

1 Manganese concentrations in Scottish groundwater

2

3 Sally C. Homoncik^a, Alan M. MacDonald^{b*}, Kate V. Heal^c, Brighid É. Ó Dochartaigh^b,4 Bryne T. Ngwenya^d.5 ^aMNV Consulting Ltd., Spinningdale, Stirling Road, Callander, Perthshire, FK17 8LE, UK

6 (Formerly The University of Edinburgh/British Geological Survey)

7 ^bBritish Geological Survey, Murchison House, West Mains Road, Edinburgh, EH9 3LA, UK8 ^c The University of Edinburgh, School of GeoSciences, Crew Building, West Mains Road,

9 Edinburgh, EH9 3JN, UK

10 ^d The University of Edinburgh, School of GeoSciences, Grant Institute, West Mains Road,

11 Edinburgh, EH9 3JW, UK

12 *Corresponding author: email: amm@bgs.ac.uk, tel: + 44 131 667 1000; fax: +44 131 668

13 2683

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⁻¹. 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⁻¹; median Mn
22 concentration was 0.013 mg l⁻¹ with 25th and 75th percentiles 0.0014 and 0.072 mg l⁻¹
23 respectively. The Scottish drinking water limit (0.05 mg l⁻¹) was exceeded for 30% of samples
24 and the WHO health guideline (0.4 mg l⁻¹) 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⁻¹ (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⁻¹ 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⁻¹) 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 mg l^{-1} , effects were first
71 noted in a group drinking concentrations 0.08 to 0.25 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 mg l^{-1} (World Health Organization, 2008), although the USA has
74 a lower health reference level of 0.3 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 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 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 µm 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⁻¹
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⁻¹) 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), HCO₃, NO₃-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 log₁₀-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 mg l^{-1} , but there was a wide variation in
169 Mn concentrations and 25th and 75th percentiles were 0.0014 mg l^{-1} and 0.072 mg l^{-1} ,
170 respectively. The Scottish limit for Mn in drinking water of 0.05 mg l^{-1} was exceeded in 30%
171 of samples; the WHO health guideline (WHO, 2008) of 0.4 mg l^{-1} was exceeded in 9%, and
172 the USEPA limit (USEPA, 2003) of 0.3 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 mg l^{-1} and around 20% of wells exceeded the Swedish recommended guideline value for
177 private wells of 0.3 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 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 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 mg l^{-1} and 15% exceeded the New Zealand health guideline of 0.5 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 (25th-75th 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^3 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⁻¹ and the WHO health guideline value of 0.4 mg l⁻¹ 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 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

351 **Acknowledgements**

352

353 The research was jointly funded by the British Geological Survey (BGS) and the School of
354 GeoSciences, The University of Edinburgh. The authors are grateful to BGS/SEPA for
355 access to groundwater data and to the following BGS staff for help and comments: Derek
356 Ball, Fiona Fordyce, Martin Gillespie, David Kinniburgh, Pauline Smedley and Stuart
357 Horsburgh. This paper is published with permission of the Executive Director of the British
358 Geological Survey (NERC).

359

360

361 **References**

362

363 Astron. Private Water Supplies: Technical Manual. Scottish Executive, Edinburgh, 2006.

364 BGS. Manganese in stream sediments: Great Britain. G-BASE Geochemical Map. Keyworth,
365 Nottingham, UK, 2009.

366 BGS. Baseline Scotland: groundwater chemistry data. British Geological Survey

367 <http://www.bgs.ac.uk/data/baselineScotland/home.html> [accessed online on 1

368 February 2010]

369 Bouchard M, Laforest F, Vandelac L, Bellinger D, Mergler D. Hair manganese and

370 hyperactive behaviours: pilot study of school age children exposed through tap water.

371 Environ Health Persp 2007; 115: 122-127.

372 Bourg ACM, Bertin C. Seasonal and spatial trends in manganese solubility in an alluvial

373 aquifer. Environ Sci Technol 1994; 28: 868-876.

374 Casale RJ, LeChevallier MW, Pontius FW. Review of manganese control and related

375 manganese issues. American Water Works Association (AWWA) Research

376 Foundation and AWWA, Denver, 2002.

377 Collins JF, Buol SW. Effects of fluctuations in the Eh-pH environment on iron and/or

378 manganese equilibria. Soil Sci 1970; 110: 111-118.

