

Iron and manganese in New Zealand's groundwater

Christopher J. Daughney

Institute of Geological and Nuclear Sciences, PO Box 30368, Lower Hutt, New Zealand

Abstract

Groundwater is used extensively in New Zealand for urban and rural water supply, agriculture and industry, and thus the quality of existing supplies must be monitored and protected. This investigation focuses on groundwater concentrations of iron (Fe) and manganese (Mn), which can pose health risks and cause a variety of engineering and aesthetic problems at high concentrations. This study used a compilation of close to 10,000 groundwater samples that had been collected by 15 regional authorities and analysed for Fe and/or Mn. The median values for dissolved Fe and Mn were 0.08 and 0.01 g m⁻³, respectively. Of the samples tested, 36% exceeded the aesthetic guideline values for Fe (0.2 g m⁻³) and 39% exceeded the values for Mn (0.05 g m⁻³). Of the samples tested for Mn, 15% exceeded the maximum allowable value for health (0.5 g m⁻³). Groundwaters from aquifers in basalt, shellbed and sandstone are the least likely to have high concentrations of Fe and/or Mn, whereas groundwaters from gravel and sand aquifers are the most likely to have elevated Fe and/or Mn concentrations. The groundwater Fe and Mn concentrations are not correlated to one another or to pH or water extraction depth, so (redox) equilibrium-based models do not accurately predict Fe and Mn concentrations in groundwaters.

Introduction

Groundwater is used extensively in New Zealand for urban and rural water supply, for agriculture and for industry. Approximately

one quarter of the New Zealand population depends exclusively on groundwater for its drinking water; groundwater is the sole source of water for the cities of Napier, Hastings, Wanganui, Lower Hutt and Christchurch (Davies, 2001). Many smaller towns are fully or partially dependent on groundwater for a water supply, and a large number of farms use groundwater for domestic supplies. Agriculture is a substantial user of groundwater, primarily for irrigation, but also for frost control. The fruit and animal processing industries, brewing, dairy, metal smelting and processing, and even fish farming use groundwater as a water supply. In total, between 30 and 50% of the abstract water use in New Zealand is from groundwater resources (Fenemor and Robb, 2001; White, 2001). Because groundwater is used by so many individuals, organisations and industries across New Zealand, the quality of existing groundwater resources must be monitored and maintained.

Of interest in this communication are the concentrations of iron (Fe) and manganese (Mn) in New Zealand's groundwaters. As components of groundwater, Fe and Mn are rarely anthropogenic, but rather are introduced to groundwater through natural interactions of water with rock. Nonetheless, high Fe and/or Mn concentrations in groundwater are problematic and pose potential health risks. The 1995 Drinking Water Standards for New Zealand (DWSNZ) indicate that dissolved Fe or Mn concentrations in excess of 0.2 or 0.05 g m⁻³, respectively, can cause numerous engineering

and aesthetic problems (e.g. clogging of pipes, staining of laundry, unpleasant smell or taste), and dissolved Mn concentrations greater than 0.5 g m^{-3} pose a health risk (Ministry of Health, 1995). Groundwaters that exceed the DWSNZ guidelines for Fe and/or Mn can be found in most regions of New Zealand, and are particularly common in the Otago, Bay of Plenty, Southland, Marlborough and Waikato regions (Rosen, 2001). Despite the frequency of elevated levels of these elements in groundwaters, and the associated risks, detailed maps at the national scale of Fe and Mn concentrations in groundwater are not available. In addition, relationships between high Fe and Mn concentrations and factors such as aquifer geology and water extraction depth have not been examined at a national scale (Rosen, 2000).

Fe and Mn concentrations in groundwater are monitored by several organisations in New Zealand. For example, the Institute of Geological and Nuclear Sciences (GNS) operates a National Groundwater Monitoring Programme (NGMP) (Rosen, 1997; Rosen, 1999; White and Rosen, 2002). As of 2002, the NGMP involved quarterly sampling of 107 wells, with sample sites in areas under 12 regional councils and 3 unitary authorities (Gisborne, Tasman and Marlborough). Work related to the NGMP has shown that 27% of the wells monitored through the programme have median dissolved Fe concentrations greater than 0.2 g m^{-3} , 32% of the wells have median dissolved Mn concentrations greater than 0.05 g m^{-3} , and 15% of the wells have median dissolved Mn concentrations greater than 0.5 g m^{-3} (Rosen, 2001). Groundwater monitoring programmes are also operated by regional, district and city councils independently of the NGMP. Through such programmes, over 3000 groundwater samples are collected and analysed in New Zealand every year. These programmes involve the collection and analysis of groundwater using a variety of

protocols, for a variety of purposes. Finally, many other groundwater analyses are conducted for compliance monitoring. Despite the number of groundwater samples collected annually in New Zealand, the individuals and organisations collecting the data are not, at present, routinely sharing or collating their data.

This paper presents a collation and analysis of data pertaining to dissolved and total Fe and Mn concentrations in New Zealand's groundwaters. Data were provided by 15 local governmental organisations, and in conjunction with data from the NGMP, chemical analyses of 9784 water samples from 2827 locations were available. The data set included analyses of soluble (dissolved) Fe (denoted here as Fe_s) from 429 sites, total Fe (Fe_T) from 2703 sites, soluble Mn (Mn_s) from 212 sites, and total Mn (Mn_T) from 1994 sites. These data were used to generate maps of Fe and Mn concentrations in New Zealand's groundwaters, and assess relationships between Fe and Mn concentrations and pH, aquifer lithology, water extraction depth, and the supplier of the data.

Methods

A total of 9784 groundwater samples were analysed, from 2827 locations across New Zealand (Table 1). The majority of these groundwater samples were collected and analysed by regional council staff for their own groundwater monitoring programmes. For this investigation, regional authority groundwater staff were asked to supply all available groundwater data for which Fe and Mn concentrations were known, along with a site identifier (site name) and location. In addition, information on date of sample collection, aquifer lithology and aquifer depth were requested if available. Within each region, groundwater samples were also collected from selected sources by regional council staff in accordance with the protocols

Table 1 – Sources of data used in this investigation.

Data supplier and abbreviation	# Analyses	# Locations*	
Auckland Regional Council (ARC)	109	23	(6)
Environment Bay of Plenty (EBOP)	645	62	(6)
Environment Canterbury (ECAN)	3265	1000	(6)
Environment Southland (ES)	507	441	(7)
Environment Waikato (EW)	540	340	(10)
Gisborne District Council (GDC)	605	18	(6)
Hawke's Bay Regional Council (HBRC)	672	24	(7)
Horizons Manawatu-Wanganui (HMW)	700	69	(4)
Marlborough Regional Council (MRC)	119	45	(7)
Northland Regional Council (NRC)	170	63	(8)
Otago Regional Council (ORC)	830	321	(7)
Taranaki Regional Council (TRC)	62	9	(6)
Tasman District Council (TDC)	568	87	(10)
Wellington Regional Council (WRC)	840	320	(10)
West Coast Regional Council (WCRC)	152	11	(7)
Total	9784	2827	(107)

* Values in parentheses show the number of wells sampled in conjunction with the National Groundwater Monitoring Programme.

of the NGMP, operated in collaboration with GNS. These data are held within a GNS database, and were extracted to obtain sample location (northing and easting), water extraction depth (defined as depth of the well screen), aquifer lithology, pH, and concentrations of Fe and Mn. The concentrations of other analytes (e.g. Na, Ca, K, etc.) were not compiled in this survey. Water extraction depth does not reflect depth of the water table for a given sample or whether the aquifer was confined or unconfined, because water level data and hydrogeology were not compiled in this study. Sample locations are presented in Figure 1.

