Review of the Environment Southland baseline groundwater quality monitoring programme

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Quarterly sampling in March, June, September and December is appropriate for assessment of temporal trends and seasonal patterns.

Parameters that are currently monitored should continue to be monitored in the future, and dissolved oxygen, redox potential and SiO_2 should be added. A synoptic survey of As concentrations should be conducted soon, and wells that have not yet been analysed for ^{18}O and/or age dated should be targeted for this purpose.

The sampling methods described in the manual are well explained and quite good, but field measurements should always be made with a flow cell, and all samples for cation or anion analysis should be field filtered.

Current status of groundwater quality in Southland

Six monitoring sites have median As concentration above the drinking water guideline value, four sites have median Mn concentration above the aesthetic guideline value, one site has NO_3 above the guideline value, and 18 sites exceed guideline values for bacterial counts. Median values of all other analytes at all other sites are below their respective guideline values.

More than 50% of the monitoring sites show high variability in NO_3, K and/or Total Coliforms, probably indicating that they are non-secure (c.f. Close et al., 2000). Roughly 30% of the monitoring sites show high variability in Fe, Mn and/or DRP, probably due to low median concentrations of these substances and possibly due to lack of field filtration.

At most sites, most monitored parameters remain constant with time, or are changing slowly (at less than 10% of the median per year). Twelve sites show significant trends in NO_3 concentration, although at only six sites is NO_3 increasing, and at only four is it increasing rapidly.

In general, temperature varies significantly by season in an expected pattern, and median K concentration shows a seasonal pattern that is probably related to flushing from the soil zone during seasons of high rainfall. Other monitored parameters do not vary by season.

Groundwaters in the vicinity of Mossburn, Lumsden and Gore (i.e. map sheets D43, E44, F44) are probably river-recharged and they are typically relatively dilute and Ca-HCO_3 dominated. Groundwaters in the vicinity of Edendale, Winton and Invercargill show higher concentrations of Na, K, Cl and SO_4, suggesting recharge by coastal rain (higher Na, Cl) and accumulation of salts (Na, K, Cl, SO_4) during passage of the recharge waters through soil in agricultural areas.

In general, groundwater chemistry does not show a strong relationship to depth. However, weak correlations suggest that substances likely to be introduced by human/agricultural activities (e.g. K, NO_3, SO_4) have highest values in shallow groundwater, whereas substances likely to be introduced during natural water-rock interaction (e.g. Fe, Mn, DRP, SiO_2) reach their highest values in deeper groundwaters.

Geochemical relationships

The median concentration of an analyte cannot be used to predict trends in its concentration over time.

For most analytes, the median concentration and its variability are uncorrelated. However, For Total Coliforms, the median count is strongly correlated to the MAD.

For any given analyte, the rate of concentration change and the amount of variability in concentration are uncorrelated.

The median concentrations of several pairs of different analytes are significantly correlated. In some cases, if the median concentration of one parameter is missing (e.g. Br, F, SiO_2), it can be estimated reasonably well from the median concentrations of other analytes.

The rates at which the concentrations of different analytes are changing are uncorrelated. If the rate of concentration change of one parameter is missing or has not been determined, it cannot be estimated based on the rates of concentration change of other analytes.

The median, variability and trend of most monitored parameters show no significant relationship to aquifer lithology. However, the median, variability and/or trend of Fe, NO_3, NH_4 or SO_4 are often different in lignite compared to other aquifers, presumably due to the low redox potentials expected for groundwaters in organic-rich material.

The median, variability and trend of most monitored parameters show no significant relationship to aquifer confinement. However, confinement category has a significant impact on medians of NO_3 and NH_4, on variability of DRP, NO_3 and Mn, and on trends in SO_4. These significant differences are likely controlled by redox potential, and suggest that unconfined aquifers tend to be oxidised whereas confined aquifers tend to be anoxic.

The median, variability and trend of most monitored parameters show no significant relationship to groundwater use. However, sites where groundwater is used for stock have lower medians, variabilities and/or trends in Ca, Mg, DRP, NO_3 and/or SO_4 compared to sites where groundwater is used for domestic purposes. This may indicate an impact of septic tanks on groundwater in domestic wells.

The various forms of well head protection appear to have no effect on the median, variability or trend of any of the monitored parameters.

^{18}O is correlated to median Cl, Na and Conductivity, which reflects a differentiation between rainfall-recharge and river-recharge. There are no correlations between ^{18}O and medians, trends or variabilities of any other parameters.

Only 17 sites have been analysed for ^{15}N, 15 of which had values indicative of soil organic nitrogen, and two of which had values indicative of human or animal waste. There are no apparent correlations between ^{15}N and any other monitored parameter.

Younger groundwaters (CFC/SF_6 age) tend to have higher median concentrations of NO_3 and K, presumably due to modern intensification of agriculture, whereas older groundwaters tend to have higher median concentrations of DRP and HCO_3, which presumably accumulate over time due to natural water-rock interaction. Relationships to the variability of DRP and to trends in Na can be tentatively used to estimate groundwater age where it hasn't yet been measured.

Overall control of groundwater quality in Southland

Natural water-rock interaction and human/agricultural impacts constitute opposing forces that affect groundwater geochemistry in Southland. These two forces vary in relative strength across sub-regions of Southland.

A sufficient quantity of data is now available for definition of baseline groundwater quality in Southland. An approach based on rank-percentiles of parameters is appropriate to account for variations in groundwater quality caused by natural and/or anthropogenic factors. It is also appropriate to develop different definitions of baseline for recognisably different categories of groundwater.

Groundwater quality in Southland is comparable to that of gravel-hosted groundwaters in other parts of New Zealand, but Southland aquifers typically have higher median concentrations of NO_3. The number of Southland sites at which groundwater quality is either improving or degrading with time exceeds the national average based on the NGMP data.

1.0 INTRODUCTION

Since March 2000, Environment Southland has operated a baseline groundwater monitoring programme. The primary objectives of the monitoring programme are:

- To provide data that describe the temporal and spatial variation in groundwater levels and quality in the Southland Region
- To enable the establishment of a baseline of groundwater quality and level information from which the presence, direction and magnitude of trends can be determined
- To improve characterisation of the hydrogeology of aquifers in the Southland Region

The information provided from the groundwater monitoring programme is intended to be incorporated into a pressure-state-response framework, in order to:

- Quantify pressures being placed on the groundwater resources of Southland
- Monitor resulting changes in the natural condition of the resource
- Develop appropriate management responses to the issues identified from monitoring.

The Southland groundwater monitoring network presently includes seven sites sampled as part of the National Groundwater Monitoring Programme (NGMP) and 35 sites comprising the Environment Southland groundwater quality network (Figure 1). Although parts of separate monitoring programmes, the NGMP sites and the Southland monitoring sites are sampled with similar frequency, at the same times of the year, and the samples are analysed for a similar range of parameters. In addition to the 35 sites sampled as part of the Southland baseline monitoring programme, approximately 15 sites have been sampled quarterly for nitrate only since March 2002, and a number of sites have been sampled on a one-off basis for a range of indicator parameters. Samples collected as part of the NGMP are analysed by the Institute of Geological & Nuclear Sciences laboratory in Wairakei, whereas samples from the Southland monitoring sites are analysed by the Environment Southland in-house laboratory.

The Institute of Geological & Nuclear Sciences was contracted to review the Environment Southland groundwater monitoring programme and comment on the following topics:

- Programme design, including an assessment of objectives, sites selected, sampling frequency, parameters measured and sampling methods
- Current status of groundwater quality in Southland, including assessment of spatial and temporal trends
- Nature and causes of geochemical relationships observed in the data, including relationships to site location, aquifer lithology, aquifer confinement, groundwater use and well head protection
- Overall assessment of groundwater quality in Southland, including definition of baseline hydrochemistry and comparison to groundwater quality in other parts of New Zealand

The organisation of this report follows the presentation of topics as given above. Data analysis and statistical methods employed are described in the relevant sections of this review. Documents describing the objectives of the Environment Southland groundwater monitoring programme and sampling methodology are included as Appendices 1 and 2, respectively. Guidelines for the collection of samples for the NGMP are described by Rosen et al. (1999). The locations of the monitoring sites are shown in Figure 1. Specific details of the Southland monitoring sites, as provided by Environment Southland, are provided in Appendix 3, and the raw hydrochemical data are provided in Appendix 4.

2.0 SAMPLING PROGRAMME

2.1 Sampling objectives

The objectives of the groundwater monitoring programme are appropriate. However, in order to apply the pressure-state-response framework, data that describe the various pressures on groundwater quality must be collected.

The objectives of the sampling programme, as outlined in the Monitoring/Investigation Strategy document, are appropriate. The definition of baseline water quality is a very important goal, as evidenced by new legislation with this same goal throughout Europe and North America. The framework of pressure-state-response is also appropriate. However, information related to pressure was not supplied for the purpose of this review. Ideally, pressures should be quantified much like other hydrochemical parameters, in order to facilitate comparison. If abstraction rates and volumes are suspected pressures, then values should be recorded at each monitoring site at each monitoring interval. Similarly, if stocking density is a suspected pressure, then it should be recorded quarterly at each monitoring site. Clearly, the measurement of suspected pressures would require a fair degree of effort, especially for a parameter like stocking density, which might not have a straight-forward definition. Nonetheless, if the pressure-state-response framework is to be employed, then data describing the various pressures are essential, and ideally these data should be numeric and easily related, spatially and temporally, to the data describing state (i.e. groundwater hydrochemical data).

2.2 Site selection

The sites for the baseline monitoring programme and the NO_3 surveys are appropriate in number, style and location, but sites could be added near Toa, Mabel Bush, Browns and Hamilton Burn to improve coverage in these areas and to constrain baseline water quality of subtly different categories of groundwater.

The criteria used for the selection of monitoring sites, as described in the sampling manual, are appropriate for the goals of the monitoring programme. In particular, it is important to select sites that can be monitored regularly for many years, to provide valuable continuity of data.

The sites sampled in the Southland monitoring programme, together with seven the NGMP sites, are sufficient for assessment of baseline groundwater quality. The distribution of these sites provides sufficient spatial coverage for recognition of differences in groundwater quality in various sub-regions of Southland (Figure 1).

One or two additional sites, monitored for a full suite of parameters, in each of the following areas would improve coverage in areas where it is presently sparse: 1) the vicinity of Hamilton Bush, south of Mossburn and west of Lumsden; 2) the vicinity of Toa, Mokotua or Oteramika, south of SH1 between Invercargill and the Matarua River; 3) the vicinity of Mabel Bush, north of SH1 between SH6 and the Matarua River; and 4) the vicinity of Browns, east of SH6 near SH96. These four areas should be typified by groundwaters of subtly different chemistry, as described in Section 5.1. Thus additional sites in these specified areas would not only increase the spatial coverage of the monitoring programme, but would provide valuable information for definition of "typical" quality of these different groundwater types.

The sites selected for the NO_3 monitoring programme are appropriate, when considered together with the data from the baseline monitoring sites. In particular, the NO_3 monitoring sites around the Waikaia and Waimea Plains are important, because they show NO_3 levels that are relatively high for the type of groundwater expected in the area (see Section 5.1).

2.3 Sampling frequency

Quarterly sampling in March, June, September and December is appropriate for assessment of temporal trends and seasonal patterns.

The current sampling schedule allows for suitably robust assessment of temporal trends (Section 3.3) and seasonal patterns (Section 3.4), because the sampling intervals bracket the periods of highest and lowest temperature and rainfall. Sampling less frequently at sites where groundwater chemistry is relatively constant is an option, but it is not recommended. This is because constancy of water chemistry does not necessarily go hand-in-hand with groundwater security; such sites may be just as susceptible to pressures on groundwater quality, but these pressures may not yet be present. Sampling more frequently would not provide a great deal more information, because seasonality appears to have a small effect on the values of most monitored parameters.

2.4 Parameters measured

Parameters that are currently monitored should continue to be monitored in the future, and dissolved oxygen, redox potential and SiO_2 should be added. A synoptic survey of As concentrations should be conducted soon, and wells that have not yet been analysed for ^{18}O and/or age dated should be targeted for this purpose.

The suite of parameters measured at the baseline monitoring sites is appropriate for characterisation of groundwater chemistry, and for recognition of spatial and temporal trends.

A synoptic survey of As concentrations should be conducted, because to date, As has been measured at only six sites (through the NGMP), and all had concentrations above the MAV of 0.01 mg/L (see Section 3.1). The groundwaters at these six NGMP sites do not appear to be abnormal or unusual in any way with respect to other monitoring sites in Southland, and thus elevated As concentrations may be found in groundwaters from other parts of the region. Field filtration is recommended for As monitoring, because of the tendency of As to associate with colloidal iron oxides.