379 DeSimone LA. Quality of water from domestic wells in principal aquifers of the

380 United States, 1991-2004: US Geological Survey Scientific Investigations

381 Report 2008-5227, 139 p., 2008.

382 Donnelley RR. Drinking Water Quality in Scotland 2007. Drinking Water Quality Regulator

383 for Scotland, 2008.

384 EC. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for

385 human consumption. Official Journal 1998; L330: 32-54.

- 386 Gounot, A-M. Microbial oxidation and reduction of manganese: Consequences in
387 groundwater and applications. *FEMS Microbiol Rev* 1994; 14: 339-350.
- 388 Graham MC, Gavin KG, Farmer JG, Kirika A, Britton A. Processes controlling the retention
389 and release of manganese in the organic rich catchment of Loch Bradan. *Appl*
390 *Geochem* 2002; 17: 1061-1067.
- 391 Graham MT, Ó Dochartaigh BÉ, Ball DF, MacDonald AM. Using transmissivity, specific
392 capacity and borehole yield data to assess the productivity of Scottish aquifers.
393 *Quarterly Journal of Engineering Geology and Hydrogeology* 2009; **42**: 227-235
- 394 Hem JD. Chemical factors that influence the availability of iron and manganese in aqueous
395 systems. *Geol Soc Am Bull* 1972; 83: 443-450.
- 396 Hem JD. Study and Interpretation of the Chemical Characteristics of Natural Water (3rd Ed.).
397 US Geological Survey Water-Supply Paper 2254, 1985.
- 398 Keen CL, Zidenberg-Cherr S. Manganese toxicity in humans and experimental animals. In:
399 Klimis-Tavantzis DJ, editor. *Manganese in Health and Disease*. CRC Press, London,
400 1994, pp. 193-205.
- 401 Kondakis XG, Makris N, Leotsinidis M, Prinou M, Papapetropoulos T. Possible health
402 effects of high manganese concentrations in drinking water. *Arch Environ Health*
403 1989; 44: 175-178.
- 404 Lind CJ, Hem JD, Roberson CE. Reaction products of manganese bearing waters In: Averett,
405 RC, McKnight DM, editors. *Chemical Quality of Water and the Hydrologic Cycle*.
406 Lewis Publishers, Michigan, USA, 1987, pp. 271-302.
- 407 Ljung K, Vahter M. Time to re-evaluate the guideline value for manganese in drinking water?
408 *Environ Health Persp* 2007; 115: 1533-1538.

- 409 MacDonalD A, Ó Dochartaigh BÉ Baseline Scotland; an overview of available groundwater
410 chemistry data for Scotland. British Geological Survey Commissioned Report,
411 CR/05/239N. British Geological Survey, Keyworth, Nottingham, 2005.
- 412 MacDonalD A, Robins NS, Ball DF, Ó Dochartaigh BÉ. An overview of groundwater in
413 Scotland. Scot J Geol 2005; 41: 3-11.
- 414 Marshall KC. Biogeochemistry of manganese minerals. In: Trudinger PA, Swaine DJ,
415 editors. Biogeochemical Cycling of Mineral-Forming Elements. Elsevier/North
416 Holland Publishing Co., 1979, pp. 253-286.
- 417 Morgan JJ, Stumm W. The role of multivalent metal oxides in limnological transformations,
418 as exemplified by iron and manganese. In: Jaag O, editor. Advances in Water
419 Pollution Research. Proceedings of the Second International Conference, August
420 1964, Tokyo. Pergamon Press, 1965; 1: 103-131.
- 421 Nealson KH. Microbial cycle of manganese. In: Krumbein WE, editor. Microbial
422 Geochemistry. Blackwell, Oxford, 1983, pp. 191-221.
- 423 Robins NS. Groundwater quality in Scotland: major ion chemistry of the key groundwater
424 bodies. Sci Total Environ 2002; 294: 41-56.
- 425 Shand P, Edmunds WM, Lawrence AR, Smedley PL, Burke S. The natural (baseline) quality
426 of groundwater in England and Wales. British Geological Survey Research Report
427 RR/07/06. British Geological Survey, Keyworth, Nottingham, 2007.
- 428 Sly LJ, Hodgkinson MC, Arunpairojana V. Deposition of manganese in a drinking water
429 distribution system. Appl Environ Microbiol 1990; 56: 628-639.
- 430 Thamdrup B. Microbial manganese and iron reduction in aquatic sediments. Advances in
431 Microbial Ecology 2000; 16:41-84
- 432 USEPA. Health Effects Support Document for Manganese. EPA 822-R-03-003. US
433 Environmental Protection Agency, Washington, DC, 2003.