In conducting their own groundwater monitoring programmes, individual regional councils use a variety of methods for collecting, preserving, transporting and analysing groundwater samples. These methods may change over time, particularly if surveys with specific objectives are undertaken, and in some cases, the methods are not recorded. In general, water samples were collected from bores or wells using plastic bottles. If the source was not flowing (artesian) or used for production, the well was purged prior

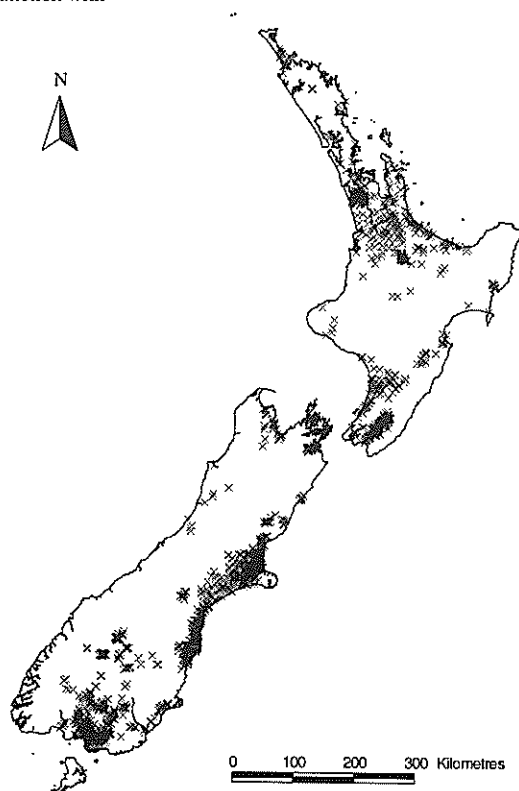


Figure 1 – Groundwater sample locations.

to sampling. A variety of criteria were used to assess the adequacy of the well purging operation. In some cases, the well was purged of a particular volume of water (typically three well volumes); in others, the well was purged for a standard amount of time (judged to be appropriate based on the experience of the sampler). In yet other cases, the well was purged until the conductivity, pH and/or temperature of the extracted water appeared to be stable over time. Finally, in some cases, the well was purged until the water appeared visually clear. Following the purging of the well, a field measurement of pH was usually made (for roughly 75% of the samples collected). Most of the groundwater samples were not filtered in the field. Those samples that were field-filtered were passed through a disposable 0.45 μm membrane using a disposable syringe. For the remainder of this paper, analyses of field-filtered samples are assumed to reflect the fraction of the metal that is soluble (Fe_S and Mn_S). Analyses of unfiltered samples are assumed to reflect total metal concentrations (Fe_T and Mn_T). In most (but not all) cases, the groundwater samples were acidified immediately after collection, usually with a few drops of concentrated nitric acid. Roughly half of the water samples were transported to the laboratory on ice; the remaining samples were not chilled during transport. In most cases, the water samples reached the laboratory within 48 hours of collection. The water samples were analysed at a variety of laboratories, some commercial and some operated by regional councils. Metal concentrations were analysed using Inductively Coupled Plasma Mass Spectroscopy, Inductively Coupled Plasma Optical Emission Spectroscopy, or Flame or Graphite Furnace Atomic Absorption Spectroscopy. Several other elements and parameters may have been analysed along with Fe and Mn, but were not compiled for this investigation. Variations in the methods used for sample

collection, preservation, transportation and analysis, such as those described above, can cause significant biases, artefacts and errors in the data (Freeze and Cherry, 1979; Domenico and Schwartz, 1990).

In addition to the groundwater samples collected by regional councils for their own monitoring programmes, groundwater samples were collected from selected sources in accordance with the protocols of the NGMP, which have been the same since 1997 (Rosen, 1997). Groundwater samples were collected four times per year (March, June, September and December) by regional council staff. Prior to sample collection, wells were purged of three well volumes of standing water, and pH and/or conductivity were monitored for stability. From each site, unfiltered, filtered (0.45 μm), and filtered and acidified (nitric acid) samples were collected using plastic bottles provided by GNS. All samples were placed on ice in chilly bins immediately after collection and for the duration of their transportation to the GNS Analytical Facility in Wairakei. Details of the analytical methods used are described by Rosen (1997). The groundwater samples analysed through the NGMP provide a useful baseline against which analyses from individual regional council monitoring programmes can be meaningfully compared.

All data were compiled using a spreadsheet, and statistical analyses were made following Sokal and Rohlf (1995). Often, analyses taken on different dates were available for a single location. In this case, the multiple analyses were averaged, and the average value was used in all subsequent statistical tests. Thus, all statistical tests were weighted to account for the number of analyses available from each location. Each numerical field was tested for outliers using Dixon's test on ordered arrays, and all outliers were removed. The outliers identified in this manner appeared to represent data entry errors. Each numerical

field was tested for homogeneity of variance using Bartlett's test and for normality using the Kolmogorov-Smirnov test. Appropriate statistical tests were then selected to evaluate relationships between Fe_S , Fe_T , Mn_S and Mn_T , and between each of these and pH, water extraction depth, aquifer lithology, and data supplier.

Results and discussion

Descriptive statistics for Fe_S , Fe_T , Mn_S , Mn_T , pH and water extraction depth provide a general introduction to the data (Table 2). These statistics were calculated after outliers ($\alpha = 0.01$) were removed (1, 3, 1, 1, 0 and 2 outliers in Fe_S , Fe_T , Mn_S , Mn_T , pH and water extraction depth, respectively). The number of data points available for each variable ranged from 212 for Mn_S to 2703 for Fe_T . In only 35 cases were data for all six variables available from single locations. Fe_S , Fe_T , Mn_S and Mn_T were not normally distributed (see below), so the median, rather than the average, was used as an indicator of the central tendency of each variable. Based on the available data, the median values for dissolved Fe and Mn concentrations were calculated to be 0.08 and 0.01 $g\ m^{-3}$, respectively. Of the 430 groundwaters analysed for Fe_S , 36% were above the DWSNZ aesthetic

guideline (0.2 $g\ m^{-3}$), and of the 214 samples analysed for Mn_S , 39% were above the DWSNZ aesthetic guideline (0.05 $g\ m^{-3}$) and 15% were above the health guideline (0.5 $g\ m^{-3}$).