SiO_2 should be monitored quarterly at all sites, because it provides a means of differentiating younger river-recharged groundwaters (SiO_2 c. 10 mg/L) from older, more evolved groundwaters (SiO_2 c. 25-40 mg/L).

Regular monitoring of dissolved oxygen concentration and redox potential should be conducted in the field, assuming that the required meters are available. Measurements should be made in a flow cell to prevent contact of the groundwater with the atmosphere. If measured correctly, these two parameters provide valuable information on the redox state of the groundwater. pH should always be measured in the field using a temperature-compensated electrode calibrated against three buffers (pH 4, 7, 10).

A complete survey of tracer compounds would be very useful. ^{18}O should be measured in all wells, because it provides useful information on recharge mechanism, and because it has already been measured at several sites (Section 4.1). Age dates by CFC, tritium or SF_6 as appropriate would also be worthwhile (Section 4.12).

2.5 Sampling methods

The sampling methods described in the manual are well explained and quite good, but field measurements should always be made with a flow cell, and all samples for cation or anion analysis should be field filtered.

For measurement of parameters in the field, a flow cell is recommended for all parameters, but especially for dissolved oxygen and redox potential. Conductivities measured in the field are in excellent agreement with measurements made in the lab (Figure 2). However, pH measured in the lab does not correlate well to pH measured in the field (Figure 3). This is probably because pH often drifts after the sample is collected, even when a sample bottle is filled without air bubbles. The pH measured in the field is probably more representative of the in-situ pH, and so care should be taken to obtain an accurate measurement, through the use of a flow cell and a temperature-compensated electrode calibrated with three buffers (pH 4, 7, 10).

The adequacy of purge time should be based primarily on conductivity and temperature, and values for "stability" should be included in the field manual (c.f. Rosen et al., 1999). In the event that conductivity, temperature and/or other field parameters do not reach their respective stability criteria even after a long period of purging, then the sample should be collected and the drift in the field parameters should be recorded on the field sample sheet (e.g. % per minute). The purge volume should also be recorded, and assessed against the standing volume of water in the bore. Note that calculation of the standing volume of water should take into account the diameter of entire bore annulus, not just the casing diameter – if a sand pack is present around the casing, it should also be purged.

Field filtration is recommended for all sites, for all samples to be analysed for cations or for anions. The need for field filtration is indicated by the large proportion of samples that do not pass the charge balance test (Table 1). From Figure 4, it is apparent that most of the samples that do not pass the charge balance test err on the high side, indicating an apparent excess of cations. This is to be expected for unfiltered samples, because many cations can exist in the form of colloidal minerals such as carbonates, silicates and oxyhydroxides. When a solution containing these minerals is acidified, the solids can dissolve, elevating the concentrations of cations such as Ca, Mg, Na, K, Fe and Mn; some of the anions released (e.g. OH, SiO_2) are not considered in the charge balance equation. The high relative variabilities of Fe and Mn observed at several Southland monitoring sites (Table 1) provides further evidence that a significant proporation may be present in the colloidal phase (Section 3.2). Thus meaningful measurement of Fe and Mn concentrations requires field filtration.

3.0 CURRENT STATUS OF GROUNDWATER QUALITY IN SOUTHLAND

3.1 Median values of monitored parameters relative to New Zealand Drinking Water Guidelines

Six monitoring sites have median As concentration above the drinking water guideline value, four sites have median Mn concentration above the aesthetic guideline value, one site has NO_3 above the guideline value, and 18 sites exceed guideline values for bacterial counts. All other analytes at all other sites are below their respective guideline values.

The median concentration of each analyte was calculated at each monitoring site (Table 1), because it is less sensitive to extreme values in the dataset than the mean and thus provides a more resistant measure of central tendency (Helsel and Hirsch, 1992). Estimation methods are often required for calculation of median values for water quality data, because the dataset typically includes censored values reported as being less than some detection limit. In this analysis, a log-probability regression method (Helsel and Cohn, 1988) was employed to calculate the median (see also Daughney and Reeves, 2003a). This method provides a reasonable estimate of the median even when up to 70% of the available results are reported as being below some detection limit. Median values of all parameters were compared to their respective Maximum Allowable Values (MAVs) based on the Drinking Water Standards for New Zealand (New Zealand Ministry of Health, 2000). In Table 1, median values in excess of the relevant guideline value are shown in red text. Note that if fewer than eight samples from a site had been analysed for the parameter of interest, or if more than 70% of the results were below an analytical detection limit, median values in Table 1 are given in italics to indicate lower confidence in the calculation. The raw data provided by Environment Southland are compiled in Appendix 4.

Six monitoring sites had median As concentrations above the MAV of 0.01 mg/L. This is a concern, because these six sites appear to be the only ones at which As concentrations have ever been analysed (they are all NGMP sites). The groundwaters at these six sites do not appear to be abnormal or unusual in any way with respect to other monitoring sites in Southland. By extension, it is possible that many of the other monitoring sites that have not yet been tested for As might have elevated concentrations of this substance. It should be noted that As has only been analysed once at the six sites in question, and so the calculated median should be considered to bear a relatively large uncertainty. It should also be noted that samples to be analysed for As should be field-filtered, to acquire data that can be interpreted against the drinking water guidelines (the MAV pertains to dissolved As concentration).

Four monitoring sites had median Mn concentration in excess of the guideline value set for aesthetic reasons (0.05 mg/L). None of the sites had median Mn concentrations above the MAV set for health reasons (0.5 mg/L). Of the four sites with median Mn concentration above the aesthetic guideline value, three are characterised by reduced (anoxic) groundwaters, as evidenced by low concentrations of NO_3 and measurable concentrations of NH_4 and/or Fe. In anoxic groundwaters, Mn is likely present in dissolved form, as the ion Mn^{2+} or a complex thereof. The remaining site has a significant concentration of NO_3, which indicates a degree of oxygenation in the aquifer, which in turn suggests that a portion of the Mn might be present in oxidised colloidal Mn(IV) oxide minerals. The form of Mn in the groundwater is potentially of importance, because, as in the case of arsenic, the guideline values pertain to dissolved concentrations only. Hence if the samples were not field filtered, then the measured concentration would reflect the total Mn concentration, including Mn present in colloidal or mineral form. If this is true, then at least one of the sites may not actually be in excedence of the aesthetic guideline value for Mn.

Only one monitoring site (E45/0009) has a median NO_3 concentration in excess of the MAV set for health reasons (11.3 mg/L as N). Of the sites with median NO_3 concentration below 11.3 mg/L, 18 have median NO_3 concentration greater than ½ the MAV, and three have median NO_3 concentration greater than ¾ the MAV. The majority of sites have been analysed for NO_3 several times, and so the calculated median concentrations are reasonably robust.

Eighteen of the monitoring sites have median values of bacterial counts that exceed the MAV set for health reasons (1 cfu/100 ml). The bacterial counts considered include Total Coliforms, Feacal Coliforms, and Escherichia coli. Of these parameters, Total Coliform counts are measured most commonly in Southland, with the majority of sites having been assessed between five and ten times. At most of the sites with median bacterial counts in excess of the MAV, more than half of the samples collected give bacterial counts above the detection limit of the assay (typically 1 cfu/100ml). The number of sites with bacterial counts in excess of MAV and the proportion of samples from each site showing detectable pathogens indicate that bacterial contamination of groundwater is the most pervasive problem in Southland.

3.2 Variability of monitored parameters

More than 50% of the monitoring sites show high variability in NO_3, K and/or Total Coliforms, probably indicating that they are non-secure (c.f. Close et al., 2000). Roughly 30% of the monitoring sites show high variability in Fe, Mn and/or DRP, probably due to low median concentrations and possibly due to lack of field filtration.

The median absolute deviation (MAD) was calculated for each analyte at each monitoring site as a means of assessing variability (Table 1). The MAD is a measure of the spread of analytical results and is analogous to the standard deviation, but the MAD is less subject to biasing by extreme values (Helsel and Hirsch, 1992). In Table 1, if the calculated MAD is greater than 10% of the corresponding median, it is listed in bold orange text. There is no strict scientific justification for a cut-off at the 10% level, but Close et al. (2000) have suggested that if the standard deviation is more than 5% of the average for certain analytes, the site is likely affected by significant seasonal variation, groundwater abstraction, landuse change, or some similar process. Note that if fewer than eight samples from a site had been analysed for the parameter of interest, or if more than 70% of the results were below an analytical detection limit, MAD values in Table 1 are given in italics to indicate lower confidence in the calculation.

Table 1 shows that at least 38 of the 69 monitoring sites (i.e. 55%) have MAD in excess of 10% of the median concentration for NO_3. In general, MAD increases with median NO_3 concentration, but the correlation is biased by a small number of points with high leverage (see Section 4.12). Close et al. (2000) have suggested that high relative variability in NO_3 concentration can be used to identify non-secure wells, though Close et al. (2000) used a slightly different method to assess relative variability than has been used in this report.

Nonetheless, it is clear that many of the Southland monitoring wells exhibit characteristics of non-security, which is to be expected considering their depths and aquifer lithologies.

Table 1 also shows that Total Coliform counts also often display high relative variability. Indeed, of the 15 sites with median Total Coliform counts above the detection limit (1 cfu/100 ml), 12 (i.e. 80%) have MAD greater than 10% of the median. This indicates that bacterial indicator parameters are almost always highly variable, such that median counts must be interpreted with caution.

Table 1 also shows that K concentration often displays high relative variability. The cause of this variability is not clear, but it may be related to a seasonal effect such as fertiliser loading or rainfall recharge volume. It is worth noting that K is one of the few variables that show a correlation between MAD and measured groundwater age (see Section 4.12). This correlation suggests that high relative variability in K might be a means of identifying younger groundwaters.

Table 1 indicates that many sites commonly have MAD in excess of 10% of the median for Fe, Mn and DRP. For these three parameters, relative variability (MAD/Median) may appear high because the median concentrations are often very low. For Fe and Mn, lack of field filtration may also give rise to significant relative variability, because Fe and Mn often exist in colloidal mineral form. If the sampling procedure allows for any period of time where gravitational settling might occur, then the amount of colloidal Fe or Mn transferred into the sample bottle could vary significantly between sampling rounds.

Four sites display high relative variability for eight or more parameters (E45/0009, E45/0010, E46/0093, F45/0171). There appears to be nothing that distinguishes these four sites from any others in Southland (use, confinement, lithology, well head protection, depth, northing, easting).

3.3 Temporal trends in monitored parameters

At most sites, most monitored parameters remain constant with time, or are changing slowly (at less than 10% of the median per year). Sixteen sites show significant trends in NO_3 concentration, although at only 12 sites is NO_3 increasing, and at only 6 is it increasing rapidly.

The rate of change of each analyte was assessed statistically at each site (Table 1). In this study, the term ‘trend’ is used to describe a monotonic (i.e. linear) increase or decrease in a parameter over time. It is important to note that an analyte may show significant variation over time, as manifested by a relatively large MAD, but if the variation does not follow a consistent direction over time, then a significant trend will not exist. Trends were identified using the Mann-Kendal test (Helsel and Hirsch, 1992) with a confidence interval of 95%. If a trend in any parameter at any site was significant at the 95% confidence interval, then the magnitude of the trend was assessed with Sen’s slope estimator. This method yields the median rate of change in the analyte (units per year) for the entire historical record available for the site in question. Trends that are not significant at the 95% level are assigned a value of zero. Finally, if the calculated trend is significant at the 95% level and if it is more than 10% of the median, it is given in bold red text. Again, there is no strict scientific justification for the 10% cut-off, but it is intended to highlight sites where the analytes are changing relatively rapidly. Note that if fewer than eight samples from a site had been analysed for the parameter of interest, or if more than 70% of the results were below an analytical detection limit, trends in Table 1 are given in italics to indicate lower confidence in the calculation.

Table 1 indicates that several monitoring sites show significant (i.e. non-zero) trends in one or more analytes, but in general, rates of change are less than 10% of the median concentration. A limited number of sites show significant and relatively rapid trends, where the rate of concentration change (per year) exceeds 10% of the median.

Twelve sites show significant trends in NO_3 concentration, of which eight sites have trends in NO_3 that exceed 10% of the median. In this regard, NO_3 is definitely the parameter that most frequently shows a rapid rate of change. Of the 12 sites showing significant trends in NO_3 concentration, at six, NO_3 concentration is decreasing over time. At the six sites where NO_3

is increasing, at only four is it increasing rapidly (rate exceeds 10% of the median). In general, the trends in Cl, K and/or SO_4 follow trends in NO_3, suggesting that these analytes are controlled by common factors, probably related to human or agricultural impact, as suggested by Daughney and Reeves (2003b) (see also Sections 5.1 and 5.3).

3.4 Seasonality of monitored parameters

Temperature varies significantly by season in an expected pattern, and median K concentration shows a seasonal pattern that is probably related to flushing from the soil zone during seasons of high rainfall. Other monitored parameters do not vary by season.