- 434 Wasserman GA, Liu X, Parvez F, Ahsan H, Levy D, Factor-Litvak P, Kline J, van Geen A,
435 Slavkovich V, Lolocono NJ, Cheng Z, Zheng Y, Graziano JH. Water manganese
436 exposure and children's intellectual function in Araihaazar, Bangladesh. Environ
437 Health Persp 2006; 114: 124-129.
- 438 World Health Organization. Guidelines for Drinking-water Quality (3rd Ed incorporating the
439 1st and 2nd Addenda), Volume 1 recommendations. World Health Organisation,
440 Geneva, 2008, available online at
441 http://www.who.int/water_sanitation_health/dwq/gdwq3rev/en/ [accessed 19 August
442 2009].
- 443
- 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 $\log_{10}\text{Mn}$</i>		<i>Predicting $\log_{10}\text{Fe}$</i>	
	<i>Incl. Fe</i>	<i>Excl. Fe</i>	<i>Incl. Mn</i>	<i>Excl. Mn</i>
pH	0.001 (-)	<0.001 (-)	0.855 (+)	0.146 (+)
Eh	0.022 (-)	<0.001 (-)	0.001 (-)	<0.001 (-)
DO	<0.001 (-)	<0.001 (-)	0.152 (+)	0.220 (+)
SEC	0.638 (+)	0.169 (+)	0.066 (+)	0.011 (+)
DOC	0.187 (+)	0.060 (+)	0.105 (+)	<0.001 (+)
HCO ₃	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 ₃ -N	0.331 (-)	0.096 (-)	0.214 (-)	0.222 (-)
$\log_{10}\text{Fe}$	<0.001 (+)	---	---	---
$\log_{10}\text{Mn}$	---	---	0.000 (+)	---
Number of samples	119	129	119	125
R ² 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 $\log_{10}\text{Mn}$</i>		<i>Predicting $\log_{10}\text{Fe}$</i>	
	<i>4 predictors</i>	<i>Excl. Fe</i>	<i>6 predictors</i>	<i>Excl. Mn</i>
pH	0.011 (-)	0.005 (-)	0.563 (+)	0.961 (+)
Eh	0.001 (-)	<0.001 (-)	0.011 (-)	<0.001 (-)
DO	0.037 (-)	0.036 (-)	0.999 (-)	0.608 (-)
SEC	---	---	0.286 (+)	---
DOC	---	---	0.047 (+)	0.007 (+)
$\log_{10}\text{Fe}$	0.077 (+)	---	---	---
$\log_{10}\text{Mn}$	---	---	0.322 (+)	---
Number of samples	59	62	34	41
R ² 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).