Maps showing groundwater concentrations of Fe_S , Fe_T , Mn_S and Mn_T indicate that most regions of New Zealand have elevated levels of Fe, Mn or both (Figs. 2-5). The maps of Fe_S and Mn_S highlight sample locations with average concentrations in excess of DWSNZ aesthetic guidelines (0.2 and 0.05 $g\ m^{-3}$, respectively), and maps of Fe_T and Mn_T highlight sample locations with concentrations in the upper quartile of the population (3.5 and 2.0 $g\ m^{-3}$, respectively).

Tests for normality and homogeneity of variance indicated that the data subsets were log normal but heteroscedastic (of unequal variance) ($\alpha = 0.05$) in most cases (for Fe_S , Fe_T , Mn_S and Mn_T grouped either by data supplier or aquifer lithology). To facilitate the log transformation, concentrations recorded as zero or "below detection" were assigned a value equal to 0.55 times the detection limit of the analysis (Sanford *et al.*, 1993). In addition, some data subsets had less than five values for a given analyte. These were considered insufficient to perform statistical analyses, so were not considered

Table 2 – Descriptive statistics for concentrations of dissolved and total iron and manganese ($g\ m^{-3}$), pH and Water Extraction Depth for samples used in this study.

Statistic	Fe_S	Fe_T	Mn_S	Mn_T	pH	WED
Median	0.08	0.12	0.33	0.24	6.7	22.8
Minimum	< 0.001	< 0.001	< 0.001	< 0.001	4.0	1.1
Maximum	47.0	42.5	12.4	54.0	10.7	863
# Samples	430	2701	214	1996	2498	2370

Fe_S – Soluble iron concentration ($g\ m^{-3}$) Fe_T – Total iron concentration ($g\ m^{-3}$) Mn_S – Soluble manganese concentration ($g\ m^{-3}$) Mn_T – Total manganese concentration ($g\ m^{-3}$) WED – Water extraction depth (m)

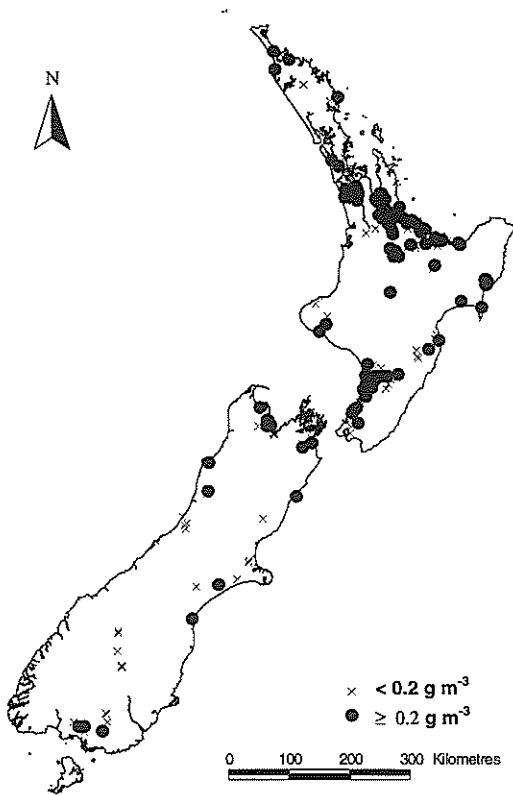


Figure 2 – Locations of groundwater sample points with average dissolved Fe concentrations greater than (large dots) or less than (small crosses) 0.2 g m^{-3} (DWSNZ aesthetic guideline – Ministry of Health 1995).

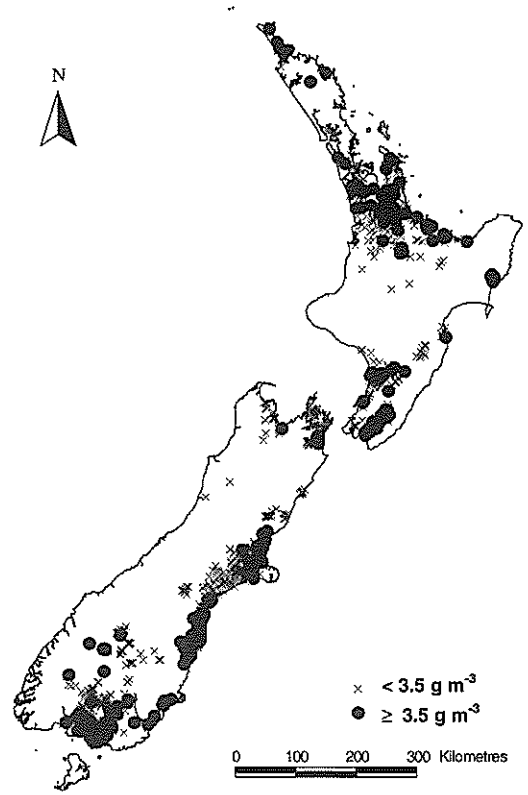


Figure 3 – Locations of groundwater sample points with average total Fe concentrations greater than 3.5 g m^{-3} (large dots) or less than 3.5 g m^{-3} (small crosses) (upper quartile).

further. The non-normality of the data reflects a large proportion of samples with very low concentrations of Fe and Mn. This indicates that the majority of samples collected were representative of “background” concentrations of these elements, i.e. the data sets were not biased by collection of a large proportion of samples from areas deemed to be “contaminated” with Fe and/or Mn.

As a result of the heteroscedasticity, the student’s t-test (assuming unequal variances) was applied to log-transformed data to evaluate relationships between the concentrations of Fe and Mn in groundwater and

aquifer lithology or the regional council that supplied the data. Based on the t-test, the majority of regions (data suppliers) were shown to have equivalent ($\alpha = 0.05$) distributions of concentrations of Fe_S , Fe_T , Mn_S and Mn_T (Table 3, Fig. 6). Gisborne District Council (GDC) is the only exception, having a higher ($\alpha = 0.05$) median concentration of Fe_T than any other region. This similarity of Fe and Mn concentrations across all regions of New Zealand can be interpreted in several ways. First, because the concentrations of Fe and Mn vary more within individual regions than they vary