The Kruskal-Wallis test was employed to test for significant differences in the medians of indicator parameters, based on the season in which the sample was collected. The Kruskal-Wallis test is non-parametric, and thus it does not require the assumption that the parameters being assessed follow the normal distribution (Helsel and Hirsch, 1992). In this regard, the Kruskal-Wallis test is more robust than analysis of variance (ANOVA), which is often used for a similar purpose.

Seasonality was assessed by assigning each sample to one of four categories, based on its date of collection. Season 1 includes samples collected from March to May, season 2 runs from June to August, season 3 runs from September to November, and season 4 runs from December to February. These seasons, and their date limits, were selected based on the Southland groundwater monitoring programme, which stipulates that samples should be collected quarterly from each site, in or near March, June, September and December of each year. For these analyses, only groundwaters in unconfined aquifers were considered, and all such sites in Southland were considered as a single group.

The median values of most monitored parameters show no significant relationship to season. However, significant differences by season were observed for the median values of temperature and K. The tests are summarised in Appendix 5, along with summary statistics and Box-Whisker plots.

The seasonal variation in temperature is expected. Groundwater temperature is highest in season 1, which runs from March to May, and lowest in season 2, from June to August. Seasons 3 and 4 show expected mid-range temperatures. Concentrations of K show an opposite pattern, where median values are highest in season 2 (June to August) and lowest in season 3 (September to November). This pattern is probably related to flushing of accumulated K from the soil zone during seasons of higher rainfall.

3.5 Assessment of groundwater chemistry with respect to site location

Groundwaters in the vicinity of Mossburn, Lumsden and Gore (i.e. map sheets D43, E44, F44) are probably river-recharged and they are typically relatively dilute and Ca-HCO_3 dominated. Groundwaters in the vicinity of Edendale, Winton and Invercargill show higher concentrations of Na, K, Cl and SO_4, suggesting rainfall recharge and greater human/agricultural impact.

Variations in the median, MAD and/or trend of monitored parameters as a function of site location were investigated with the Kruskal-Wallis test, and with bubble plots showing parameter variation by northing and easting. Spatial variations in geochemistry were also assessed using hierarchical cluster analysis (HCA), but discussion of these results is deferred to Section 5.1.

Initially, the Kruskal-Wallis test was employed to test for significant differences in the medians, MADs or trends of indicator parameters between sites located on different 1:50k map sheets. The assignment of sites to categories based on map sheet location was based on northings and eastings and site names provided by Environment Southland. The monitoring sites considered here covered nine 1:50k map sheets: D43 (2 sites), D45 (3 sites), D46 (2 sites), E44 (6 sites), E45 (6 sites), E46 (9 sites), F44 (5 sites), F45 (5 sites) and F46 (6 sites). Eleven NGMP sites were also considered in the analysis, but these were considered together in a single category, with the aim of discerning any differences in monitored parameters between the NGMP monitoring sites and the Southland monitoring sites, as might arise due to differences in sampling protocol. Although the boundaries of the map sheets are arbitrary lines for categorisation, this exercise was intended to be a preliminary exploration of the data in spatial terms.

Roughly half of the monitored parameters showed significant difference in median, MAD and/or trend between the ten categories based on location, with differences in Cl, HCO_3, Mg, Na, DRP, SO_4, pH, Conductivity and ^{18}O being among the most significant. The results of the tests are summarised in Table 2 and Figure 5, and the tests themselves, along with summary statistics and Box-Whisker plots, are compiled in Appendix 6.

The observed differences in median values (Figure 5) can be explained by the fact that the map sheets segregate monitoring wells into classes that differ by altitude, recharge mechanism, and proximity to mountains and hills. Groundwaters from wells in map sheets D43, E44 and F44 typically have the lowest ^{18}O values, suggesting that they are recharged by rivers fed by high altitude rain. Accordingly, groundwaters from these wells (sheets D43, E44 and F44) also typically have the lowest conductivities, and the lowest concentrations of Na and Cl. The observed median values of ^{18}O, conductivity, Na and Cl suggest that sites in map sheet D43, E44 and F44 are characterised by groundwaters that are fairly dilute, “river-like” in composition, and are probably recharged by rivers originating in the nearby hills (see also Sections 4.10 and 5.1). On the other end of the spectrum, groundwaters from wells in map sheets D45, D46, E45, E46, F45 and F46 typically have higher ^{18}O values, higher conductivities, and higher concentrations of Na, K, Cl and/or SO_4. Groundwaters in these areas are probably recharged by lower altitude rain, which would accumulate Na, K, Cl and SO_4 during their passage through the soil zone during recharge.

Groundwaters from wells in different map sheets also appear to show different trends and/or MADs in Na, K, Cl and/or SO_4 (Figures 6 and 7). Specifically, groundwaters from wells in map sheets D45, E45 and F45 typically show the highest MADs and rates of concentration change for Na, K, Cl and/or SO_4. Groundwaters from wells in other map sheets typically have less variability in these parameters, nor do they show increasing trends in these parameters over time. Each of these substances might be expected to accumulate in soil, and so it is possible that high relative variabilities and/or increasing trends are related to a change or intensification of land use. Additional monitoring data would be required to adequately test this hypothesis.

Following analysis by the Kruskal-Wallis test as described above, a series of bubble plots were used to illustrate relationships between location and median values of Na, K, Ca, Mg, Cl, HCO_3, SO_4, and NO_3. Bubble plots were also created to illustrate relationships between location and trends in K, SO_4, NO_3 and Total Coliform counts. All plots are included in Figure 8.

The bubble plots for median concentrations corroborate the conclusions based on the Kruskal-Wallis test (above). Median concentrations of Cl and Ca are clearly lowest in groundwaters proximal to the hills in the vicinity of Mossburn in the Waimea Plains north of Gore, and highest in groundwaters near Winton, Invercargill and Edendale. Spatial relationships in Na, K and Mg are more subtle, but generally follow patterns observed for Ca and Cl. Median NO_3 and SO_4 concentrations are highest in groundwaters in the alluvial aquifers between the Ararima and Oreti Rivers near Winton and along the Mataura River between Gore and Edendale. However, spatial interpretation of median NO_3 and SO_4 concentrations requires care, because these substances will usually be relatively low in moderately reduced aquifers. For example, at sites D46/0003, D46/0031, E46/0110, E46/0096, E46/0098, Clarke and Thompson, median NO_3 and SO_4 concentrations are relatively low, and at several of these sites, median concentrations of Fe, Mn and/or NH_4 are relatively high. Two of these sites (E46/0096, E46/0098) are known to tap lignite aquifers, and the hydrochemistry at these sites is clearly indicative of anoxic conditions. The other sites mentioned above do not show the same level of anoxia, but the groundwaters are probably partially reduced. Taken together, these sites form a ring around Invercargill where hydrochemistry is probably controlled by organic materials in the aquifers. These sites are quite valuable to the monitoring programme, because they show that low NO_3 concentrations do not necessarily indicate limited human/agricultural impact.

The bubble plots for MADs and trends are more difficult to interpret. The MADs and trends of K, SO_4, NO_3 and Total Coliforms reach their highest values at monitoring sites between the Ararima and Oreti Rivers near Winton and along the Mataura River between Gore and Edendale. Although the cause of this temporal variability cannot be reliably determined with the available data, it may be related to factors or pressures such as abstraction or intensified land use.

3.6 Assessment of groundwater chemistry with respect to well depth

In general, groundwater chemistry does not show a strong relationship to depth. However, weak correlations suggest that substances likely to be introduced by human/agricultural activities (e.g. K, NO_3, SO_4) have highest values in shallow groundwater, whereas substances likely to be introduced during natural water-rock interaction (e.g. Fe, Mn, DRP, SiO_2) reach their highest values in deeper groundwaters.

Regression analyses were conducted to examine relationships between well depth and the medians, MADs and trends of monitored parameters. For these analyses, all Southland monitoring sites were considered as a group. The T statistic was used to determine if the regression slope was significantly different from zero, and the Pearson coefficient was used to assess the strength of the correlation. Regression equations, graphs and related statistics are compiled in Appendix 7.

There are no strong correlations between depth and the median, MAD or trend of any monitored parameter. The lack of correlation might be caused by consideration of all monitoring sites in a single group, or it might be caused by uncertainty in the reported depth (i.e. relative to the screened interval of the well or the water table).

The weak relationships between depth and monitored parameters generally suggest that human/agricultural activities have most visible impact on shallow groundwaters, whereas natural water-rock interaction has most impact on deeper groundwaters. For example, median concentrations and MADs of NO_3, K and SO_4 are usually highest in shallow groundwaters. In contrast, median concentrations and MADs of Fe, NH_4 DRP and SiO_2 are highest in deeper groundwaters. Note that the relationships between depth and NO_3, NH_4, Fe, Mn and SO_4 are probably controlled to some degree by redox potential, and indicate that deeper groundwaters are more likely to be anoxic than shallow groundwaters.

4.0 GEOCHEMICAL RELATIONSHIPS

4.1 Relationships between medians and trends of monitored parameters

The median concentration of an analyte cannot be used to predict trends in its concentration over time.

It would be instructive to know, for example, if the sites where NO_3 concentration was increasing most rapidly were also the sites with the highest median NO_3 concentrations. To address this and similar hypotheses, regression analyses were performed for each analyte to assess the strength of correlation between the median concentration and rate of concentration change. To conduct these analyses, all Southland monitoring sites (including NGMP sites in Southland) were considered as a group. The T statistic was used to determine if the regression slope was significantly different from zero, and the Pearson coefficient was used to assess the strength of the correlation. Regression equations, graphs and related statistics are compiled in Appendix 8.

For some analytes, correlations between median concentration and rate of concentration change were significant, but in all cases, the correlations were relatively weak. A similar lack of correlation between median concentration and rate of concentration change was reported by Daughney and Reeves (2003b).

The lack of correlation between median concentration and rate of concentration change is not surprising in a geochemical context. For example, consider two groundwaters with very low rates of Ca change over time. One might be a young dilute rainfall-dominated groundwater with low Ca concentration, where the rate of change in concentration is low because the rainfall has a relatively constant Ca concentration. The other could be an older groundwater with higher Ca concentration, where the rate of change in Ca concentration is low because the groundwater has reached saturation with respect to some Ca-bearing mineral. As a second example, consider two groundwaters that are both impacted by agricultural activities and have high concentrations of NO_3. One groundwater may be subjected to increased stocking, so that the already high NO_3 concentration could be increasing over time. The other groundwater might be impacted by reduced agricultural impact, so that the NO_3 concentration might actually be decreasing over time.

4.2 Relationships between medians and variability of monitored parameters

For most analytes, the median concentration and the variability are uncorrelated. However, For Total Coliforms, the median count is strongly correlated to the MAD.

It would be instructive to know, for example, if the sites with the highest variability (i.e. MAD) in NO_3 concentration were also the sites with the highest median concentration of NO_3. Such a relationship could arise in shallow unconfined aquifers, where high NO_3 concentrations might result from ease of infiltration, and high MAD might reflect seasonal climatic effects. To address this and similar hypotheses, regression analyses were performed for each analyte to assess the strength of correlation between the median concentration and the MAD. As above, all Southland monitoring sites (including NGMP sites in Southland) were considered as a group. The T statistic was used to determine if the regression slope was significantly different from zero, and the Pearson coefficient was used to assess the strength of the correlation. Regression equations, graphs and related statistics are compiled in Appendix 9.

For most analytes, correlations between median concentration and MAD were either very weak or insignificant. Total Coliform count was the only analyte that showed a strong correlation between median and MAD. This relationship indicates that where Total Coliform counts are highest, they will also be most variable.

4.3 Relationships between trends and variability of monitored parameters

For any given analyte, the rate of concentration change and the amount of variability in concentration are uncorrelated.

These tests were performed to examine relationships between the variability of an analyte and its rate of concentration change over time. A correlation between the rate and the MAD might arise, for example, in a shallow unconfined aquifer susceptible to both seasonal variability (high MAD) and a continued geochemical pressure (high rate of change). As above, all Southland monitoring sites (including NGMP sites in Southland) were considered as a group. The T statistic was used to determine if the regression slope was significantly different from zero, and the Pearson coefficient was used to assess the strength of the correlation. Regression equations, graphs and related statistics are compiled in Appendix 10.

For most analytes, correlations between rate of concentration change and MAD were either very weak or insignificant. In some cases, apparently strong correlations were the result of just one or two points with very high influence on the regression.

4.4 Relationships between medians of different monitored parameters

The median concentrations of several pairs of different analytes are significantly correlated. In some cases, if the median concentration of one parameter is missing, it can be reasonably well predicted from median concentrations of other analytes.

