Final author submission: Science of the Total Environment 408 (2010) 2467–2473

Manganese concentrations in Scottish groundwater

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Abstract

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

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

1 Introduction

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

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

Furthermore, several studies in different environmental settings have reported significant associations between exposure to Mn in groundwater-sourced drinking water supplies and adverse human health effects. For example, Wasserman et al. (2006) identified a significant negative relationship between well water Mn concentration (0.004-3.91 mg l^{-1}) and measures of intellectual function in 142 children of 10 years of age in Bangladesh (notable difference in intellectual function between <0.2 mg l^{-1} group and > 1 mg l^{-1} group). Mn exposure associated with drinking water was also significantly positively related with hyperactive classroom behaviours in a study of 46 children in Québec (Bouchard et al., 2007). In adults, exposure to elevated Mn concentrations in drinking water has been associated with manganism, a Parkinson-like disorder. In a study in Greece (Kondakis et al., 1989), neurological symptoms of chronic Mn poisoning were found to increase with exposure to Mn from groundwater-sourced water supplies in three populations of adults with similar social and dietary characteristics (concentrations ranging from 0.0036 to 2.3 mg l^{-1}, effects were first noted in a group drinking concentrations 0.08 to 0.25 mg l^{-1}). Because of the association between Mn intake and neurological effects , the WHO current guideline concentration for Mn in drinking water is 0.4 mg l^{-1} (World Health Organization, 2008), although the USA has a lower health reference level of 0.3 mg l^{-1} (USEPA, 2003). In the studies by Wasserman et al. (2006) and Kondakis et al. (1989) there was evidence of a dose-response relationship between the severity of neurotoxic effects and exposure to Mn in well water suggesting that exposure to Mn concentrations *below* the WHO guideline value could still result in adverse health effects, with children most vulnerable (Ljung and Vahter, 2007). Consequently Bouchard et al. (2007) recommend that further research is required to establish adequate guidelines for Mn in drinking water.

The occurrence and concentration of Mn in groundwater is controlled by many factors, the main ones being rock geochemistry, water chemistry and microbiological activity. Some rock types, such as mafic and ultramafic rocks, shale, greywacke and limestone, contain high concentrations of Mn, which can lead to elevated concentrations in soil and sediment through weathering processes. Water chemistry, in particular pH, redox potential (Eh), dissolved oxygen (DO), and dissolved organic carbon (DOC), is instrumental in mobilising Mn and controlling its speciation and concentration in the water environment. Manganese occurs mainly as the reduced soluble Mn^{2+} at lower pH and Eh, but is oxidised to form precipitates in the presence of oxygen and at higher pH (Hem, 1985). Hence in equilibrium conditions Mn is likely to occur as Mn^{2+} at pH<7 and at Eh as high as 800 mV. Complexation with humic substances (e.g. Graham et al., 2002) inhibits Mn oxidation and precipitation, although complexation with inorganic ligands, such as sulphate or hydrogen carbonate, is suggested to have only a limited effect on Mn speciation and concentration, apart from at very high ligand concentrations (Hem, 1972). Micro-organisms can play an important role in Mn mobilisation in the environment and can both enhance or inhibit concentrations in groundwater. The effects can be direct, through enzymatic catalysis of Mn oxidation and reduction and specific binding by cell-associated materials, or indirect, by altering the pH and Eh conditions of the micro-environment, thereby influencing Mn speciation and concentration (Nealson, 1983). The impact of microbiological activity on Mn behaviour in water is frequently evident in the accumulation of oxidised Mn in biofilms on surfaces such as pipes (Sly et al., 1990). The factors described above frequently interact to determine Mn concentrations in groundwater. For example, Bourg and Bertin (1994) and Gounot (1994) attributed spatial and temporal changes in Mn concentrations in two alluvial aquifers in France to different mineralogical forms of Mn and also to the reduction of solid Mn oxides to the dissolved form in anaerobic conditions generated by microbial degradation of organic matter.