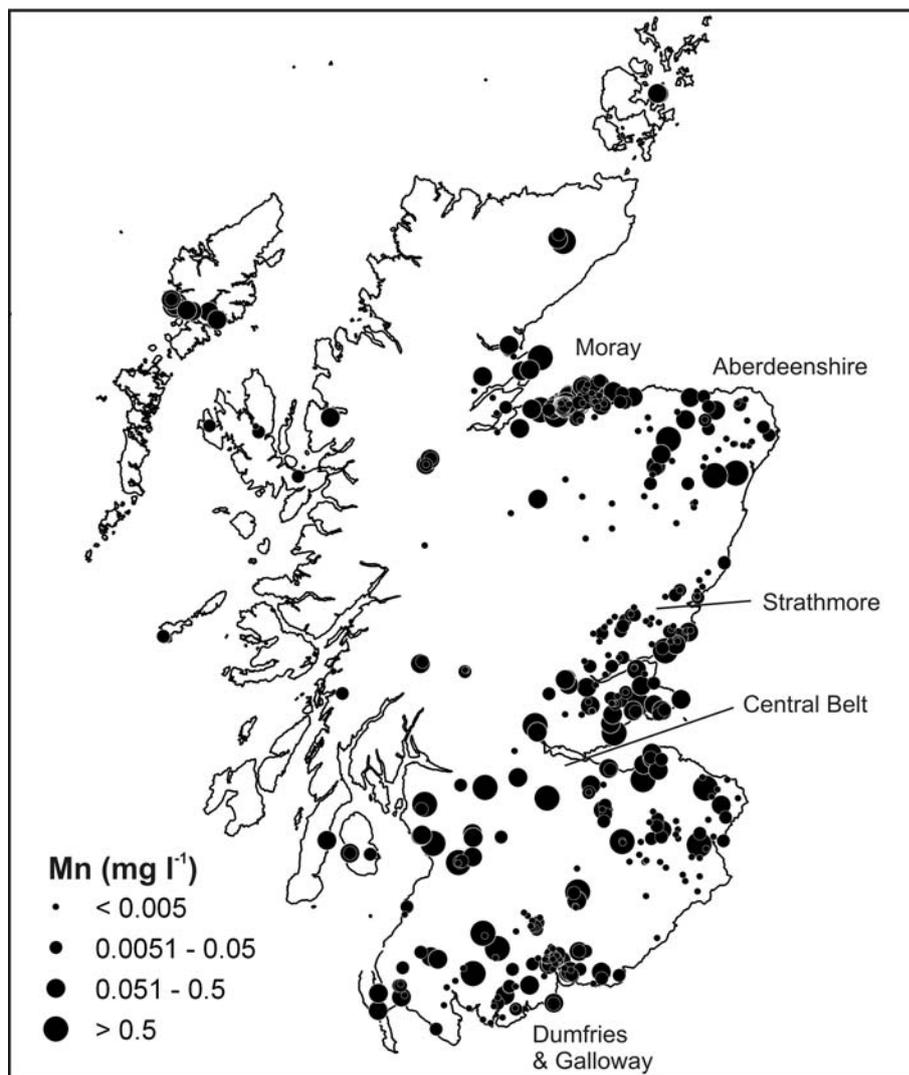
465 Figure 3 Cumulative frequency plot for Mn groundwater concentrations for the Scottish
466 dataset (n = 475).

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)

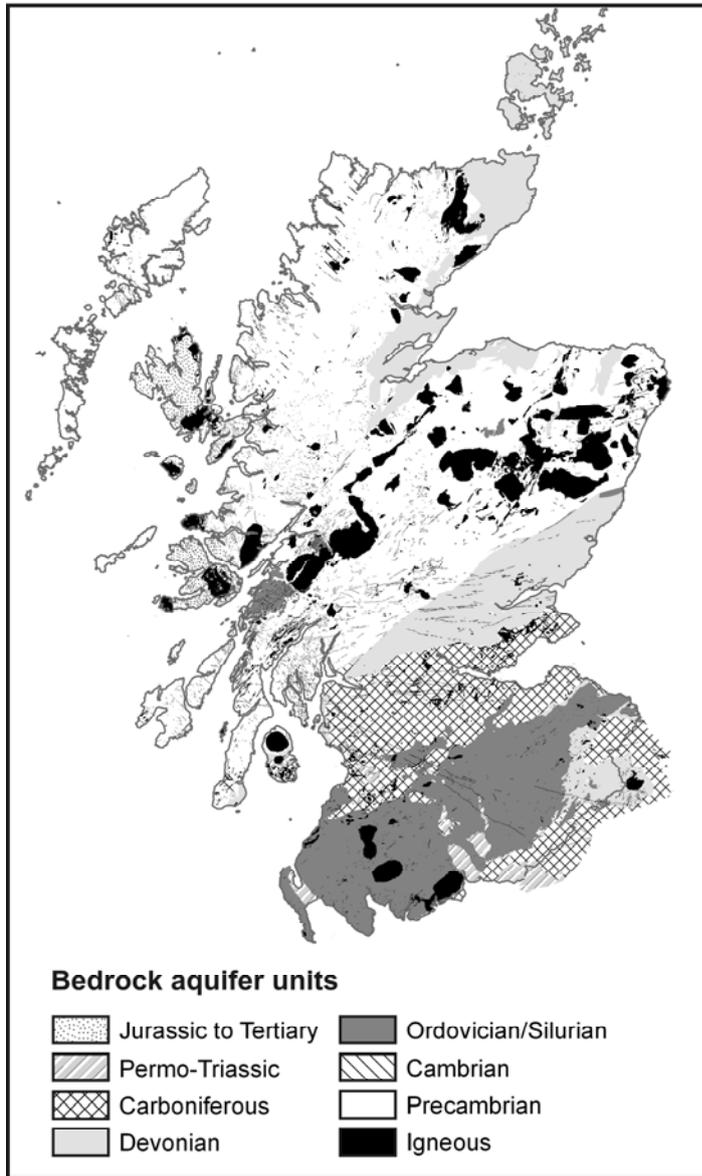
473 Figure 7 Scatter plot of Mn versus Fe concentrations for the Scottish dataset (n = 195,
474 adjusted $R^2 = 0.25$)