A multiple-variable analysis was conducted to search for significant correlations between the median values of different analytes in the different Southland monitoring sites. This procedure was designed to summarise several fields of quantitative data, in this case including the median concentrations (mg/L) of Br, Ca, Cl, F, Fe, HCO_3, K, Mg, Mn, Na, NH_4, NO_3, DRP, SiO_2 and SO_4.

The data were plotted on tiered multivariate graphs (Figure 9). This procedure revealed eleven pairs of variables that showed relatively strong correlations (Appendix 11). These pairs of variables are listed below, along with their Pearson coefficients (r) for the Southland monitoring data and the number of data pairs (n) used in the evaluation. The Pearson coefficients for the NGMP dataset as a whole (Daughney and Reeves, 2003a) are also given for reference (n = 107).

Br and Ca	Southland r = -0.65	n = 19	NGMP r = 0.31
Br and Cl	Southland r = 0.65	n = 19	NGMP r = 0.87
Ca and HCO_3	Southland r = 0.73	n = 55	NGMP r = 0.78
Cl and F	Southland r = 0.84	n = 16	NGMP r = 0.18

Cl and Na	Southland r = 0.73	n = 55	NGMP r = 0.86
F and Na	Southland r = 0.84	n = 16	NGMP r = 0.45
F and NO_3	Southland r = -0.81	n = 16	NGMP r = -0.49
F and SiO_2	Southland r = 0.70	n = 16	NGMP r = 0.06
HCO_3 and SiO_2	Southland r = 0.71	n = 19	NGMP r = 0.13
K and SiO_2	Southland r = -0.64	n = 19	NGMP r = 0.42
Na and SiO_2	Southland r = 0.85	n = 19	NGMP r = 0.45

Based on these correlations, if the median concentration of one parameter is missing, it can be reliably predicted from median concentrations of other analytes. Equations describing simple linear relationships between the above pairs of variables are presented in Appendix 11. Multiple linear regressions have also been developed to predict concentrations of Br, F and SiO_2, all of which are not typically monitored in Southland. The multiple linear regressions indicate that Br concentration can be predicted from Ca and Cl (r = 0.71), F can be predicted from Cl and NO_3 (r = 0.94), and SiO_2 can be predicted from Cl, HCO_3 and K (r = 0.98) (Appendix 12).

4.5 Relationships between trends in different monitored parameters

The rates at which the concentrations of different analytes are changing are uncorrelated. If the rate of concentration change of one parameter is missing or has not been determined, it cannot be estimated based on the rates of concentration change of other analytes.

A multiple-variable analysis was conducted to search for significant correlations between the rates of concentration change of different analytes in the Southland monitoring sites. This procedure was designed to summarise several fields of quantitative data, in this case including the rates of change of concentrations (mg/L per year) of Br, Ca, Cl, F, Fe, HCO_3, K, Mg, Mn, Na, NH_4, NO_3, DRP, SiO_2 and SO_4.

The data were plotted on tiered multivariate graphs (Figure 10). This procedure revealed only one pair of variables (Cl and F) that showed a relatively strong correlation between their rates of change (Appendix 13). Several other pairs of variables appeared to be correlated in terms of concentration change, but in fact the relationships were biased by a small number of points with exceedingly large influence (leverage) on the regression.

4.6 Assessment of groundwater chemistry with respect to aquifer lithology

The median, MAD and trend of most monitored parameters show no significant relationship to aquifer lithology. However, the median, MAD and/or trend of Fe, NO_3, NH_4 or SO_4 are often different in lignite compared to other aquifers, presumably due to the low redox potentials expected for groundwaters in organic-rich material.

The Kruskal-Wallis test was employed to test for significant differences in the medians, MADs and trends of indicator parameters between aquifers of different lithology. The Kruskal-Wallis test is non-parametric, and thus it does not require the assumption that the parameters being assessed follow the normal distribution (Helsel and Hirsch, 1992). In this regard, the Kruskal-Wallis test is more robust than analysis of variance (ANOVA), which is often used for a similar purpose.

The assignment of sites to lithology classes was based on information provided by Environment Southland. Four aquifer lithology classes were used, namely alluvial gravel (31 sites), claybound gravel (5 sites), lignite (2 sites) and limestone (1 site). There is naturally some uncertainty associated with the assignment of sites to these lithology categories, and this should be considered in the discussion that follows. Sites with no available information about aquifer lithology were also considered in the Kruskal-Wallis test.

The majority of monitored parameters show no significant difference in median, MAD or trend between the four categories of aquifer lithology. However, significant differences by aquifer lithology were observed for median values of Fe, NH_4, NO_3 and pH, for MADs of Fe and NO_3, and for trends in DRP and SO_4. The results of the tests are summarised in Table 2, and the tests themselves, along with summary statistics and Box-Whisker plots, are compiled in Appendix 14.

Median values of Fe, NH_4 and NO_3 differ significantly between the different lithology categories. Median concentrations of Fe and NH_4 are significantly higher in the lignite aquifers than in any of the other lithologies. Conversely, median NO_3 concentrations are significantly lower in lignite aquifers. These variations pertain to redox state. Fe and NH_4 should in theory only be dissolved in anoxic groundwaters, whereas NO_3 should only be present in oxidised groundwaters. Lignite aquifers contain large quantities of organic carbon which acts as a reductant. This leads to low redox potential (i.e. anoxia), thus explaining the high concentrations of Fe and NH_4 and the low concentration of NO_3.

The MAD of Fe is higher in lignite aquifers than in any other category, and the MAD of NO_3 is lower in lignite than in any other category. Again, this effect is related to the tendency of lignite aquifers to be reduced (anoxic), and to the control of redox potential on the solubility of Fe and NO_3. Because Fe can dissolve in anoxic groundwaters, it is logical that its MAD is high in lignite; because NO_3 cannot dissolve in anoxic groundwater, its MAD is low in lignite. To generalise, the MAD of a substance is most likely to be smallest when its median concentration is held near zero by some geochemical or biochemical process.

The role of redox potential also explains the significant variation of trends in SO_4 between the different aquifer lithologies. SO_4 trends are lower in lignite than in any other aquifer class. Like NO_3, SO_4 tends to be removed from anoxic groundwaters by microbial activity. Because its concentration in lignite is typically low, it is logical that its rate of change should also be low, when compared to other aquifer lithologies.

The Kruskal-Wallis tests also show that median pH is significantly higher in the one limestone aquifer than in any other lithology. Although this statement is based on only one observation in a single limestone aquifer, it is geochemically reasonable, because the dissolution of limestone involves the consumption of protons, resulting in an upward shift in pH (Langmuir, 1997).

Finally, trends in DRP were observed to vary significantly by aquifer lithology, being lower in lignite than in any other category. The reason for this relationship is unclear.

4.7 Assessment of groundwater chemistry with respect to aquifer confinement

The median, MAD and trend of most monitored parameters show no significant relationship to aquifer confinement. However, confinement category has a significant impact on medians of NO_3 and NH_4, on MADs of DRP, NO_3 and Mn, and on trends in SO_4. These significant differences are likely controlled by redox potential, and suggest that unconfined aquifers tend to be oxidised whereas confined aquifers tend to be anoxic.

The Kruskal-Wallis test was employed to test for significant differences in the medians, MADs or trends of indicator parameters between aquifers of different confinement. The Kruskal-Wallis test is non-parametric, and thus it does not require the assumption that the parameters being assessed follow the normal distribution (Helsel and Hirsch, 1992). In this regard, the Kruskal-Wallis test is more robust than analysis of variance (ANOVA), which is often used for a similar purpose.

The assignment of sites to confinement classes was based on information provided by Environment Southland. Three aquifer confinement classes were used, namely unconfined (28 sites), semiconfined (3 sites) and confined (2 sites). There is naturally some uncertainty associated with the assignment of sites to these confinement categories, and this should be considered in the discussion that follows. Sites with no available information about aquifer confinement were excluded from the Kruskal-Wallis test.

The majority of monitored parameters show no significant difference in median, MAD or trend between the three categories of aquifer confinement. However, significant differences by aquifer confinement were observed for median values of NH_4 and NO_3, for MADs of Mn, DRP and NO_3, and for trends in SO_4. The results of the tests are summarised in Table 2, and the tests themselves, along with summary statistics and Box-Whisker plots, are compiled in Appendix 15.

The significant differences in median NO_3 and NH_4 by confinement category probably reflect the role of redox potential, as discussed above. The Kruskal-Wallis test indicates that median concentrations of NO_3 tend to be lowest in confined aquifers and highest in unconfined aquifers, whereas median NH_4 concentrations behave oppositely. Because NO_3 and NH_4 are theoretically dominant in oxidised or reduced groundwaters, respectively, the observed difference by aquifer confinement suggest that unconfined aquifers tend to be oxidised, whereas confined aquifers are more likely to be anoxic. This hypothesis is supported by observed variations in other redox-sensitive compounds besides NO_3 (e.g. NH_4, Mn, SO_4), as described below.

An alternative explanation for significant differences in median NO_3 and NH_4 by confinement category is related to groundwater age. Specifically, if a groundwater pre-dates the period of intensive agriculture in Southland (c. 30 years), then it may display a lower median NO_3 concentration than a younger groundwater. If confined aquifers typically host older groundwaters than unconfinded aquifers, then a significant difference in median NO_3 concentration might be expected. Unfortunately, there is insufficient data to perform a reliable statistical assessment of age variation by aquifer confinement. Relationships between age and values of monitored parameters are discussed further in Section 4.12.

The significant differences in trend of SO_4 by confinement category probably also reflect the role of redox potential. The Kruskal-Wallis test indicates that SO_4 concentrations are higher and positive in unconfined aquifers and lower and negative in confined aquifers. SO_4 is only soluble in oxidised groundwaters; in anoxic waters, it is removed by microbial sulfate reduction. The observation that SO_4 concentrations are often decreasing over time in confined aquifers suggests that many of these aquifers may be anoxic. The observed increase in SO_4 concentration in unconfined aquifers may be indicative of increasing human/agricultural impact in near-surface, oxidised environments.

The MAD of NO_3 is observed to be lower in confined aquifers than in any other confinement category. Following the discussion above, if confined aquifers are likely to be anoxic, then the median concentration of NO_3 will likely be near zero, and therefore the MAD of NO_3 must also be accordingly small. A similar geochemical control causes the MAD of Mn to be lower in unconfined aquifers than in confined aquifers. Namely, Mn is theoretically only soluble in anoxic groundwater, which would be expected more often in confined than in unconfined aquifers. Because the solubility of Mn is limited in unconfined aquifers, its MAD is accordingly low, compared to confined (anoxic) aquifers. This same process may also explain the observation that the MAD of DRP tends to be higher in confined than in unconfined aquifers. DRP is not controlled by redox solubility, but its median concentration in near-surface aquifers is typically observed to be low, perhaps because of limitation of phosphorus by algae in surficial recharge waters. In summary, the MAD of a parameter is most likely to vary significantly between confinement categories if its median concentration is held near zero in one or more of the categories by some geochemical or biochemical process.

4.8 Assessment of groundwater chemistry with respect to groundwater use

The median, MAD and trend of most monitored parameters show no significant relationship to groundwater use. However, sites where groundwater is used for stock have lower medians, MADs and/or trends in Ca, Mg, DRP, NO_3 and/or SO_4 compared to sites where groundwater is used for domestic purposes.

The Kruskal-Wallis test was employed to test for significant differences in the medians, MADs or trends of indicator parameters between different categories of groundwater use. The Kruskal-Wallis test is non-parametric, and thus it does not require the assumption that the parameters being assessed follow the normal distribution (Helsel and Hirsch, 1992). In this regard, the Kruskal-Wallis test is more robust than analysis of variance (ANOVA), which is often used for a similar purpose.

The assignment of sites to categories related to groundwater use was based on information provided by Environment Southland. Four groundwater use classes were defined, namely domestic (11 sites), stock (10 sites), a combination of domestic and stock use (11 sites) or something other (2 sites, e.g. school). There is naturally some ambiguity associated with the assignment of sites to these groundwater use categories, and this should be considered in the discussion that follows. Moreover, it appears that the use categories are based on the use of groundwater at the site, not on the land use around the site, but there should be a correlation between the two. Sites with no available information about aquifer confinement were excluded from the Kruskal-Wallis test.

The majority of monitored parameters show no significant difference in median, MAD or trend between the four categories of groundwater use. However, significant differences by use category were observed for median values of NO_3, DRP, SO_4, and Total Coliforms, for

MADs of Ca, Mg, NO_3 and SO_4, and for trends in SO_4. The results of the tests are summarised in Table 2, and the tests themselves, along with summary statistics and Box-Whisker plots, are compiled in Appendix 16.