There is increasing evidence (Robins, 2002; MacDonald and Ó Dochartaigh, 2005) that Mn is often present in Scottish groundwaters at concentrations in excess of the Scottish drinking water supply limit of 0.05 mg l^{-1}(as defined by the Water Supply (Water Quality)(Scotland) Act 2001) and may be in excess of the WHO guideline value of 0.4 mg l^{-1}. In Scotland groundwater is the main source of water for an estimated 30,000 private water supplies and approximately 7% of public water supplies and is also a major contributor to environmental flows, through baseflow to rivers and streams (MacDonald et al., 2005). Concerns related to excessive Mn concentrations are greatest for private water supplies, which are generally groundwater based, but are not subject to such stringent testing as public water supplies so that elevated concentrations could go unnoticed.

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

2 Methods

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

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

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

The final dataset contained data for Mn in groundwater from 475 sites across Scotland (Figure 1). Data were divided into nine geological categories, based on the principal geological units from which samples were taken (Figure 2). Categories were chosen to enable comparison with previous work on characterising Scottish aquifers (MacDonald and Ó Dochartaigh, 2005) and to contain sufficient numbers of samples for analysis to determine the effect of geology on Mn concentrations. Relationships between Mn and a number of other physicochemical parameters measured in the same samples (where available) which are likely to influence Mn concentrations (Eh, pH, DO, DOC, specific electrical conductance (SEC), HCO_3, NO_3-N, Fe, Ca, Mg) were examined using scatter plots and multiple linear regression to assess the effect of water chemistry on Mn concentrations. Mn and Fe concentrations were $\log_{10}$-transformed for the regression analyses, conducted in Minitab v.15, in order to normalise the data distributions. P values were used to test significance at 95% probability.

3 Results

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

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

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

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

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

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

3.2 Analysis of data for the Devonian sedimentary aquifer

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

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

4 Discussion

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

4.1 Geology as a control on Mn concentrations

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

4.2 pH and redox conditions as controls on Mn concentrations

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

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

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

4.3 Fe as a control on Mn concentrations

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

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

4.4 Implications for groundwater monitoring

The research results have particular implications for monitoring of private water supplies in Scotland, which are often groundwater based. Water quality standards for private supplies in Scotland are derived from EC regulation, and monitoring and protection is carried out by local authorities. The level of monitoring depends on whether a private water supply is classified as Type A (providing 10 m^3 or more per day, supplying 50 or more people, or used for commercial or public activity) or Type B supplies (all others) (Astron, 2006). Chemical parameters are tested for in both types of supply, but Type A supplies are subject to more regular and stringent testing and enforcement of water quality regulations than Type B, which are only monitored on a discretionary basis (Donnelley, 2008). Therefore, Mn may not be tested and high concentrations can go undetected.

Another major issue is sampling protocol. Samples collected for routine monitoring carried out by the regulatory bodies are often not filtered or acidified in the field, giving unreliable Mn data. In creating the dataset used for this Scottish study, a comparison was undertaken between samples collected with good and poor protocol for 40 locations. For samples with poor field protocol Mn concentrations were consistently underestimated by more than an order of magnitude. In addition, for a reliable measure of exposure to Mn for public health reasons, samples would need to be taken throughout the year to capture natural variations. The range of Mn concentrations encountered in each geological unit also has implications for groundwater monitoring. Manganese concentrations in excess of the Scottish limit of 0.05 mg l^{-1} and the WHO health guideline value of 0.4 mg l^{-1} were found in each aquifer unit, and there was more variability within each unit than between them. Therefore, developing hazard maps identifying areas of potential elevated Mn concentrations from geology alone are unlikely to be effective. Monitoring therefore needs to be widespread.