475

476 Figure 1

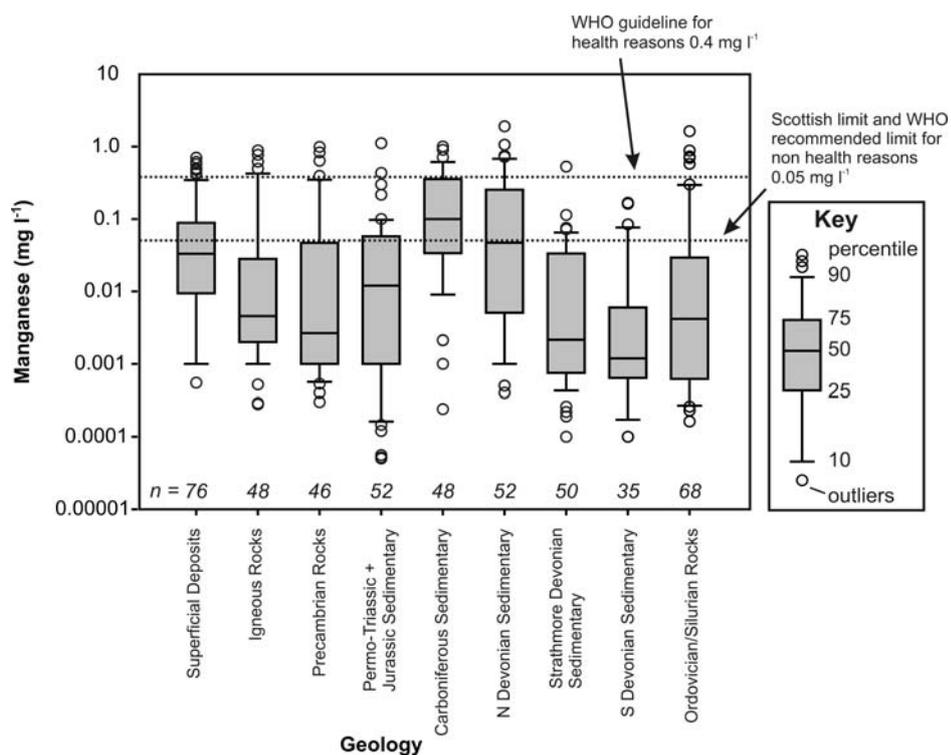
477



478

479 Figure 2

480



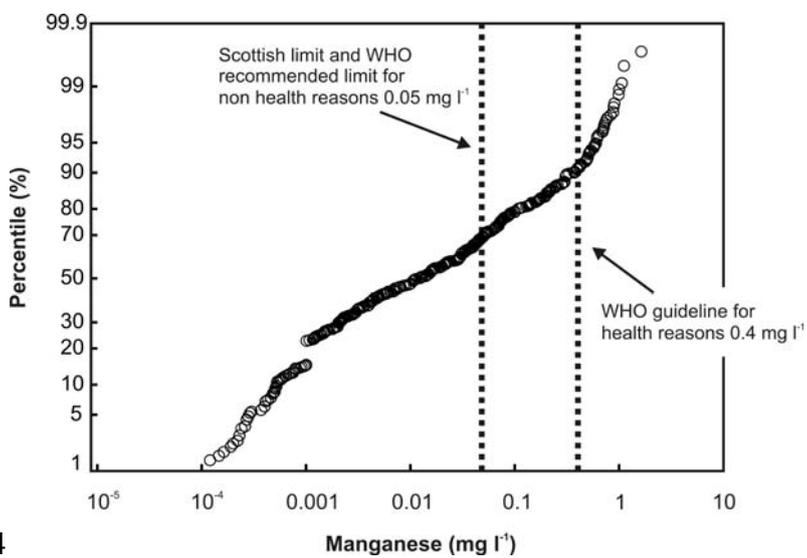
481

482 Figure 3

483

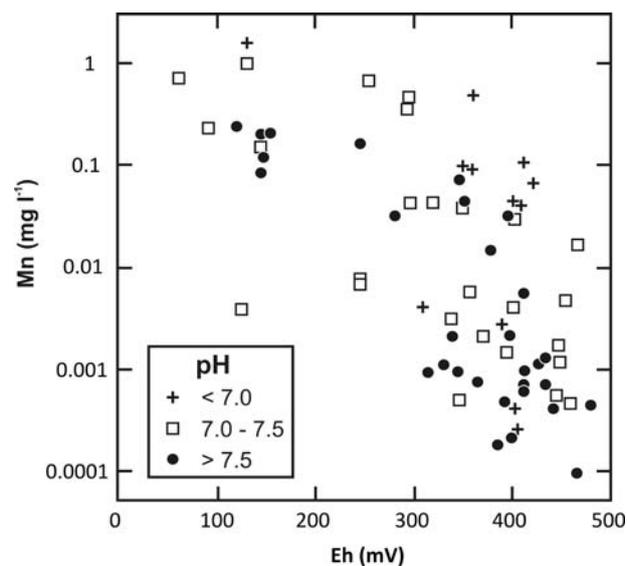