Observed relationships between median concentrations and groundwater use categories are not easy to interpret. For example, the Kruskal-Wallis test indicates that Total Coliform counts are highest at sites where groundwater is used for stock. This would imply that the stock is the source of the bacteria. However, if this were the case, then median NO_3 concentration should follow the same pattern, but in fact median NO_3 is typically lowest at sites where in groundwater is used for stock. Similarly, median SO_4 concentrations are lowest at sites in the stock use category and highest for sites in the domestic use category. The observation that median concentrations of NO_3 and SO_4 are highest at sites where groundwater is used for domestic purposes may be related to the existence and/or proximity of domestic septic tanks.

Likewise, observed relationships between MADs and the groundwater use categories are not easy to interpret. The monitored parameters with MADs that differ significantly between the groundwater use categories (Ca, Mg, NO_3, SO_4) tend to have the highest variability at sites used for domestic purposes. Such differences in MAD based on groundwater use may be related to rate or variability in abstraction, or on the proximity of domestic septic tanks to these wells, but these suggestions are only tentative.

Finally, SO_4 is the only monitored parameter with trends that differ significantly by groundwater use category. As for median and MAD, the trends in SO_4 are observed to be higher at sites where groundwater is used for domestic purposes. The reason for this is unclear, but again, might be due to the position of such wells relative to domestic septic tanks.

4.9 Assessment of groundwater chemistry with respect to well head protection

The various forms of well head protection appear to have no effect on the median, MAD or trend of any of the monitored parameters.

The Kruskal-Wallis test was employed to test for significant differences in the medians, MADs or trends of indicator parameters between different degrees of well head protection. The Kruskal-Wallis test is non-parametric, and thus it does not require the assumption that the parameters being assessed follow the normal distribution (Helsel and Hirsch, 1992). In this regard, the Kruskal-Wallis test is more robust than analysis of variance (ANOVA), which is often used for a similar purpose.

The assignment of sites to categories describing well head protection was based on information provided by Environment Southland. The available information described whether or not the well head was covered, sealed by a concrete pad, located inside a shed, and/or isolated from livestock. To provide an overall descriptor of well head protection, the presence or absence of each form of protection was given a value of 1 or 0, respectively, and the four numbers were summed. This resulted in a single number for each site between 0 and 4, where the lower values corresponded to lower degrees of well head protection. Finally, the median, MAD and trend in each monitored parameter was independently compared to the well head descriptor. Sites with no available information about well head protection were excluded from the Kruskal-Wallis test.

None of the monitored parameters showed significant difference in median, MAD or trend between the categories of well head protection. The results of the tests are summarised in Table 2.

4.10 Relationships between ^{18}O and monitored parameters

^{18}O is correlated to median Cl, Na and Conductivity, which reflects a differentiation between rainfall-recharge and river-recharge. There are no correlations between ^{18}O and medians, trends or MADs of any other parameters.

Regression analyses were conducted to examine relationships between ^{18}O and the median concentrations of other analytes. For these analyses, all Southland monitoring sites were considered as a group. The T statistic was used to determine if the regression slope was significantly different from zero, and the Pearson coefficient was used to assess the strength of the correlation. Regression equations, graphs and related statistics are compiled in Appendix 17.

^{18}O is positively correlated to median Cl, Na and to Conductivity, but shows only weak relationships with the median concentrations of other analytes. There are no significant correlations between ^{18}O value and the rate of change of concentration of any analyte, or to the MAD of any analyte.

The relationship between ^{18}O and Cl, Na and Conductivity is probably related to groundwater recharge mechanism. In general, ^{18}O decreases about 0.2 ‰ with each 100 m rise in altitude, though relationships are not well constrained in Southland (Stewart and Morgenstern, 2001). Rivers, which are fed by high-altitude rainfall, typically have low (more negative) ^{18}O values (c. -10 ‰), and Cl about 8 mg/L, Na about 6 mg/L and Conductivity on the order of 100 uS/cm (Langmuir, 1997). Groundwaters that are recharged primarily by rivers would be expected to have ^{18}O, Cl, Na and Conductivity values in this neighbourhood. Low altitude rainfall typically has more positive positive ^{18}O values (c. -7 ‰). Groundwaters recharged by rain might show higher Cl, Na and Conductivity, reflecting accumulation of these ions during infiltration through the soil zone. Substances such as Na, Cl, K and SO_4 would be concentrated in soil due to evapotranspiration and agricultural activities, and concentrations of Na and Cl in rain are naturally highest near the coast. See Section 5.1 for further discussion.

4.11 Relationships between ^{15}N and monitored parameters

Only 17 sites have been analysed for ^{15}N, 15 of which had values indicative of soil organic nitrogen, and two of which had values indicative of human or animal waste. There are no apparent correlations between ^{15}N and any other monitored parameter.

Regression analyses were conducted to examine relationships between ^{15}N and the median, MAD and trend in concentrations of other analytes. For these analyses, all Southland monitoring sites were considered as a group. The T statistic was used to determine if the regression slope was significantly different from zero, and the Pearson coefficient was used to assess the strength of the correlation.

There were no significant identifiable relationships between ^{15}N and the median, MAD or trend of any other monitored parameter. ^{15}N values did not appear to show any relationship to sample location. Of the 17 sites at which ^{15}N had been measured, 15 sites had values in the range expected for typical soil organic nitrogen (c. 5 – 10 ‰, Chapelle, 1993). Two of the monitoring sites at which ^{15}N had been measured had values indicative of human or animal waste (c. 10 – 20 ‰).

4.12 Relationships between groundwater age and monitored parameters

Younger groundwaters (CFC/SF_6 age) tend to have higher median concentrations of NO_3 and K, presumably due to modern intensification of agriculture, whereas older groundwaters tend to have higher median concentrations of DRP and HCO_3, which presumably accumulate over time due to natural water-rock interaction. Relationships to the MAD of DRP and to trends in Na can be tentatively used to estimate groundwater age where it hasn't yet been measured.

Regression analyses were conducted to examine relationships between groundwater age (CFC or SF_6, expressed in years) and the median, MAD and trends in other monitored parameters. For these analyses, all Southland monitoring sites at which age had been measured (8 sites) were considered as a group. The T statistic was used to determine if the regression slope was significantly different from zero, and the Pearson coefficient was used to assess the strength of the correlation. Regression equations, graphs and related statistics are compiled in Appendix 18.

Groundwater age is significantly correlated to the median concentrations of HCO_3, K, NO_3, DRP (Figure 11). Median HCO_3 and DRP increase with groundwater age, presumably due to water-rock interaction, whereas median K and NO_3 decrease with groundwater age, suggesting that they are added to groundwaters by modern (probably human/agricultural) activities. The variability (MAD) of K and conductivity have significant negative correlations to groundwater age, whereas the MAD of DRP has a significant positive correlation to groundwater age (Figure 12). Again, this suggests that K and conductivity are influenced by modern, possibly human/agricultural processes, while DRP accumulates to variable degree in groundwater due to natural water-rock interaction over time. Four monitored parameters show significant correlations (all positive) between their trends and groundwater age (Mn, Na, DRP and pH) (Figure 13). These relationships suggest that these substances accumulate more quickly in older groundwaters than in younger ones. For Mn, DRP and pH, this may again be a sign that these substances accumulate in groundwaters over time in response to natural water-rock interaction. The observed relationship between trend in Na and age is harder to explain, because Na would be expected to accumulate fairly quickly in younger groundwaters, especially those recharged by rain; Na also accumulates in groundwaters due to natural water-rock interaction. Clearly, more age data are required to constrain these relationships and their causes.

A multiple regression analysis was performed to identify the set of variables that best predicts groundwater age. The result suggested that the MAD of DRP and the trend in Na provided the best estimate, where

Age (years) = 10.76 + 3045.9*drpmad + 29.0561*nat

The multiple regression analysis is presented in Appendix 19, and the quality of the regression is shown in Figure 14. This relationship can be used to estimate the age of a groundwater where it has not yet been determined by CFC or SF_6 measurement, but the accuracy of the estimate has considerable uncertainty. Moreover, despite the quality of the regression, there is no obvious logic to its underlying cause.

5.0 OVERALL ASSESSMENT OF GROUNDWATER GEOCHEMISTRY IN SOUTHLAND

5.1 Factors controlling Southland groundwater chemistry

Natural water-rock interaction and human/agricultural impacts constitute opposing forces that affect groundwater geochemistry in Southland. These two forces vary in relative strength across sub-regions of Southland.

Many of the correlations between the median concentrations of different analytes are related to natural water-rock interaction (Section 4.4). The correlation between Ca and HCO_3 concentration probably reflects control of both substances by equilibration with carbonate minerals, which are readily soluble and ubiquitous in most watersheds. Most river waters and many younger or river-dominated groundwaters are Ca-HCO_3 type waters due to the rapid dissolution of carbonate minerals. The correlation between SiO_2 and F probably represents release of these substances during slow dissolution of silicate minerals in the aquifers. The correlations between Na and Cl and Br and Cl probably represent dissolution or equilibration with mineral salts. Such salts are present in rainwater (with concentration related to distance from the coast), and they tend to be concentrated in soils due to evapotranspiration and activities related to agriculture. Median concentrations of Na and Cl are also often correlated in older, more evolved groundwaters. It is often observed that groundwaters become less Ca-HCO_3 dominated and more Na-Cl dominated with age, because although carbonate minerals are common and dissolve rapidly, Na and Cl minerals have much higher solubilities, and so they are able to accumulate to much higher concentrations in groundwater given sufficient time. This may explain the observed correlations between Na, Cl, Br, F, DRP and SiO_2; all of these substances tend towards increasing concentrations in older, more evolved groundwaters.

Some of the correlations between the median concentrations of different analytes are related to human or agricultural influence. In particular, there is a strong inverse correlation between F and NO_3. As stated above, F tends to accumulate in older, more evolved groundwaters due to natural water-rock interaction. The inverse correlation with NO_3 suggests that NO_3 is present in young, less evolved groundwaters, potentially because of its introduction by human or agricultural activities. Similarly, a relatively strong inverse correlation exists between K and SiO_2. Again, this may imply that K, or a fraction of it, is introduced to younger groundwaters due to human or agricultural impact (K is also leached from aquifer minerals over time due to natural water-rock interaction). Note that K and NO_3 are not strongly correlated.

In an attempt to support the conclusions made above, Principal Components Analysis (PCA) was conducted to identify the major causes of variability in the data. PCA was conducted with log-transformed and scaled median concentrations (mg/L) of Br, Ca, Cl, F, Fe, HCO_3, K, Mg, Mn, Na, NH_4, NO_3, DRP, SiO_2 and SO_4. Where Br, F or SiO_2 concentrations had not been measured, they were estimated using the regression equations given in Appendix 12.

PCA revealed four significant components (Eigenvalue > 1) that were collectively able to describe 81% of the variability in the original data (Appendix 21). Figure 15 shows a plot of the weightings of the two main components, which cumulatively describe 52% of the variation in the original data. The plot shown in Figure 15 is very similar to results obtained by Daughney and Reeves (2003a) using all of the data from the National Groundwater Monitoring Programme.

Principal Components Analysis suggests that natural water-rock interaction and human/agricultural impacts constitute opposing forces that control groundwater geochemistry in Southland. Redox potential, Total Dissolved Solids (TDS), and human/agricultural impact (in the form of NO_3) appear to be the dominant controls on groundwater chemistry. The former two controls are likely related to natural water-rock interaction. Both Components 1 and 2 show strong negative loadings of NO_3 and strong positive loadings of Fe, Mn and NH_4. This demonstrates the importance of redox potential, because NO_3 only dominates in oxic waters, whereas the latter three substances are only present in anoxic waters. Component 1 also shows positive weightings of all substances except NO_3. This is suggestive of a distinction between dilute waters with low TDS and more concentrated waters with high TDS. The fact that NO_3 is inversely related to TDS (i.e. to the concentrations of all other substances) suggests that the NO_3 is not naturally introduced, but rather is added to the groundwater by human or agricultural activities.

As a final investigation into factors controlling groundwater chemistry in Southland, the sites were partitioned into categories based on Hierarchical Cluster Analysis (HCA). HCA provides a means of dividing the sites into groups based on their chemical characteristics, without assuming that the group definitions are related to map sheet boundaries (as in Section 3.5). HCA was conducted using log-transformed and scaled median concentrations (mg/L) of Br, Ca, Cl, F, Fe, HCO_3, K, Mg, Mn, Na, NH_4, NO_3, DRP, SiO_2 and SO_4. Where Br, F or SiO_2 concentrations had not been measured, they were estimated using the regression equations given in Appendix 12. A total of 41 sites had information for all of these parameters, and so could be considered in HCA. Ward's linkage rule was used in the HCA, and the square of the Euclidean distance was used as the separation measure (Daughney and Reeves, 2003).