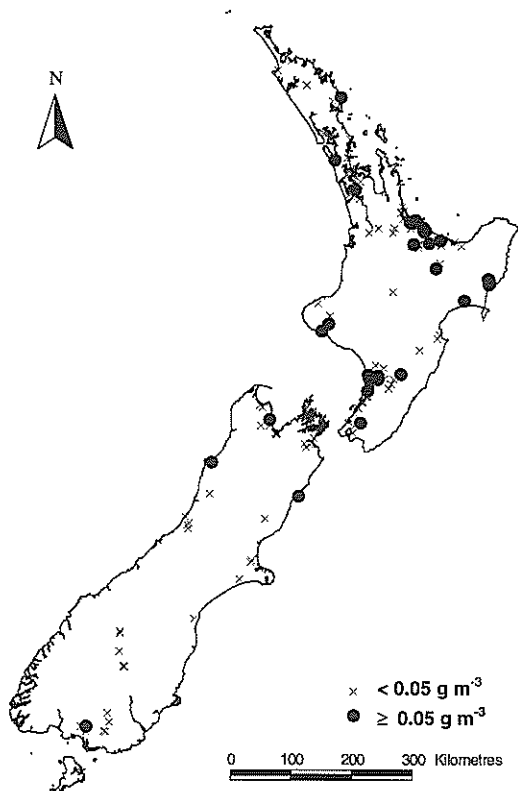


Figure 4 – Locations of groundwater sample points with average dissolved Mn concentrations greater than 0.05 g m^{-3} (large dots) or less than 0.05 g m^{-3} (small crosses) (DWSNZ aesthetic guideline – Ministry of Health 1995).

between different regions, it is not possible to detect any significant bias in the data that might be caused by sampling or analytical techniques employed by a single regional council. Second, by corollary, variations of Fe and Mn concentrations are most likely due to hydrogeochemical processes that operate on the aquifer scale (rather than on the scale of a regional council). Third, if Fe and Mn data from all of New Zealand can be assumed to be part of the same distribution, then it is reasonable to compile data from the entire country for subsequent analysis of the effects of other possible governing parameters (see below).

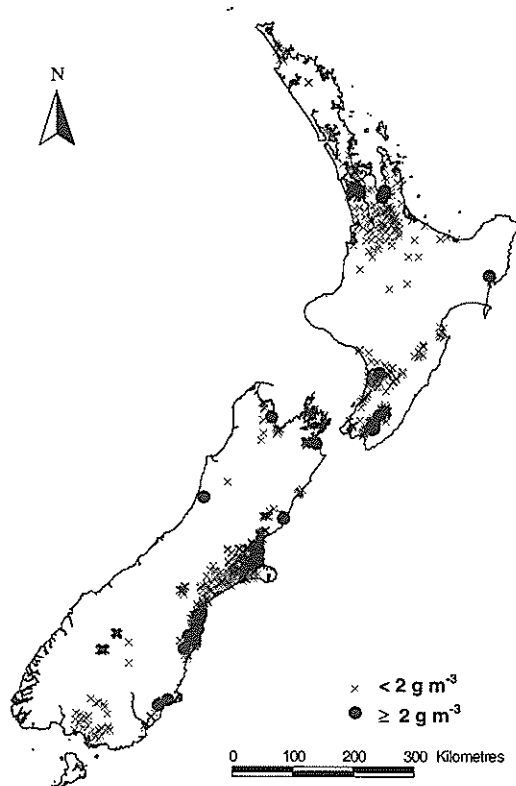


Figure 5 – Locations of groundwater sample points with average total Mn concentrations greater than 2.0 g m^{-3} (large dots) or less than 2.0 g m^{-3} (small crosses) (upper quartile).

The t-test revealed significant differences in Fe_S , Fe_T and Mn_T when they were grouped by aquifer lithology. In order to compare variables by lithology, the lithological descriptions reported by the data suppliers were grouped into 12 categories (Table 4), and descriptive statistics for Fe_S , Fe_T , Mn_S , and Mn_T were calculated for each category (Table 5, Fig. 7; the limestone category contained too few data points for meaningful analysis, so was omitted). Using the t-test, it was determined that (for $\alpha = 0.05$):

- 1) Fe_S concentrations in sand aquifers are higher than in all other aquifer types

Table 3 – Concentrations of dissolved and total iron and manganese (g m^{-3}) by regional council (data supplier).

Regional Council	Median Fe_S (Maximum)	Median Fe_T (Maximum)	Median Mn_S (Maximum)	Median Mn_T (Maximum)
ARC	0.023 (6.43)	0.215 (6.80)	0.012 (4.09)	0.038 (0.24)
EBOP	0.045 (23.57)	0.682 (18.99)	0.030 (12.44)	0.030 (0.54)
ECAN	0.006 (1.14)	0.070 (64.00)	0.001 (0.57)	0.001 (54.00)
ES	0.017 (1.44)	0.100 (58.00)	0.001 (0.97)	0.001 (0.24)
EW	0.080 (47.00)	0.370 (38.00)	0.002 (0.40)	0.030 (14.80)
GDC	2.039 (12.00)	5.314 (18.64)	0.718 (1.15)	0.554 (3.93)
HBRC	0.133 (6.70)	0.416 (9.08)	0.147 (0.51)	0.071 (0.58)
HMW	0.205 (16.80)	0.640 (31.45)	0.068 (3.03)	0.132 (3.20)
MRC	0.056 (0.68)	0.090 (8.30)	0.031 (0.37)	0.006 (12.00)
NRC	0.203 (1.37)	0.800 (24.00)	0.008 (0.69)	0.050 (0.90)
ORC	0.034 (0.15)	0.050 (46.67)	0.002 (0.01)	0.001 (11.40)
TDC	0.114 (2.95)	0.001 (18.20)	0.005 (2.57)	0.001 (4.50)
TRC	0.044 (0.17)	No data	0.004 (0.01)	0.078 (4.00)
WCRC	0.096 (1.93)	No data	0.002(0.90)	No data
WRC	0.035 (1.39)	0.360 (30.00)	0.001 (0.53)	0.001 (2.30)

Fe_S – Soluble iron concentration (g m^{-3})
 Fe_T – Total iron concentration (g m^{-3})

Mn_S – Soluble manganese concentration (g m^{-3})
 Mn_T – Total manganese concentration (g m^{-3})

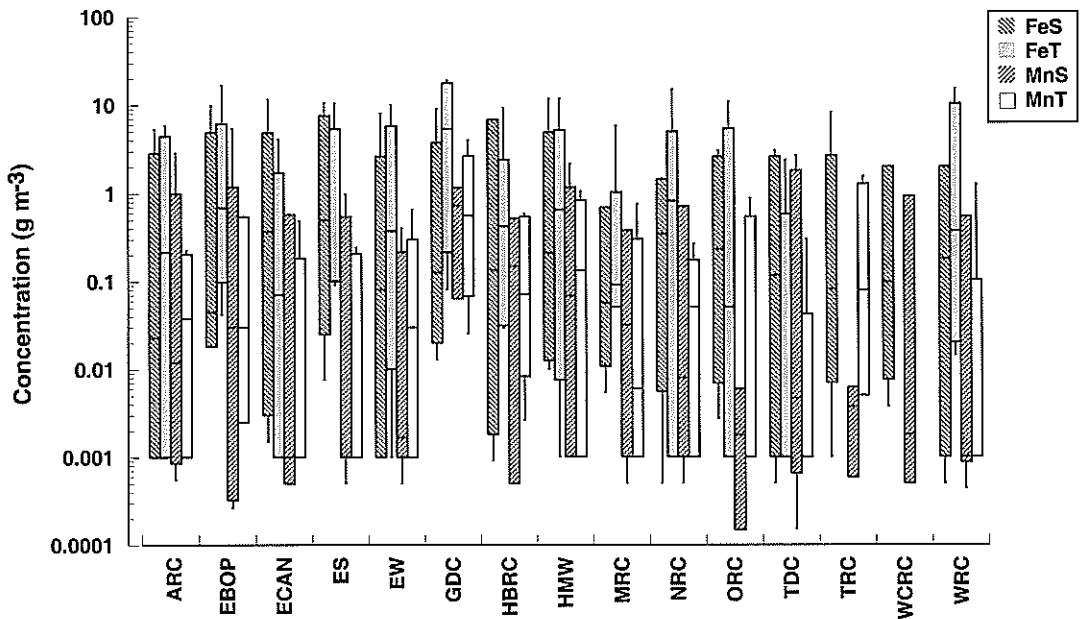


Figure 6 – Concentrations of median dissolved and total Fe and Mn by regional council (data supplier, as abbreviated in Table 1).

