	0.223 (+)
Ca	0.528 (+)	0.610 (+)	0.703 (-)	0.678 (-)
Mg	0.428 (-)	0.214 (-)	0.286 (-)	0.051 (-)
NO <sub>3</sub> -N	0.331 (-)	0.096 (-)	0.214 (-)	0.222 (-)
$\log_{10}\text{Fe}$	< <b>0.001</b> (+)	---	---	---
$\log_{10}\text{Mn}$	---	---	<b>0.000</b> (+)	---
Number of samples	119	129	119	125
R <sup>2</sup> Adjusted for sample size	50%	42%	45%	41%

450

451

452 **Table 2** P values for multiple linear regression analysis of the Devonian groundwater  
 453 samples for  $\log_{10}\text{Mn}$  and  $\log_{10}\text{Fe}$  vs. selected physicochemical parameters. The sign  
 454 in parentheses after each P value indicates whether the predictor was positively (+) or  
 455 negatively (-) related. P numbers in bold indicate significance at 95% probability.  
 456

	<i>Predicting <math>\log_{10}\text{Mn}</math></i>		<i>Predicting <math>\log_{10}\text{Fe}</math></i>	
	<i>4 predictors</i>	<i>Excl. Fe</i>	<i>6 predictors</i>	<i>Excl. Mn</i>
pH	<b>0.011 (-)</b>	<b>0.005 (-)</b>	0.563 (+)	0.961 (+)
Eh	<b>0.001 (-)</b>	<b>&lt;0.001 (-)</b>	<b>0.011 (-)</b>	<b>&lt;0.001 (-)</b>
DO	<b>0.037 (-)</b>	<b>0.036 (-)</b>	0.999 (-)	0.608 (-)
SEC	---	---	0.286 (+)	---
DOC	---	---	<b>0.047 (+)</b>	<b>0.007 (+)</b>
$\log_{10}\text{Fe}$	0.077 (+)	---	---	---
$\log_{10}\text{Mn}$	---	---	0.322 (+)	---
Number of samples	59	62	34	41
R <sup>2</sup> Adjusted for sample size	61%	58%	53%	58%

457

458

459 **Figure Captions**

460

461 Figure 1 The location of groundwater sites in Scotland sampled for manganese to an  
462 appropriate standard.

463 Figure 2 Bedrock aquifer units in Scotland (from MacDonald et al., 2005; Graham et  
464 al., 2009).

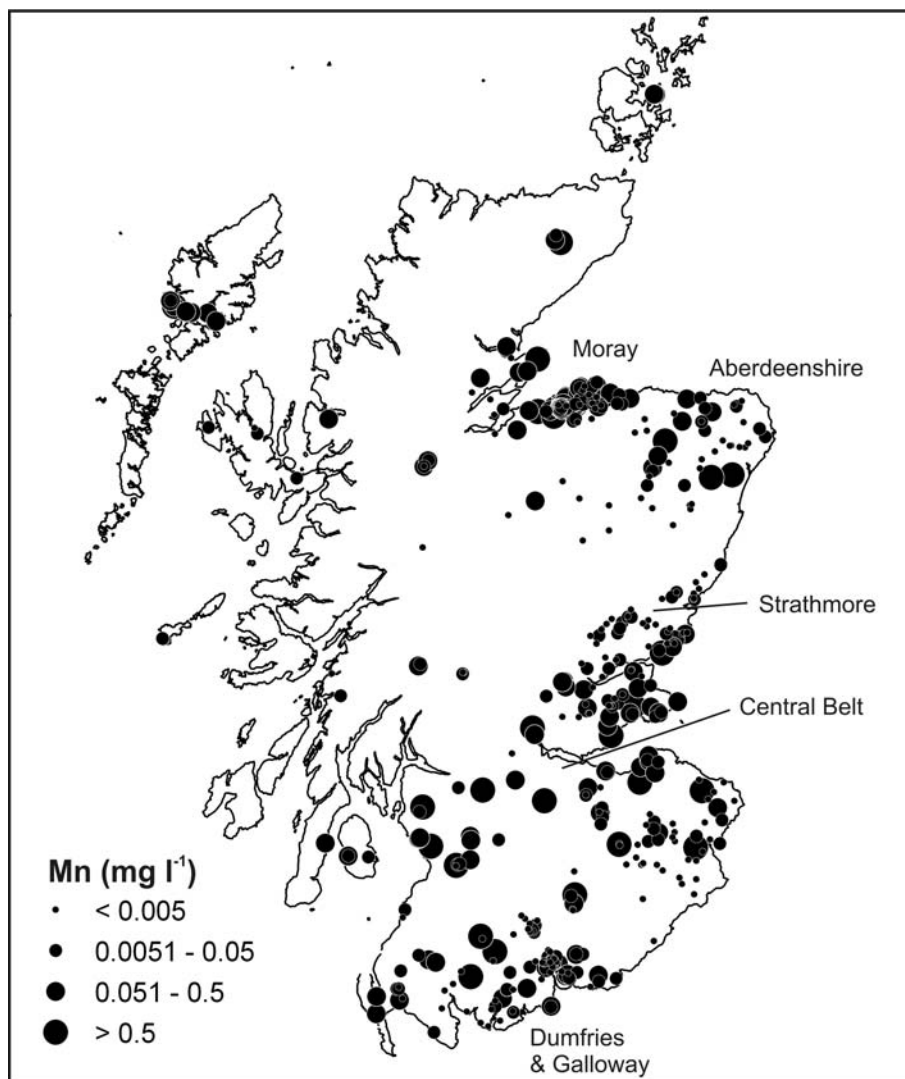
465 Figure 3 Cumulative frequency plot for Mn groundwater concentrations for the Scottish  
466 dataset (n = 475).