484

485



486 Figure 4

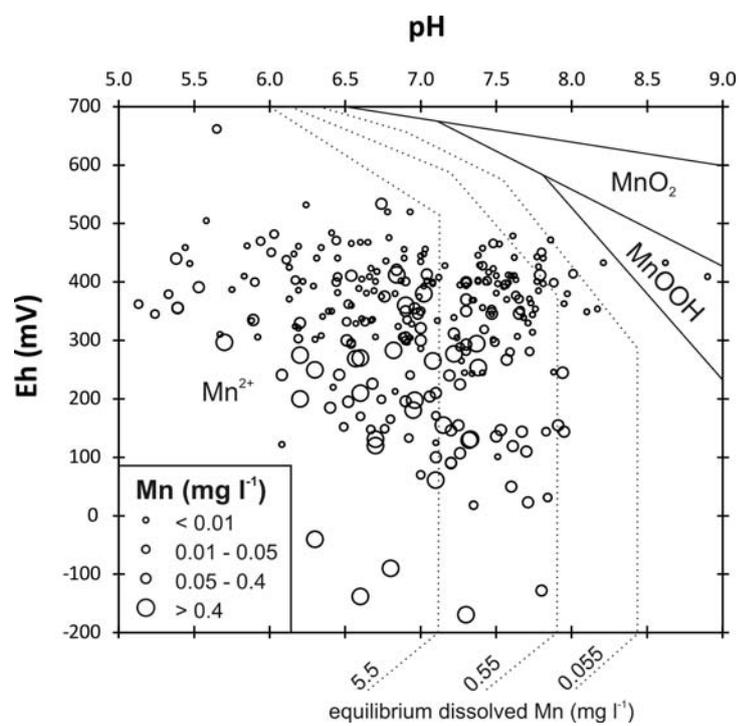
487



488

489 Figure 5

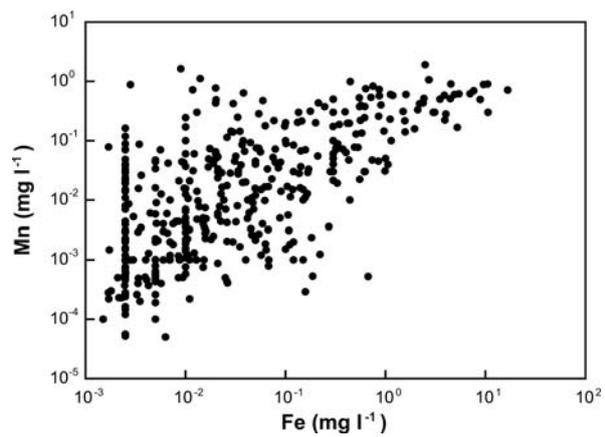
490



491

492 Figure 6

493



494

495 Figure 7

496