Table 4 – Reported aquifer lithologies and their assigned categories.

Basalt	Gravel	Greywacke	Sand
Bank Peninsula Volcanic Bombay Basalt Deep Pukekohe Basalt Drury Basalt Kiwitahi Andesite Mt Richmond Basalt One Tree Hill Basalt Shallow Pukekohe Basalt South Auckland Basalts Three Kings Basalt	Alluvial Gravels Burwood Gravel Cemented Gravel Cobbles to Granules Clay, Pebble, Lignite & Gravels Coarse Gravel Coarse Gravel & Clay Coarse Gravel Silt & Sand Cobble to Sand & Clay Fairhall River Gravels Fine Gravel & Sand Gravel & Clay Trace Gravel & Sand Gravel Sand & Clay Trace Gravels Makauri Gravel Matokitoki Gravel Mixed Gravels and Greywacke Omaka Aquifer Riccarton Gravel Shallow Fluvial Deposits Wainoni Gravel Waipaoa Gravel	Fractured Greywacke Greywacke Ignimbrite Ignimbrite Ignimbrite, Gravels, Pumice Ignimbrite, Pumice, Rhyolite Rhyolitic Ignimbrite Lignite Lignite Limestone Limestone Limestone/Mudstone Marble Marble Pumice Ash, Ignimbrites & Sand Pumice Pumice, Sand, Gravel	Cemented Coarse Sand/Grit Clay and Sand Kaawa Formation – Sands Sand Sand, Gravel Sands, Gravels, Greywackes Silt & sand Silt, Sand, Gravel, Pumice Tauranga Group Te Hapara Sand Waitemata Group Sandstone Sandstone Shellbeds Shellbeds
Clay Clay Clay & Silt Clay, Sandstone & Papastone			

Table 5 – Concentrations of dissolved and total iron and manganese (g m^{-3}) by aquifer lithology.

Aquifer Lithology	Median Fe_S (Maximum)	Median Fe_T (Maximum)	Median Mn_S (Maximum)	Median Mn_T (Maximum)
Basalt	0.020 (0.26)	0.090 (10.10)	0.006 (0.09)	0.010 (0.88)
Clay	No data	0.930 (38.00)	No data	0.085 (54.00)
Gravel	0.061 (6.03)	0.302 (42.50)	0.068 (3.03)	0.070 (4.70)
Ignimbrite	0.092 (2.47)	0.682 (3.91)	0.030 (0.95)	No data
Lignite	No data	0.060 (10.50)	No data	No data
Marble	No data	0.001 (0.070)	No data	No data
Pumice	0.102 (2.08)	0.202 (3.37)	0.013 (1.04)	No data
Rhyolite	No data	0.417 (3.79)	0.009 (1.75)	No data
Sand	0.685 (47.00)	1.140 (38.00)	0.337 (12.44)	0.111 (4.50)
Sandstone	0.012 (0.17)	0.290 (6.80)	0.024 (0.25)	0.050 (0.24)
Shellbeds	0.04 (0.16)	0.260 (5.413)	No data	0.050 (0.21)

Fe_S – Soluble iron concentration (g m^{-3}) Mn_S – Soluble manganese concentration (g m^{-3})
 Fe_T – Total iron concentration (g m^{-3}) Mn_T – Total manganese concentration (g m^{-3})

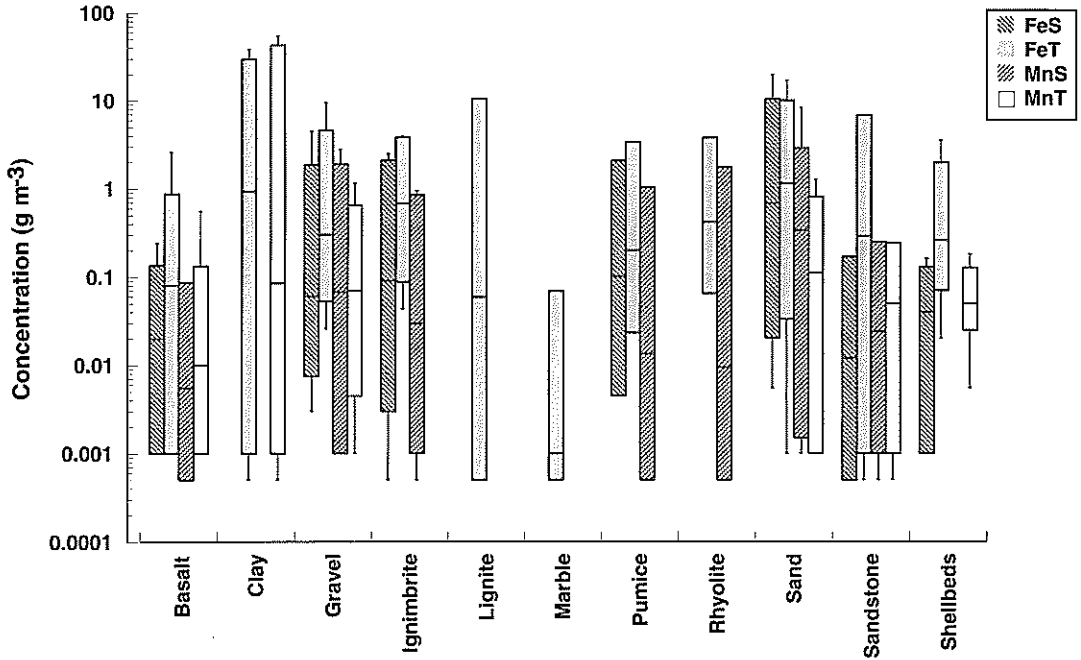


Figure 7 – Concentrations of median dissolved and total Fe and Mn by aquifer lithology.

- 2) sandstone, basalt and shellbed aquifers have statistically identical median concentrations of Fe_S
- 3) pumice, ignimbrite and gravel aquifers have statistically identical median concentrations of Fe_S
- 4) sandstone, basalt and shellbed aquifers have a statistically lower median Fe_S than pumice, ignimbrite and gravel aquifers.