467 Figure 4. Box plot of Mn concentrations, divided into the main different aquifer units in  
468 Scotland

469 Figure 5 The relation between Mn concentrations, Eh and pH for groundwater samples  
470 from the Devonian sedimentary aquifer. Eh exhibits the largest control.

471 Figure 6 Data plotted on a predominance diagram for Mn speciation (Hem 1985,  
472 PhreeqC)

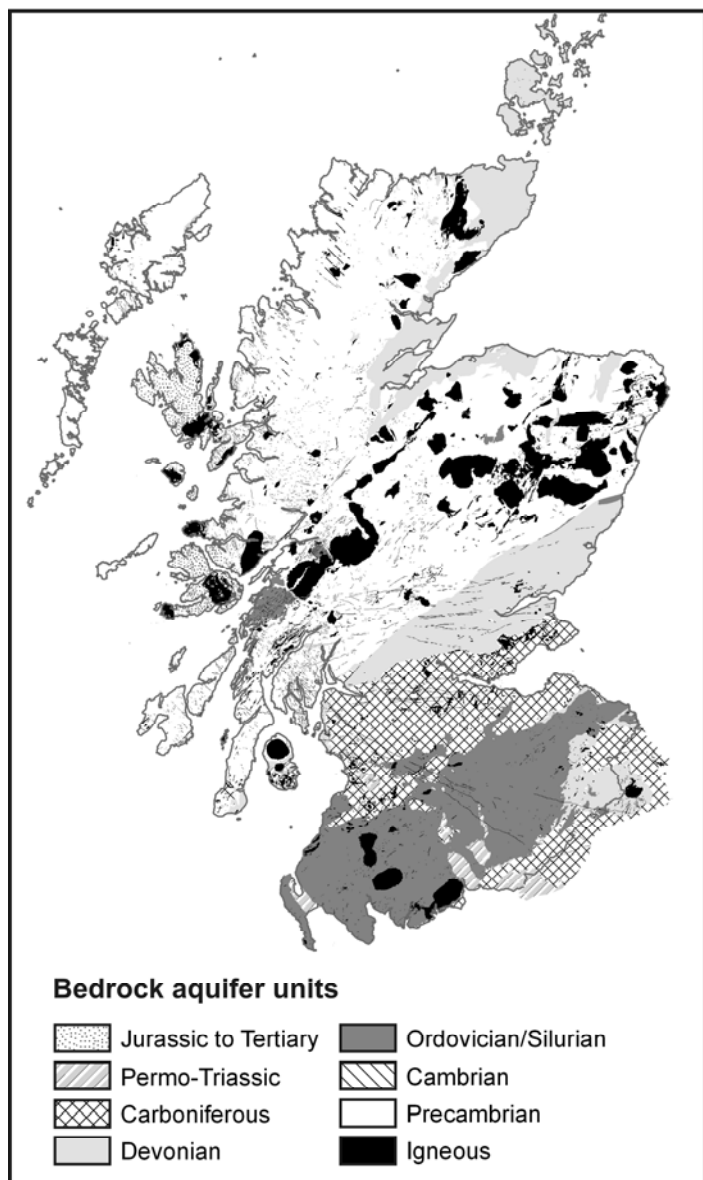
473 Figure 7 Scatter plot of Mn versus Fe concentrations for the Scottish dataset (n = 195,  
474 adjusted  $R^2 = 0.25$ )