At a relatively high separation threshold of c. 500, seven sites (cluster 1) are differentiated from the remaining 34 (Figure 16). These seven sites are located on map sheets D43, E44 and F44, proximal to the hills in the vicinity of Mossburn, Lumsden and the Waimea and Waikaia Plains (Figure 17). Table 3 shows that these seven sites have dilute (c. 140 uS/cm), Ca-HCO_3 type waters with very low Na, Cl, K and estimated SiO_2. These groundwaters also have the most negative ^{18}O values, indicating recharge by rivers and/or high altitude rain. NO_3 concentrations are generally low, on the order of 2 mg/L, but may be higher in the Waimea and Waikaia Plains.

If the separation threshold is lowered, a cluster containing just two sites can be defined. Both of these two sites tap confined lignite or lignite-bearing aquifers, and they are located immediately east of Invercargill (Figures 16 and 17). The groundwaters from these sites are differentiated from others in Southland by anoxic conditions. As a result of this anoxia, Fe and Mn are able to dissolve, and reach concentrations well in excess of those in other Southland groundwaters (Table 3). Again due to the reducing conditions, nitrogen exists as NH_4, and NO_3 is absent.

The groundwaters from the remaining 32 sites are all very similar, but can be tentatively divided into two groups based on water type (Figure 16, Table 3). Figure 17 indicates that the groundwaters with slightly more Ca-HCO3 character (cluster 3) tend to be found between the Ararima and Oreti Rivers, north of Invercargill, in the area of Winton. The groundwaters with slightly more Na-Cl character (cluster 4) are found around Invercargill, Edendale and Gore. There are several possible explanations for the geographic distribution of these two subtly different categories of groundwater. First, the groundwaters with slightly more Na-Cl character occur closer to the coast, and may thus be affected by higher salt concentrations in rainfall recharge. Second, groundwaters with slightly more Na-Cl character may result from passage through soils with higher salt content, as might result from greater evapotranspiration and/or more intensive agricultural land use. Third, the spatial distribution of cluster 3 vs. cluster 4 groundwaters might be caused by slightly different ratios of rainfall recharge (Na-Cl) vs. river recharge (Ca-HCO_3) in different areas of Southland. Finally (and least likely), groundwaters in the more Na-Cl dominated category (cluster 4) might be slightly older. This last hypothesis is reasonable, since groundwaters do tend to evolve towards more Na-Cl character with age, and, based on the topography, the regional groundwater flow regime is probably toward the coast. Additional research is required to determine which, if any, of these possible explanations are relevant to Southland.

5.2 Baseline groundwater quality in Southland

A sufficient quantity of data is now available for definition of baseline groundwater quality in Southland. An approach based on rank-percentiles of parameters is appropriate to account for variations in groundwater quality caused by natural and/or anthropogenic factors. It is also appropriate to develop different definitions of baseline for recognisably different categories of groundwater.

A definition of baseline quality is vital for effective management of groundwater resources. For example, for reasons related to human activity, the concentration of some analyte may be elevated. It is only possible to make an assessment like this if the baseline (i.e. 'normal') concentration of the analyte has been quantified. The definition of baseline quality is a central objective of the Environment Southland groundwater monitoring programme. A similar emphasis on defining baseline groundwater chemistry can be found around the world, for example in the newly established Water Framework Directive, which applies to all of the European Union.

A sufficient quantity of data is now available for a preliminary definition of the baseline groundwater quality in Southland. However, the groundwater community does not have a standard protocol for the determination or definition of baseline groundwater quality. Clearly, each parameter's level is expected to depend upon variables such as location, depth, aquifer lithology and confinement, so baseline must be defined as a range of values, rather than as a single number. In this report, rank-based percentiles are used to define the range of parameter values that define baseline. The median is used as the measure of central tendency, the 25th and 75th percentiles provide a conservative, narrow definition of baseline, and the 5th and 95th percentiles give a broader definition of baseline.

As a first approximation of baseline, data from all monitoring sites are considered together. In this approach, all data for a given parameter are assumed to come from a single distribution, regardless of site location, aquifer hydrogeology or other potentially important factors. The 5th, 25th, 50th, 75th and 95th percentiles expected for each parameter, based on all of Southland's data (including the NGMP sites in Southland), are presented in Table 3. Note that here, because Br, F and SiO_2 are not routinely monitored at many sites in Southland, their baseline concentrations were estimated using the multivariate regressions given in Appendix 12.

A second and more robust means of defining baseline groundwater quality is to break the monitoring sites up into categories based on some set of critical factors (e.g. location, lithology, confinement, etc.), and define a range of 'normal' values for each parameter (e.g. 25th and 75th or 5th and 95th percentiles). Daughney and Reeves (2003a) used HCA to divide sites from the NGMP into six categories, and they defined a range of expected parameter values for each. Following a similar approach, the Southland monitoring sites can be placed into one of four categories (Section 5.1, Figure 16): 1) relatively young, unimpacted, river-recharged groundwaters, 2) anoxic, more evolved groundwaters representative of confined organic-rich aquifers, 3) rainfall-recharged groundwaters of intermediate age and predominant Ca-HCO_3 character, showing some evidence of human/agricultural impact, and 4) rainfall-recharged groundwaters of intermediate age with slightly more Na-Cl character and a similar level of human/agricultural impact. The definitions of baseline groundwater quality for each of these four categories are presented in Table 3.

The two methods for defining baseline groundwater quality can be compared, for example, by consideration of the range of NO_3 concentrations considered to be 'normal'. If all monitoring sites are considered together, the resulting definition of baseline would suggest that median NO_3 concentrations above 5.9 mg/L (i.e. 75th percentile) anywhere in Southland are probably indicative of human or agricultural impact. Compared to data from the NGMP, where the 75th percentile in NO_3 is 3.5 mg/L, Southland appears to have relatively high concentrations of this analyte. An alternative approach would be to define the range of 'normal' NO_3 concentrations based only on sites from Category 1, which appear to include only young, river-recharged, relatively pristine groundwaters. The 75th and 95th percentiles of NO_3 in Category 1 are 3.6 and 3.9 mg/L, respectively (Table 3). The latter definition of baseline is more in agreement with the NGMP data, such that it is perhaps more appropriate to conclude that any site where median NO_3 exceeds 3.9 mg/L almost certainly shows some degree of human or agricultural impact. By extension then, many groundwaters in Southland are already in excess of the baseline value for NO_3.

5.3 Comparison of Southland groundwater quality to the rest of New Zealand

Groundwater quality in Southland is comparable to that of gravel-hosted groundwaters in other parts of New Zealand, but Southland aquifers typically have higher median concentrations of NO_3. The number of Southland sites at which groundwater quality is either improving or degrading with time exceeds the national average based on the NGMP data.

As a preliminary means of comparing Southland's groundwater quality to other parts of New Zealand, the rank-percentiles for each parameter can be compared to the corresponding data from the NGMP (Table 3). Based on the median values (50^{th} percentile), most monitored parameters have similar levels in Southland and across New Zealand as a whole. Understandably, based on the 25^{th} and 75^{th} percentiles (i.e. the inter-quartile range), the Southland data cover a narrower range of compositions, compared to data from the entire NGMP.

NO_3 is the only parameter that is distinctly different in Southland compared to the rest of New Zealand. The median NO_3 concentration in Southland groundwater is 3.4 mg/L, compared to 0.7 mg/L for all of the NGMP data. Of course, most of the Southland aquifers are oxidised, whereas many sampled in the NGMP are anoxic and thus would not be expected to have measurable NO_3. However, the median concentration of NO_3 in oxidised NGMP aquifers is 1.4 mg/L; and even at NGMP sites that show evidence of agricultural impact, the median NO_3 concentration is only 2.3 mg/L (Daughney and Reeves, 2003a). This indicates that levels of NO_3 in Southland are typically relatively high, compared to sites monitored through the NGMP.

A second approach for comparing Southland groundwater quality to the rest of New Zealand is to assign each Southland monitoring site to a category based on the cluster definitions based on median concentrations of analytes at NGMP sites, as derived by Daughney and Reeves (2003a). Daughney and Reeves (2003a) grouped the NGMP sites into six categories, based on the median concentrations of 15 chemical parameters (Tables 4 and 5). Each Southland monitoring site can be placed into one of these six categories, based on its median concentrations of the same 15 analytes (Table 1). By far the majority of Southland sites fall into clusters 1A-1 or 1A-2, suggesting that they are characterised by oxidised groundwaters showing a measurable level of human or agricultural impact. Although this result is in general agreement with statements made elsewhere in this report, it is important to note that the cluster definitions of Daughney and Reeves (2003a) have not been rigorously tested for their applicability to non-NGMP sites. Further, at many Southland sites, some of the required data for cluster assignment were lacking (e.g. concentrations of Br, F, SiO_2), and so the assignments are only tentative.

A third approach for comparing Southland groundwater quality to the rest of New Zealand is to assign each Southland monitoring site to a category based on trends observed in the NGMP data (Daughney and Reeves, 2003b). Daughney and Reeves (2003b) assigned each NGMP site to one of five categories based on the trends in the concentrations of 15 analytes (Table 6). It is only possible to assign 39 of the Southland sites to one of the NGMP trend-based clusters, because many of the Southland sites do not have all of the required hydrochemical data. Still, assignment of the Southland sites to these same categories suggests that 15 sites are exhibiting relatively slow changes in hydrochemistry over time, potentially representative of natural water-rock interaction (Table 1). The proportion of Southland site showing slow trends over time (38%) is quite a bit lower than observed for the NGMP dataset as a whole (71%). At sixteen of the Southland sites where a trend-based cluster assignment can be made, changes in groundwater chemistry suggest that human/agricultural impact is actually decreasing with time (Trend cluster P). A relatively higher proportion of Southland sites seem to have improving water quality (41%) compared to the NGMP as a whole (8%). Finally, eight of the Southland sites that could be assigned to a trend-based category seem to show water quality that is becoming worse over time (Trend Cluster I). The proportion of Southland sites showing declining water quality over time (21%) is higher than for the NGMP dataset as a whole (11%). As is the case for the median-based clusters, it is important to note that the trend-based cluster definitions of Daughney and Reeves (2003b) have not been rigorously tested for their applicability to non-NGMP sites, and that at many Southland sites, some of the required data for cluster assignment were lacking. Because of these limitations, any conclusions based on assignment of Southland sites to trend-based categories based on the NGMP data must be considered as tentative.

6.0 RECOMMENDATIONS

Data that describe the various suspected pressures on Southland groundwater quality should be compiled and if possible collected on a regular basis at each monitoring site (e.g. stock density, groundwater abstraction rate and volume). These data should then be compared to groundwater quality through the pressure-state-response framework, as recommended by the Southland baseline groundwater monitoring program. The analysis of Southland's groundwater quality indicates that many areas are already impacted by human/agricultural activities, and so the pressures or factors responsible for this must be quantified as soon as possible, so that corrective action can be taken where appropriate.

At least three monitoring sites should be added to the baseline network, one each near Toa, Mabel Bush, Browns and Hamilton Burn, to improve coverage in these areas and to constrain baseline water quality of subtly different categories of groundwater.

Quarterly sampling of all sites currently in the baseline program should continue in the future. Samples should be analysed for all of the parameters currently included in the program, and dissolved oxygen, redox potential and SiO_2 should be added.

The NO_3 monitoring sites should continue to be sampled quarterly. On at least one sampling round, these sites should also be analysed for total coliforms and for K and SO_4; these analytes may indicate human/agricultural impact in moderately reducing or anoxic groundwaters (e.g. around Invercargill), where NO_3 concentration is either low or below detection. The utility of these extra analytes should be assessed following the first 'test' sampling round, and then a decision to either discontinue or regularise their inclusion should be made.

A synoptic survey of dissolved and total As concentrations should be conducted soon, and wells that have not yet been analysed for ^{18}O and/or age dated should be targeted for this purpose.

Measurement of field parameters should be made with a flow-cell (especially for dissolved oxygen and redox potential). Samples collected for cation and anion analysis should be field-filtered.

Baseline groundwater quality should be defined as a range of values to account for natural and anthropogenic variations. Different definitions of baseline groundwater quality are required for the four different categories of groundwater in Southland; these four definitions should be applied on a geographic basis, to different sub-regions of Southland. As future monitoring data are collected, the definitions of baseline should be refined.