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

5 Conclusion

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

Acknowledgements

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

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

	Predicting $\log_{10}$Mn		*Predicting $\log_{10}$Fe*	
	Incl. Fe	*Excl. Fe*	*Incl. Mn*	*Excl. Mn*
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 (-)
$\log_{10}$Fe	**<0.001 (+)**	---	---	---
$\log_{10}$Mn	---	---	**0.000 (+)**	---
Number of samples	119	129	119	125
R^2 Adjusted for sample size	50%	42%	45%	41%

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

	Predicting $\log_{10}$Mn		*Predicting $\log_{10}$Fe*	
	4 predictors	*Excl. Fe*	*6 predictors*	*Excl. Mn*
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 (+)**
$\log_{10}$Fe	0.077 (+)	---	---	---
$\log_{10}$Mn	---	---	0.322 (+)	---
Number of samples	59	62	34	41
R^2 Adjusted for sample size	61%	58%	53%	58%

Figure Captions

Figure 1	The location of groundwater sites in Scotland sampled for manganese to an appropriate standard.
Figure 2	Bedrock aquifer units in Scotland (from MacDonald et al., 2005; Graham et al., 2009).
Figure 3	Cumulative frequency plot for Mn groundwater concentrations for the Scottish dataset (n = 475).
Figure 4.	Box plot of Mn concentrations, divided into the main different aquifer units in Scotland
Figure 5	The relation between Mn concentrations, Eh and pH for groundwater samples from the Devonian sedimentary aquifer. Eh exhibits the largest control.
Figure 6	Data plotted on a predominance diagram for Mn speciation (Hem 1985, PhreeqC)
Figure 7	Scatter plot of Mn versus Fe concentrations for the Scottish dataset (n = 195, adjusted $R^2 = 0.25$)

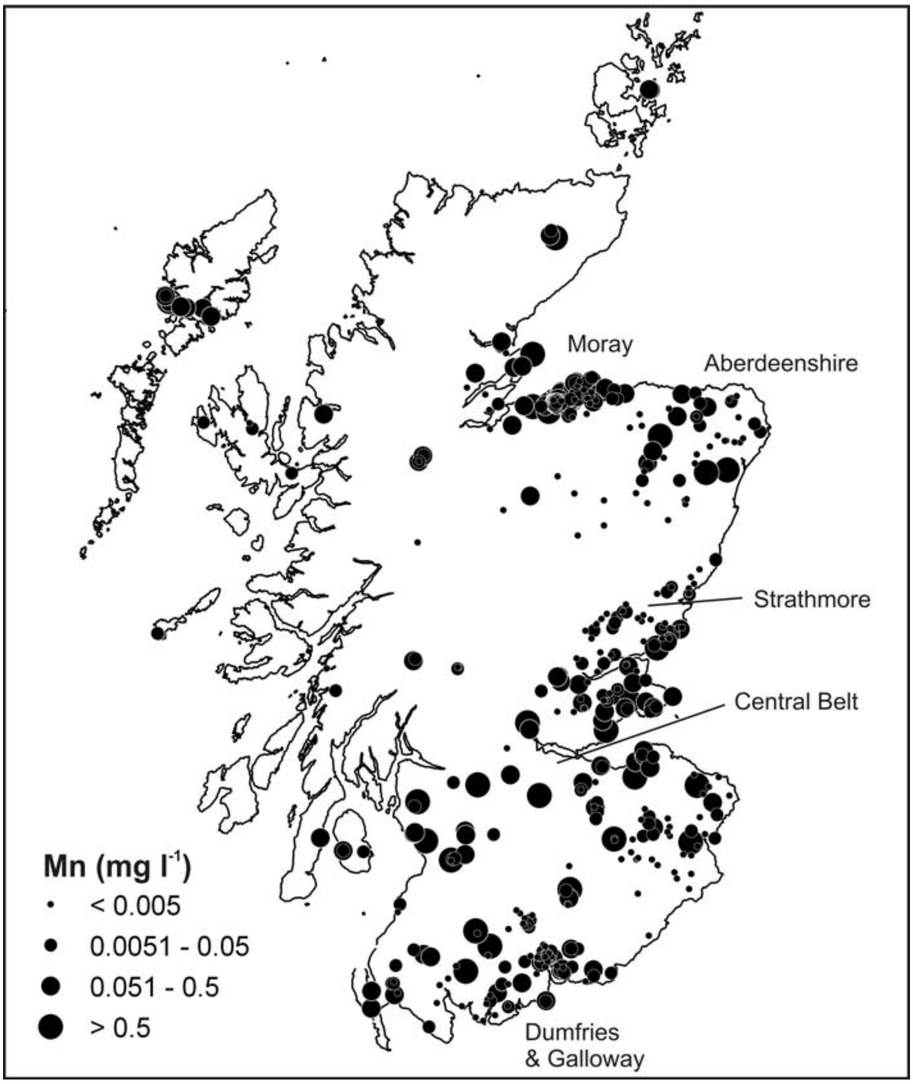
Moray
Aberdeenshire
Strathmore
Central Belt
Dumfries & Galloway
Mn (mg l^{-1})
< 0.005
0.0051 - 0.05
0.051 - 0.5
> 0.5