475

476 Figure 1

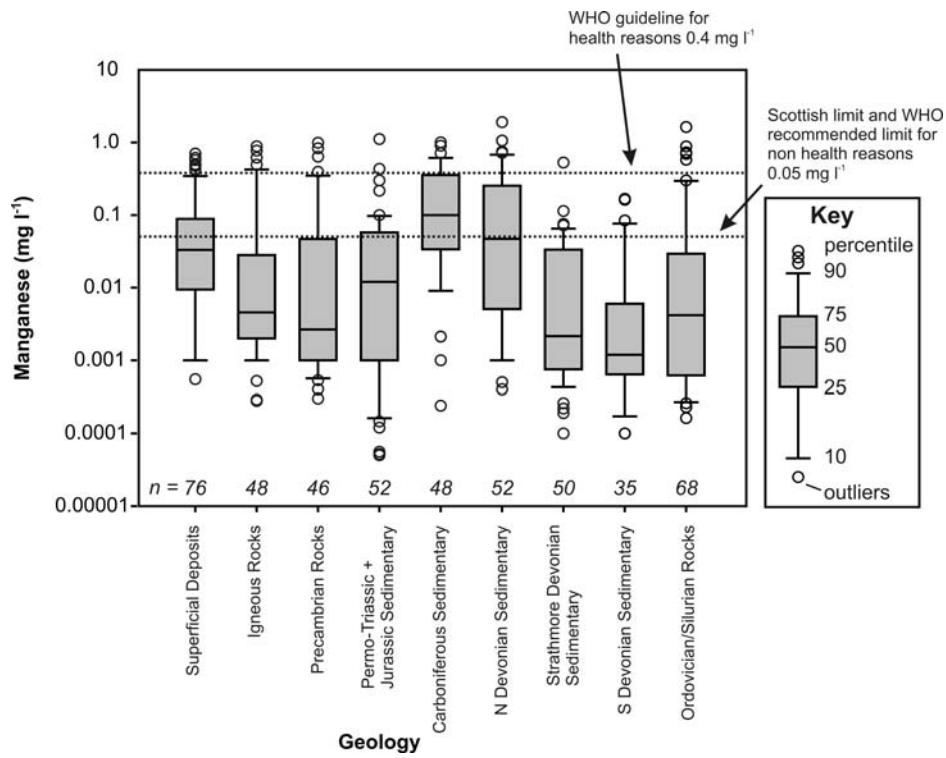
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478

479 Figure 2

480



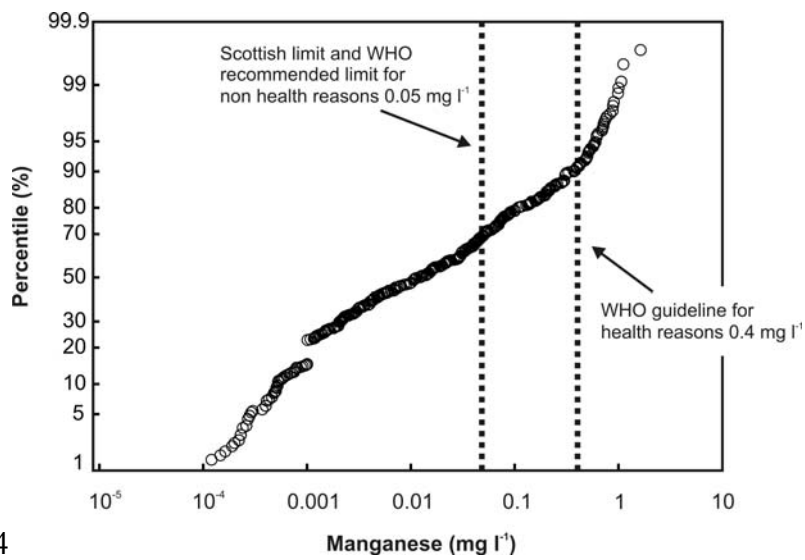
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482 Figure 3