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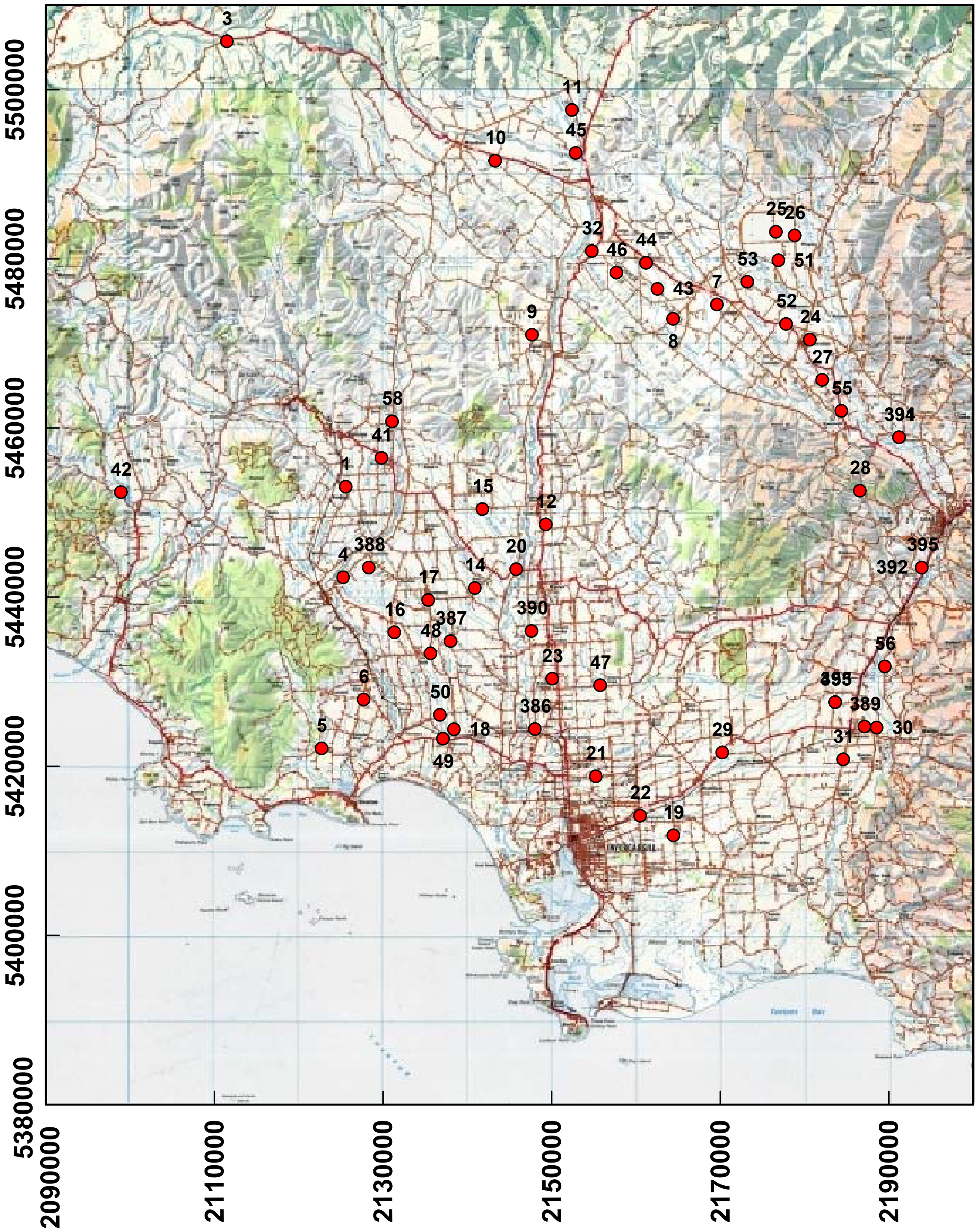
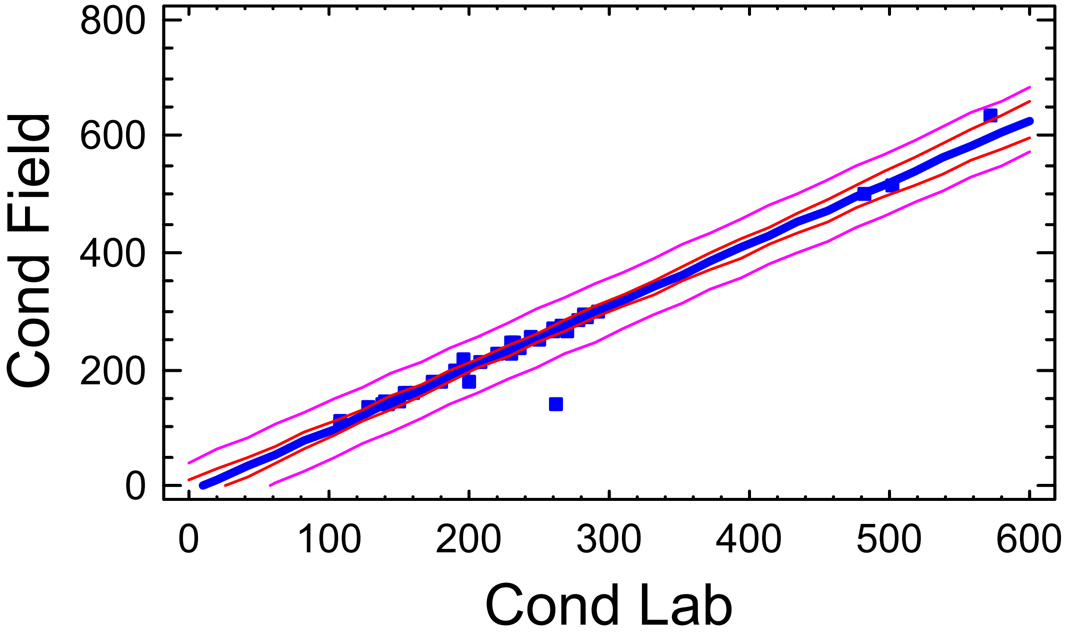


Figure 1. Location map showing groundwater monitoring sites in Southland. For clarity of presentation, full site names are not shown; the numbers refer to site identification codes used in Table 1.



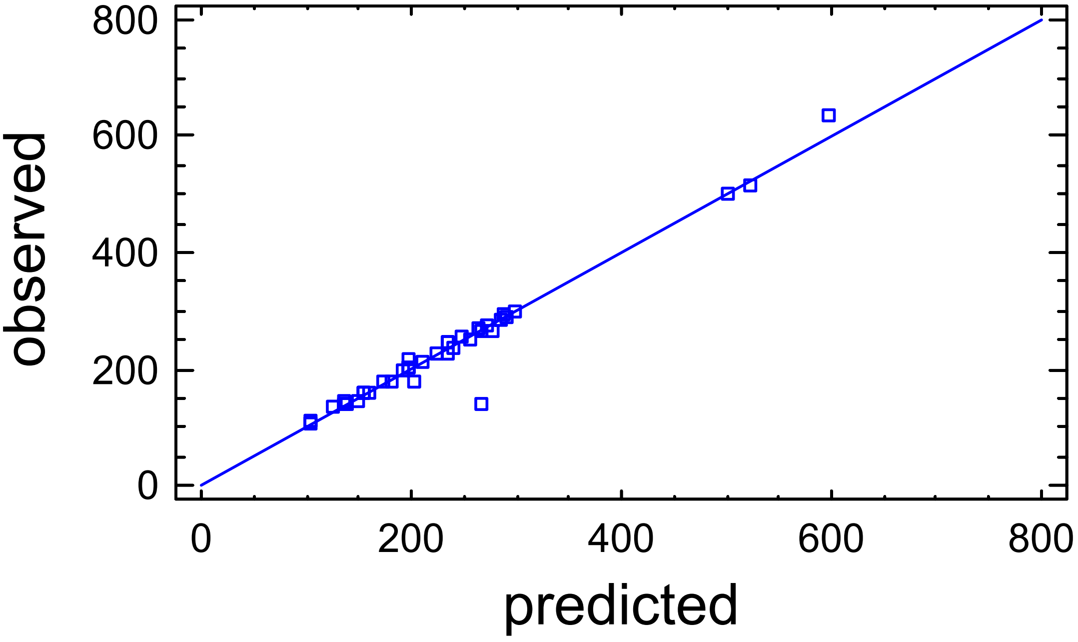


Figure 2. Linear relationship between conductivity as measured in the lab and as measured in the field. R^2 = 96% and slope and intercept are not significantly different from their ideal values of 1 and 0, respectively. The inner bounds show 95.0% confidence limits for the mean lab measurement at given values of the field measurement. The outer bounds show 95.0% prediction limits for new observations.

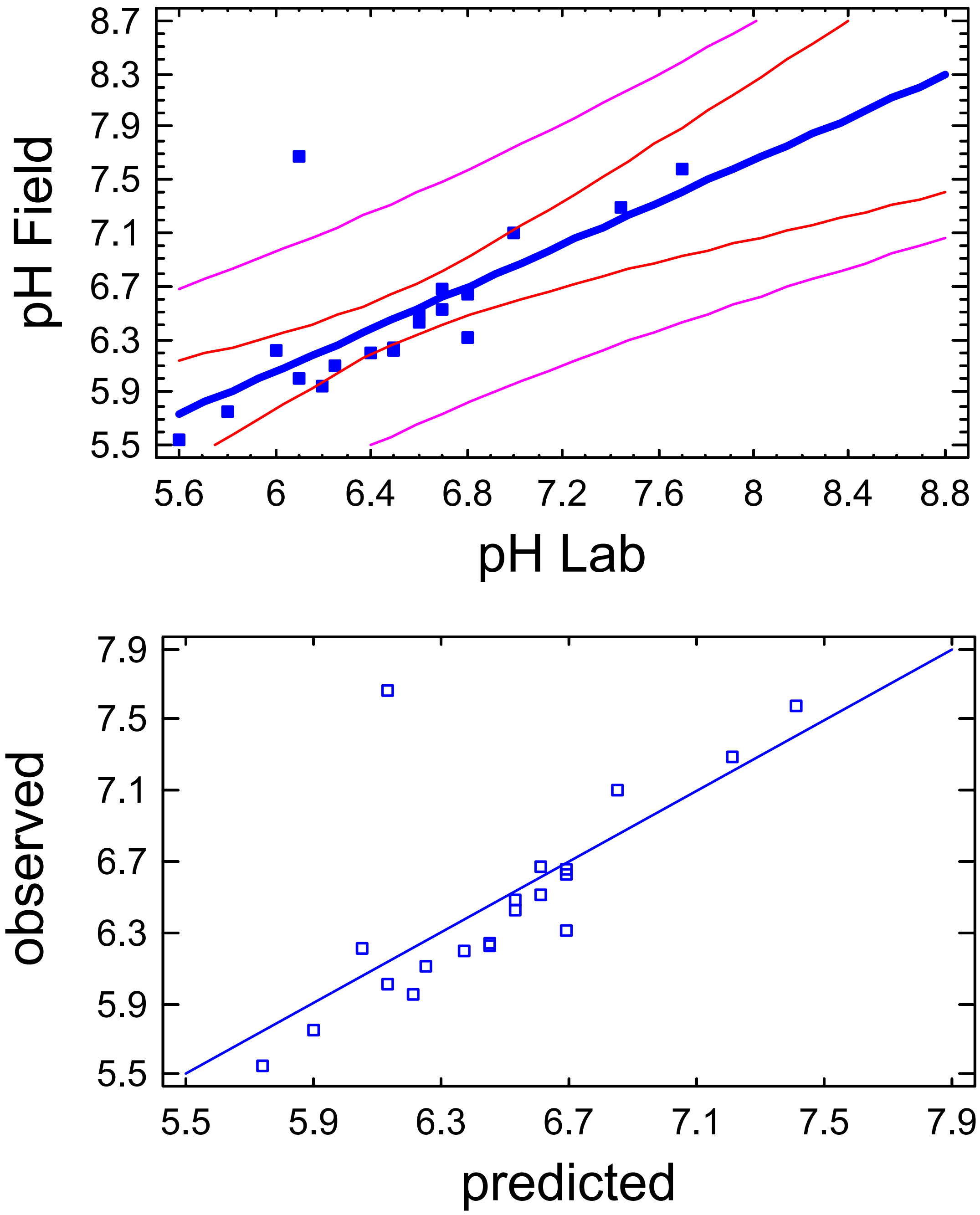


Figure 3. Linear relationship between pH as measured in the lab and as measured in the field. $R^2 = 51\%$ and slope and intercept are significantly different from their ideal values of 1 and 0, respectively. The inner bounds show 95.0% confidence limits for the mean lab measurement at given values of the field measurement. The outer bounds show 95.0% prediction limits for new observations.