This relationship can be expressed in the following notation, where numbers in parentheses represent the median Fe_S value of the aforementioned aquifer type:

Sandstone (0.012) = Basalt (0.020) = Shellbeds (0.040) < Gravel (0.061) = Ignimbrite (0.092) = Pumice (0.102) < Sand (0.685).

Thus sand aquifers are most likely to have Fe_S concentrations that exceed the DWSNZ

aesthetic guideline (0.2 g m^{-3}). Following the same procedure for Fe_T , it can be shown that:

Marble (0.001) < Lignite (0.060) = Basalt (0.090) = Pumice (0.202) = Shellbeds (0.260) = Sandstone (0.290) = Rhyolite (0.417) = Ignimbrite (0.682) < Gravel (0.302) < Clay (0.930) = Sand (1.140).

This series is broadly similar to that for Fe_S , but some lithologies move up or down one or two spots. All aquifer groups had statistically identical median concentrations of Mn_S except for sand, which was significantly higher:

Basalt (0.006) = Rhyolite (0.009) = Pumice (0.013) = Sandstone (0.024) = Ignimbrite (0.030) = Gravel (0.068) < Sand (0.337).

Only gravel and sand aquifers have median Mn_S concentrations that are greater than the DWSNZ aesthetic guideline (0.05 g m^{-3});

median Mn_S concentrations for all aquifer types are below the DWSNZ health-related guideline (0.5 g m^{-3}). Finally, the median values of Mn_T are not dependent on aquifer type:

Basalt (0.010) = Shellbeds (0.050) = Sandstone (0.050) = Gravel (0.070) = Clay (0.085) = Sand (0.111).

From the above discussion, it is clear that aquifer lithology affects the likelihood that a groundwater will have elevated concentrations of either Fe or Mn. Basalt, shellbed and sandstone aquifers generally have low but statistically equivalent concentrations of Fe_S , Fe_T , Mn_S and Mn_T . Gravel aquifers have statistically higher Fe_S , Fe_T and Mn_T concentrations than aquifers composed of basalt, shellbeds or sandstone. Sand aquifers have statistically higher Fe_S , Fe_T and Mn_S concentrations than gravel aquifers, but do not have higher Mn_T concentrations. Clay aquifers have concentrations of Fe_T and Mn_T that are similar to sand aquifers. Of the aquifer types investigated here, sand aquifers are the most likely to have Fe and Mn concentrations that exceed DWSNZ guidelines (Fe_S and Mn_S data were not available for clay aquifers).

The median pH values varied with aquifer lithology. All aquifer types had normal distributions (pH is already a log-transformed variable) with unequal variance. Using the notation introduced above, the variation of pH among aquifer lithologies was as follows:

Basalt (6.68) < Clay (6.95) = Gravel (7.12) = Sand (7.16) < Shellbeds (7.89) = Sandstone (8.21).

The pH of a groundwater can affect the amount of Fe or Mn that can be dissolved (Langmuir, 1997). However, based on the above sequence, there appears to be little relationship between pH and Fe or Mn concentrations in groundwater. For example,

basalt and sandstone aquifers both have low and statistically equivalent average Fe_S concentrations, but they have average pH values on opposite ends of the observed range. Such relationships can be further assessed through correlation analysis.

Pearson product-moment correlation coefficients (r) were calculated using log-transformed data to investigate relationships between Fe_S , Fe_T , Mn_S , Mn_T , pH and water extraction depth (Table 6, Fig. 8). The correlations between pairs of these variables ranged from $r = 0.93$ to not significantly different from zero. The significance of the differences between correlation coefficients was tested as described by Sokal and Rohlf (1995).

The strongest correlations were between Fe_S and Fe_T , and between Mn_S and Mn_T . The slope of the Mn_S - Mn_T correlation line was approximately equal to unity, implying that, for any given water sample, the soluble and

Table 6 – Pearson product-moment correlation coefficients (r) between dissolved and total iron and manganese, pH and water extraction depth.

	Fe_S	Fe_T	Mn_S	Mn_T	pH	WED
Fe_S	1	–	–	–	–	–
Fe_T	0.93 (328)	1	–	–	–	–
Mn_S	0.39 (212)	0.35 (117)	1	–	–	–
Mn_T	0.40 (225)	0.67 (2038)	0.64 (75)	1	–	–
pH	0.10* (324)	0.07* (2415)	0.08* (110)	0.04* (1765)	1	–
WED	0.17 (430)	0.06* (2712)	0.17 (192)	0.01* (1711)	0.15 (2060)	1

Fe_S – Soluble iron concentration

Fe_T – Total iron concentration

Mn_S – Soluble manganese concentration

Mn_T – Total manganese concentration

WED – Water extraction depth

Value in parentheses – Number of samples upon which the correlation is based

* Correlation coefficients not significantly different from zero

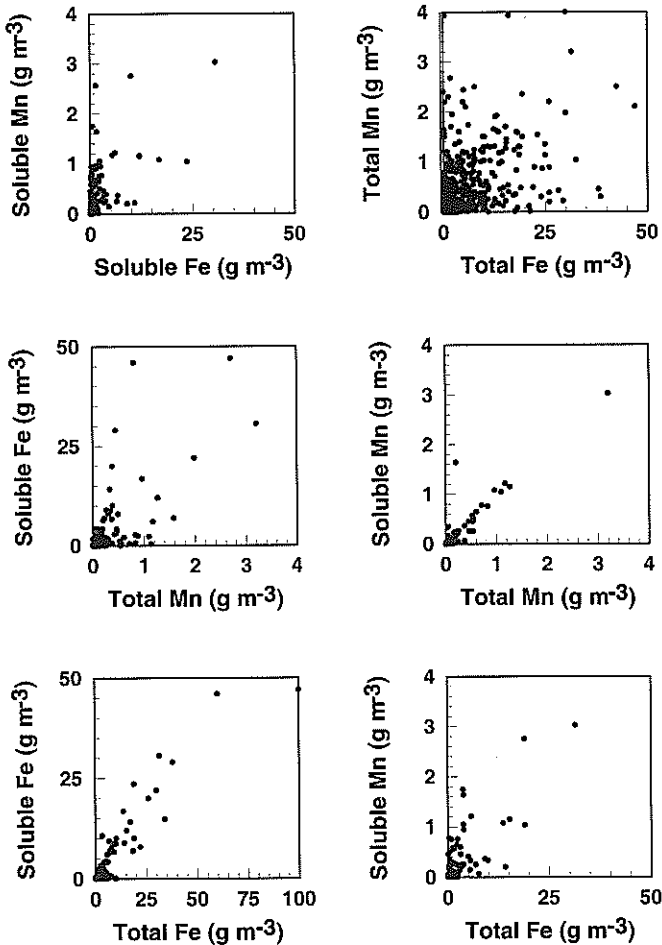


Figure 8 – Bivariate scatter plots for dissolved and total Fe and Mn. Product-moment correlation coefficients are compiled in Table 6.

total concentrations of Mn were generally approximately equal. This suggests that the major fraction of Mn in New Zealand groundwaters is soluble (not colloidal or particulate). This in turn suggests that the Mn is present in its reduced form, because the oxidised form has very low solubility in groundwater at circum-neutral pH (Langmuir, 1997). In contrast, the slope of the Fe_S - Fe_T correlation line was slightly less than unity, suggesting that a fraction of Fe exists in colloidal form in many ground-

waters. The reduced form of Fe is much more soluble than its oxidised form in most groundwaters, and in this respect, Fe and Mn are similar. However, reduced Mn is more stable across a range of pH and redox conditions than reduced Fe (Krauskopf and Bird, 1995), which may explain why Fe appears more commonly in particulate form in groundwaters. For both Fe and Mn, there are samples for which the dissolved concentration exceeds the total concentration, implying sampling or analytical error (Fig. 8).