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484

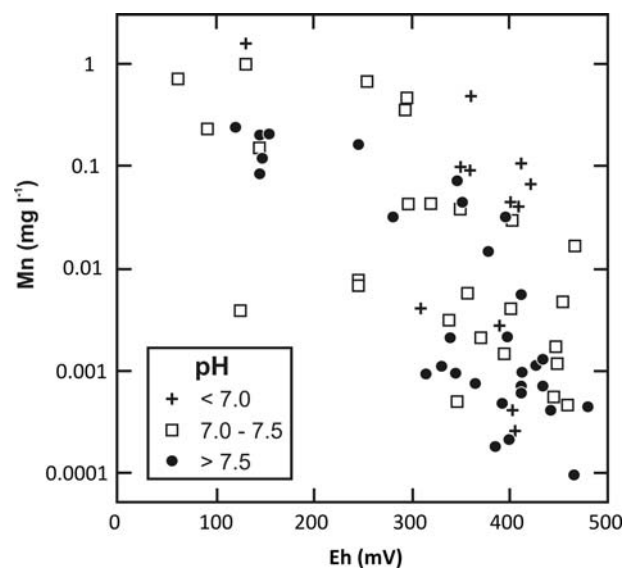
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486 Figure 4

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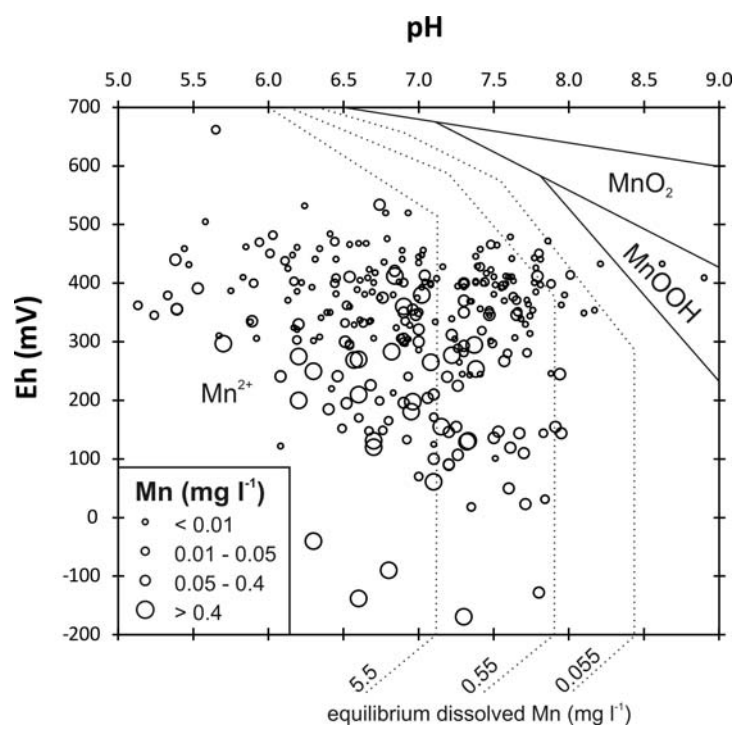




488

489 Figure 5

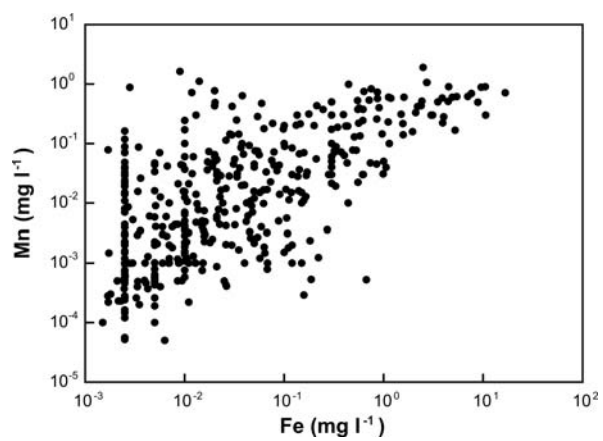
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491

492 Figure 6

493



494

495 Figure 7

496