Figure 1

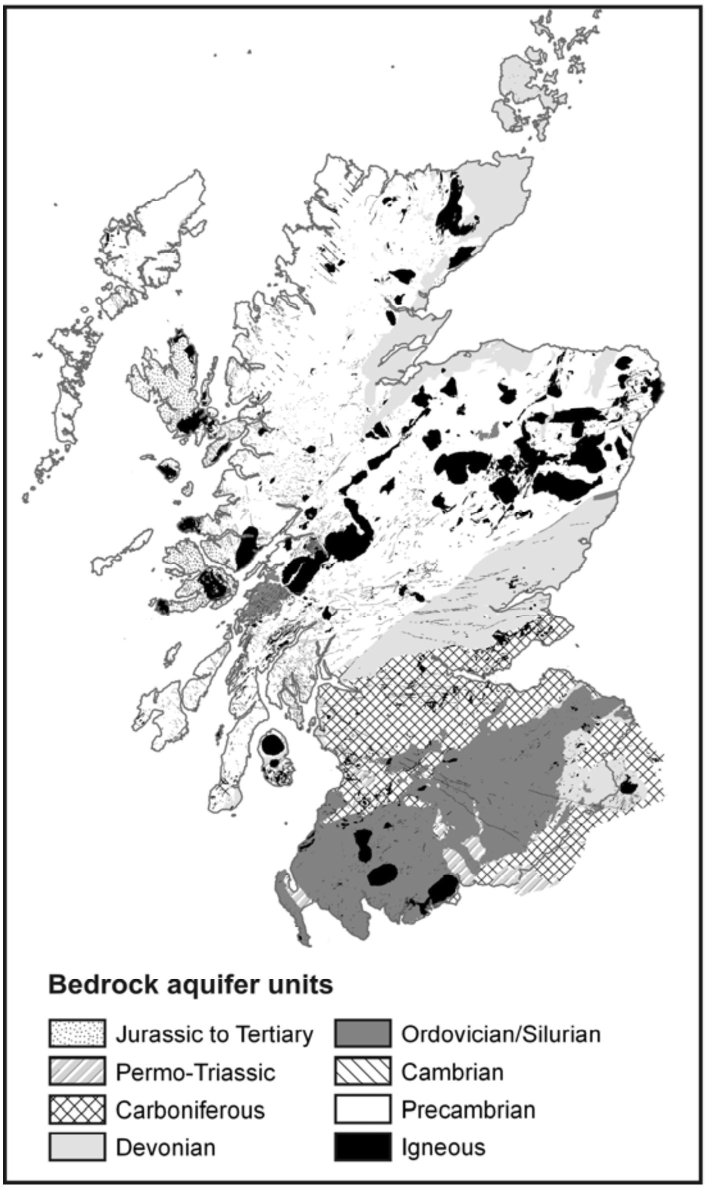
Bedrock aquifer units
Jurassic to Tertiary
Permo-Triassic
Carboniferous
Devonian
Ordovician/Silurian
Cambrian
Precambrian
Igneous