A maximum concentration of either Fe or Mn is not apparent; this suggests that the concentrations of these elements are not buffered by the presence of a solid phase, as would be the case if there were chemical equilibrium between the dissolving mineral and the aqueous phase. However, the apparent lack of maxima in Fe and Mn concentrations may indicate 1) that the dissolution of the metals from the minerals was kinetically restricted, 2) that the water samples were taken from aquifers with widely different

solid-phase concentrations of Fe- and Mn-bearing minerals, 3) that the composition of the groundwater varied extensively (particularly with respect to the concentrations of complexing ligands), 4) that the biodiversity and activity of the microbial population was widely varied, or any combination of the above.

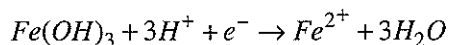
Correlations between Mn_S and Fe_S , and between Mn_T and Fe_T were weak. There are so many geochemical processes could give rise to the poor Fe-Mn correlation that the

cause(s) cannot be determined unequivocally. For example, the lack of correlation between Fe and Mn in groundwaters could reflect a lack of correlation between the total amounts of Fe and Mn in the aquifer minerals. The lack of correlation could also reflect a difference in the kinetics of Fe and Mn dissolution, such that the concentrations of the two elements would tend to become more dissimilar over time due to groundwater-rock interaction. Alternatively, the poor correlation between Fe and Mn could be due to differences in the oxidation-reduction potential of the water samples; Mn would be reduced (and thus solubilized) at redox potentials where Fe would remain oxidised (and insoluble) (Langmuir, 1997).

Correlations between concentrations of Fe or Mn and pH or water extraction depth were also weak and, in many cases, not significantly different from zero. Although pH can affect the amount of Fe and Mn that can be dissolved in groundwater (Langmuir, 1997), clearly it is not a dominant control on the Fe and Mn concentrations examined in this study. Water extraction depth should not be a *direct* control on groundwater metal concentrations, but a correlation between these variables could be explained by an indirect process. For example, if groundwaters extracted from greater depths were typically and significantly more reducing than shallow groundwaters, then a correlation between water extraction depth and metal concentration would be probable. Alternatively, a correlation between water extraction depth and metal concentration could be explained by a greater concentration of complexing ligands in deeper groundwater systems (e.g. Kharaka *et al.*, 1986; Fein and Hestrin, 1994). However, the lack of correlation between water extraction depth and concentrations of Fe and Mn in groundwater indicates that, on the national scale, such indirect relationships are not significant.

The relationship between the concentrations of dissolved Fe and Mn indicates that

the groundwaters are in redox disequilibrium. For a groundwater at redox equilibrium with the surrounding aquifer materials, the concentration of Fe in solution is buffered by the dissolution of a Fe(III)-bearing mineral, commonly an iron oxyhydroxide. If the oxyhydroxide is represented as $Fe(OH)_3$, its reductive dissolution is described by the reaction:



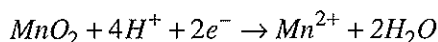
where e^- represents the electron. At redox equilibrium, the redox potential (E_H) and the concentration of Fe^{2+} are related:

$$E_H^{Fe} = E^0 + \frac{RT}{nF} \ln \frac{[H^+]^3}{[Fe^{2+}]}$$

where E^0 represents the standard potential of the half-reaction (in this case 0.975 V), R is the gas constant, T is the temperature, n is the number of electrons transferred in the reaction, F is Faraday's constant, and square brackets represent the activity of the enclosed species (mol dm^{-3}). If the dissolved Fe (Fe_S) is assumed to exist entirely as Fe(II), then, to account for hydrolysis, the concentration of Fe^{2+} can be calculated as

$$[Fe^{2+}] = [Fe_S] \frac{[H^+]}{K + [H^+]}$$

where $[Fe_S]$ is the concentration of dissolved Fe in mol dm^{-3} , and K is the thermodynamic stability constant describing the formation of $FeOH^+$ from Fe^{2+} ($10^{-10.1}$, Langmuir, 1997). Using the equations above, it is possible to calculate a theoretical E_H value for each groundwater sample for which Fe_S and pH are known (Fig. 9). Similarly, if the groundwater is at redox equilibrium with respect to Mn, the concentration of dissolved Mn^{2+} will be buffered by the reductive dissolution of an Mn-bearing mineral, most likely MnO_2 :



$$E_H^{Mn} = E^0 + \frac{RT}{nF} \ln \frac{[H^+]^4}{[Mn^{2+}]}$$

where symbols are as defined above and $E^0 = 1.23 \text{ V}$ for this reaction. Again, if it is assumed that Mn_2O_3 exists entirely as Mn^{2+} , then it is possible to calculate a theoretical redox potential for each water sample for which the concentration of dissolved Mn_2O_3 and pH are known (Fig. 9). Clearly, the redox potentials calculated from the concentrations of Fe (denoted here as E_H^{Fe}) and Mn (E_H^{Mn}) do not agree. This indicates that the groundwaters are not at redox equilibrium. Redox disequilibrium is common in groundwater systems (Lindburg and Runnells, 1984), due, in part, to the sluggish nature of electron-transfer reactions and the role of microbial catalysis. The redox disequilibrium observed here indicates that chemical speciation models will not reliably predict Fe and Mn concentrations in New Zealand groundwaters.

With the available data, it is not possible to determine *why* certain aquifer lithologies are prone to elevated concentrations of Fe and/or Mn; however, it is possible to pose a reasonable hypothesis. The data indicate that the Fe and Mn are likely dissolved and not colloidal, but that their concentrations are not

pH-dependent. The Fe and Mn concentrations do not appear to be limited by the solubility of a solid phase. It is not simply the presence of these elements in the aquifer materials that controls their concentrations in groundwater (basalts contain minerals rich in Fe and Mn, but groundwaters in basalt aquifers are not prone to elevated concentrations of Fe and Mn). This suggests that reductive dissolution is the pathway by which these elements enter groundwater (despite the redox disequilibria between them). It can therefore be hypothesized that the presence of a reductant (such as organic carbon) is the dominant factor controlling Fe and Mn concentrations in groundwater. The oxidation of the reductant would lead to reduction and solubilisation of Fe and Mn. Organic carbon may be the reductant controlling Fe and Mn solubility in New Zealand groundwaters, because it is probably present in aquifer lithologies like sand and gravel, but it is likely to be absent or limited in aquifers composed of basalt, limestone, marble, pumice, sandstone and rhyolite.

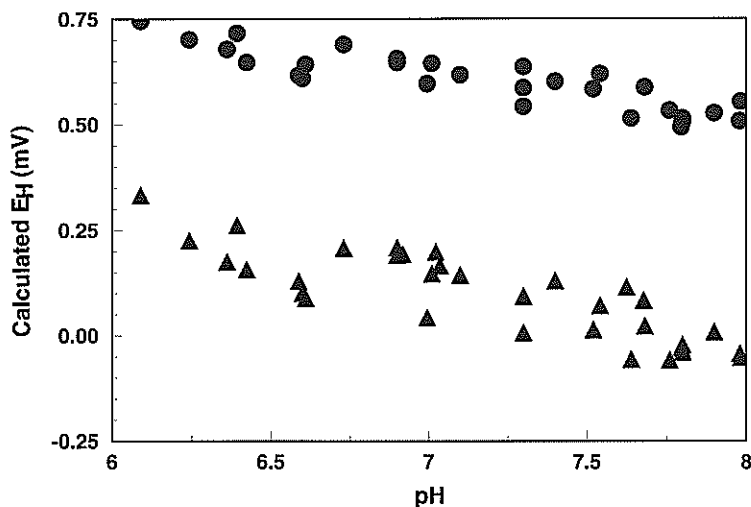


Figure 9 – E_H values calculated from pH and dissolved Fe concentration, assuming equilibrium with respect to $\text{Fe}(\text{OH})_3$ (triangles), and from pH and dissolved Mn concentration, assuming equilibrium with respect to MnO_2 (circles).

Summary

This study focused on Fe and Mn concentrations in close to 10,000 groundwater samples compiled through collaborative effort with local governmental organisations. Maps and statistical tests based on the supplier of the data indicate that many regions of New Zealand have problematic levels of Fe, Mn or both. Aquifer lithology clearly affects the likelihood that a groundwater will have elevated concentrations of these elements. Groundwaters in basalt, shellbed and sandstone aquifers are the least likely to have high concentrations of Fe and Mn, whereas groundwaters in gravel and sand aquifers are the most likely to have elevated Fe and Mn concentrations. Virtually all of the Fe and Mn appear to exist in dissolved (and thus presumably reduced) form, rather than in colloidal (particulate) form. The concentrations of Fe and Mn in a groundwater sample are not related to one another, nor are they related to pH or water extraction depth, due primarily to redox disequilibrium. It may be hypothesized that the presence of a reductant (such as organic carbon) is the dominant factor controlling Fe and Mn concentrations in groundwater.

Acknowledgements

The regional and district councils that participated in this investigation are thanked for sharing their data and for many helpful discussions. This research was initiated by Michael Rosen and Johanna Marnjizegyidubi and supported by funding from the Foundation for Research, Science and Technology.

Reviewers

This manuscript was greatly improved by the reviews of Gabor Bekesi, one anonymous reviewer, and the editorial staff of The Journal of Hydrology (NZ).

References

- Davies, H. 2001: Groundwater and health. In: *Groundwaters of New Zealand*. M.R. Rosen and P.A. White (eds.), New Zealand Hydrological Society, Wellington, 253-272.
- Domenico, P.A.; Schwartz, F.W. 1990: *Physical and Chemical Hydrogeology*. John Wiley and Sons, New York. 824 p.
- Ehrlich, H.L. 1996: How microbes influence mineral growth and dissolution. *Chemical Geology* 132: 5-9.
- Fein, J.B.; Hestrin, J.E. 1994: Experimental studies of oxalate complexation at 80°C: Gibbsite, amorphous silica, and quartz solubilities in oxalate-bearing fluids. *Geochimica et Cosmochimica Acta* 58: 4817-4829.
- Fenemor, A.D.; Robb, C.A. 2001: Groundwater management in New Zealand. In: *Groundwaters of New Zealand*. M.R. Rosen and P.A. White (eds.), New Zealand Hydrological Society, Wellington, 273-289.
- Freeze, R.A.; Cherry, J.A. 1979: *Groundwater*. Prentice Hall, New Jersey. 604 p.
- Kharaka, Y.K.; Law, L.M.; Carothers, W.W.; Goerlitz, D.F. 1986: Role of organic species dissolved in formation waters from sedimentary basins in mineral diagenesis. *SEPM Special Publication* 38: 111-122.
- Krauskopf, K.B.; Bird, D.K. 1995: *Introduction to Geochemistry*. McGraw Hill, New York.
- Langmuir, D. 1997: *Aqueous Environmental Geochemistry*. Prentice Hall, New Jersey.
- Lindburg, R.E.; Runnells, D.D. 1984: Groundwater redox reactions: An analysis of equilibrium state applied to Eh measurements and chemical modeling. *Science* 225: 925-927.
- Ministry of Health 1995: Drinking Water Standards for New Zealand. National Drinking-Water Standards Review Expert Working Group, Ministry of Health. 130 p.
- Rosen, M.R. 1997: *The National Groundwater Monitoring Network (NGMP): Structure, implementation and preliminary results*. Institute of Geological and Nuclear Sciences Science Report 97/26. 47 p.

- Rosen, M.R. 1999: The importance of long-term seasonal monitoring of groundwater wells in the New Zealand National Groundwater Monitoring Programme (NGMP). *Journal of Hydrology (New Zealand)* 38(1): 145-169.
- Rosen, M.R. 2000: Iron and manganese in New Zealand groundwater: Preliminary assessment of available data and directions of current research. In: *Fresh Perspectives: A Joint Conference of New Zealand Hydrological Society, Meteorological Society of New Zealand, New Zealand Limnological Society*, 94-95.
- Rosen, M.R. 2001: Hydrochemistry of New Zealand's Aquifers. In: *Groundwaters of New Zealand*. M.R. Rosen and P.A. White (eds.), New Zealand Hydrological Society, Wellington, 77-110.
- Sanford, R.F.; Pierson, C.T.; Crovelli, R.A. 1993: An objective replacement method for censored geochemical data. *Mathematical Geology* 25: 59-80.
- Sokal, R.R.; Rohlf, F.J. 1995: *Biometry: The Principles and Practice of Statistics in Biological Research*, 3rd edition. W. H. Freeman and Company, New York. 776 p.
- White, P.A. 2001: Groundwater resources in New Zealand. In: *Groundwaters of New Zealand*. M.R. Rosen and P.A. White (eds.), New Zealand Hydrological Society, Wellington, 47-75.
- White, P.A.; Rosen, M.R. 2002: The National Groundwater Monitoring Programme. *Water and Wastes in New Zealand* 123: 19-23.