Figure 2

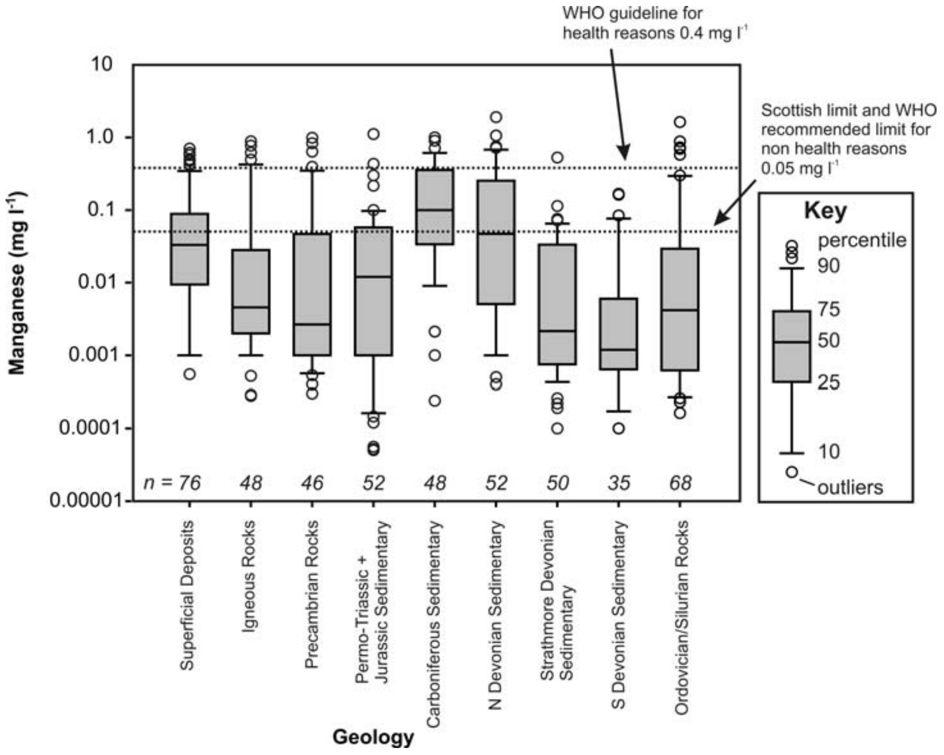

Figure 3

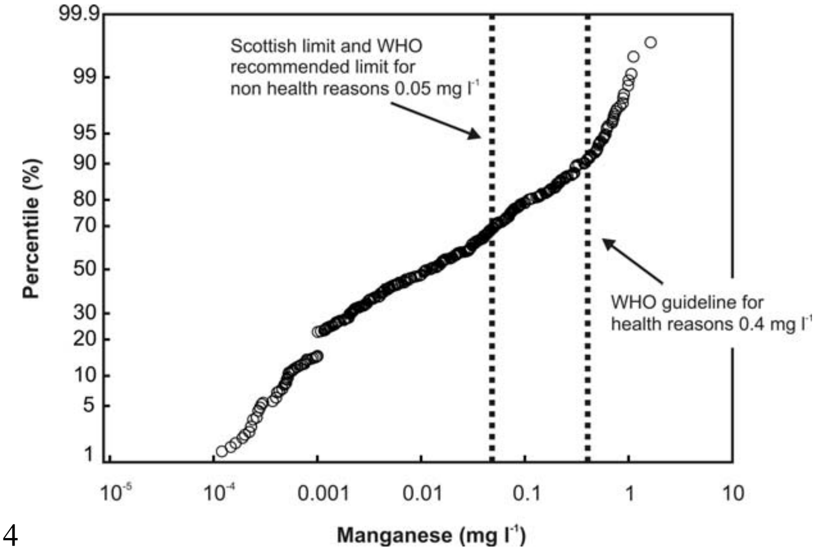

Figure 4

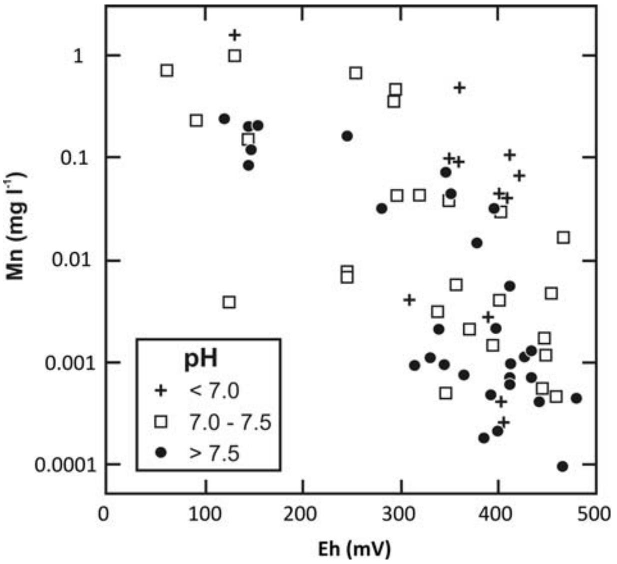

Figure 5

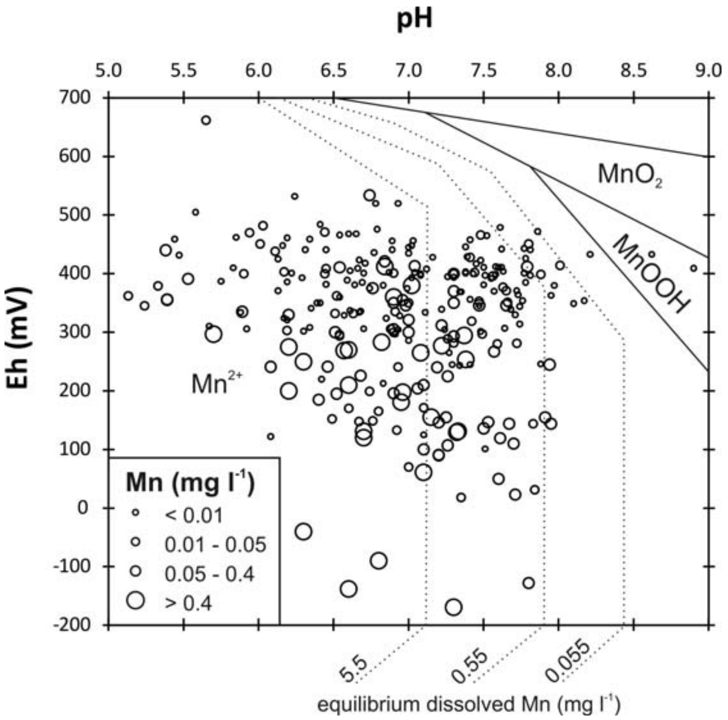

Figure 6

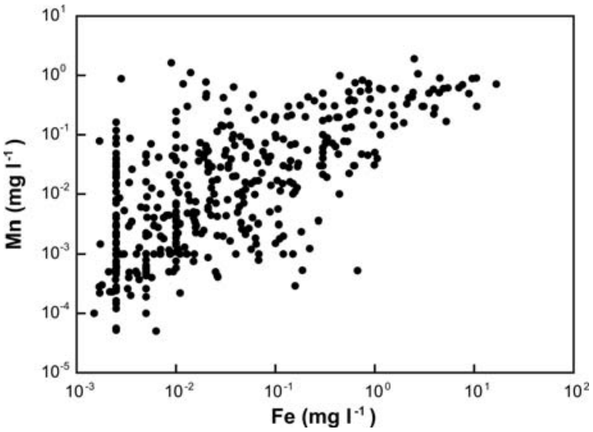
Mn (mg l⁻¹)
10¹
10⁰
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
Fe (mg l⁻¹)
10⁻³
10⁻²
10⁻¹
10⁰
10¹
10²

Figure 7