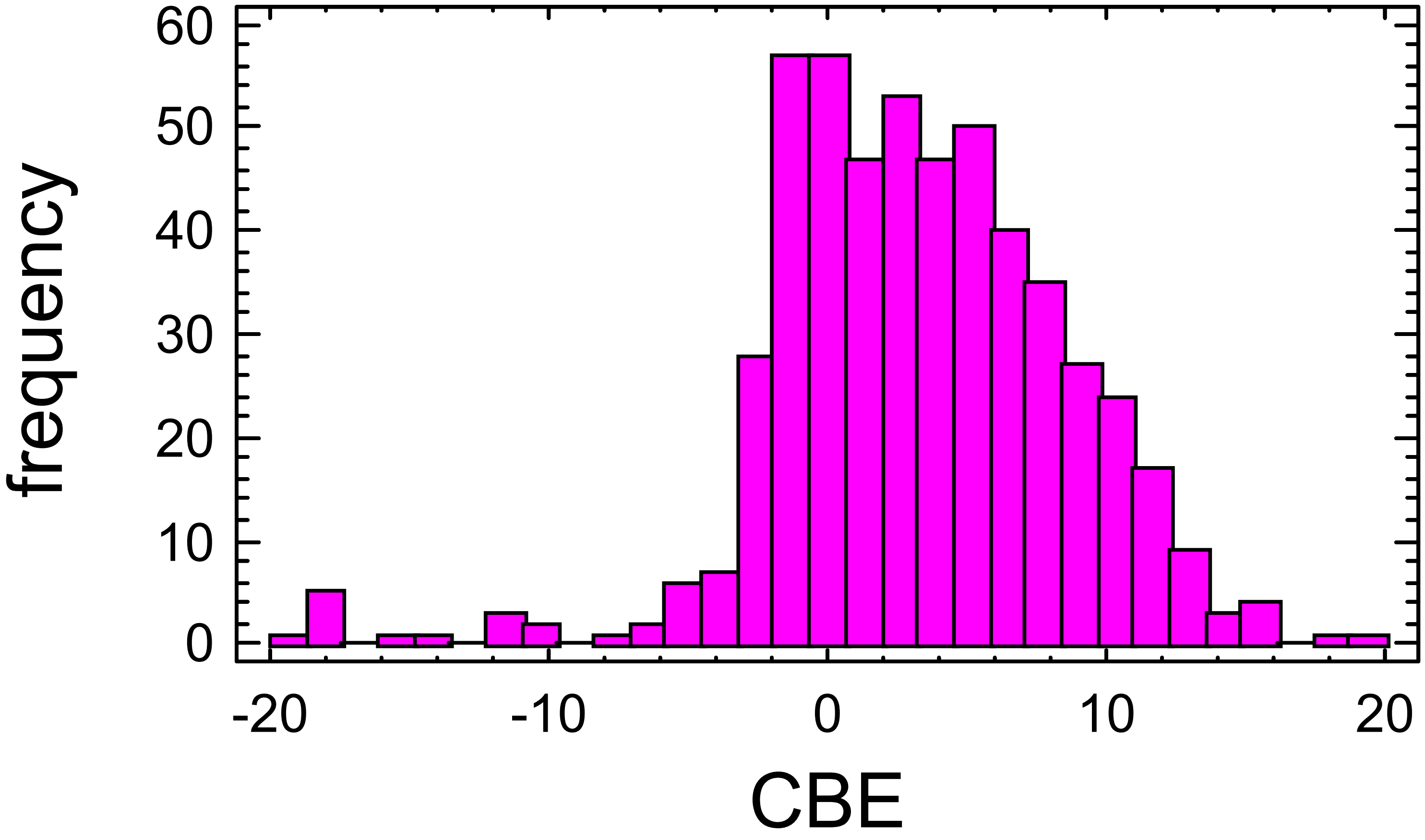


Figure 4. Histogram of % Charge Balance Error (CBE) for 533 individual groundwater samples. Samples with charge balance error greater or less than zero correspond to apparent excess concentrations of cations or anions, respectively. Acceptable limits for charge balance error vary for each sample, but are generally roughly ± 5%.

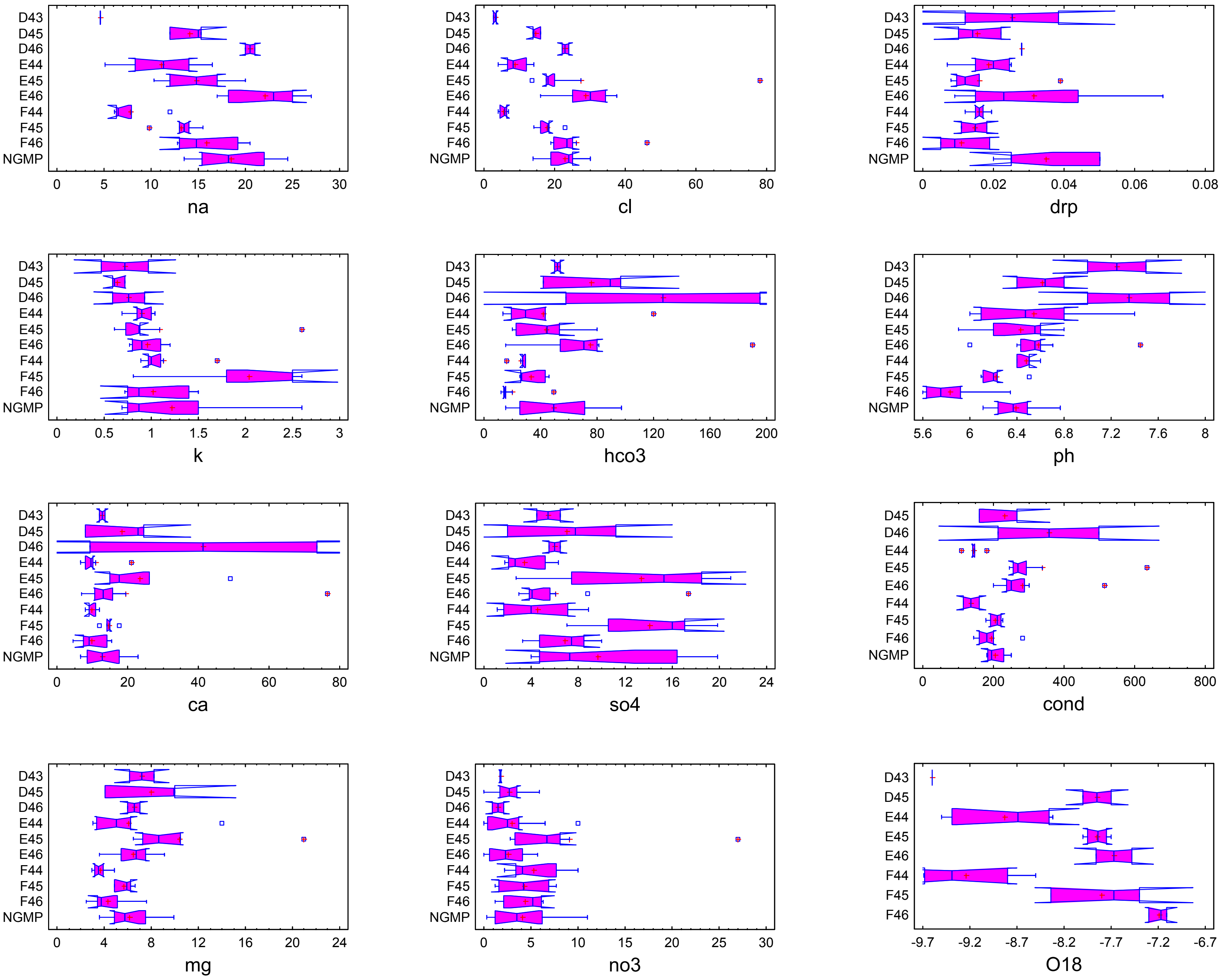


Figure 5. Box-Whisker plots showing differences in median values of selected monitored parameters by map sheet. For each category, the rectangular part of the plot extends from the lower quartile to the upper quartile, covering the centre half of each sample. The centre lines within each box show the location of the sample medians. The plus signs indicate the location of the sample means. The whiskers extend from the box to the minimum and maximum values in each sample, except for any outside or far outside points, which are plotted separately. Outside points are points which lie more than 1.5 times the interquartile range above or below the box and are shown as small squares. Far outside points are points which lie more than 3.0 times the interquartile range above or below the box and are shown as small squares with plus signs through them. Also included on the plots are notches covering a distance above and below each median. If the two notches for any pair of medians overlap, there is not a statistically significant difference between the medians at the 95% confidence level. If the two notches for any pair of medians do not overlap, there is a statistically significant difference between the medians at the 95% confidence level.

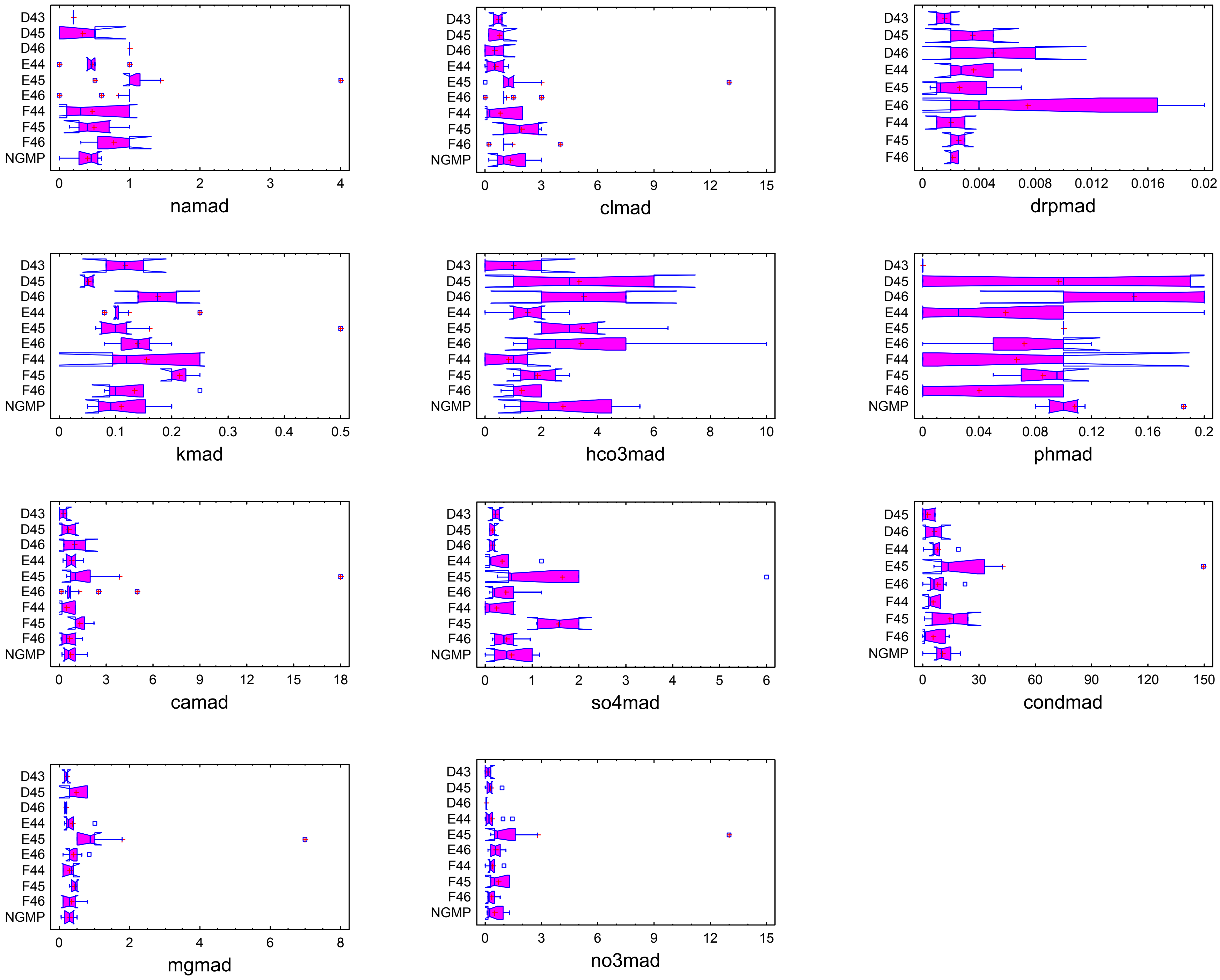


Figure 6. Box-Whisker plots showing differences in MADs of selected monitored parameters by map sheet. For each category, the rectangular part of the plot extends from the lower quartile to the upper quartile, covering the centre half of each sample. The centre lines within each box show the location of the sample medians. The plus signs indicate the location of the sample means. The whiskers extend from the box to the minimum and maximum values in each sample, except for any outside or far outside points, which are plotted separately. Outside points are points which lie more than 1.5 times the interquartile range above or below the box and are shown as small squares. Far outside points are points which lie more than 3.0 times the interquartile range above or below the box and are shown as small squares with plus signs through them. Also included on the plots are notches covering a distance above and below each median. If the two notches for any pair of medians overlap, there is not a statistically significant difference between the medians at the 95% confidence level. If the two notches for any pair of medians do not overlap, there is a statistically significant difference between the medians at the 95% confidence level.

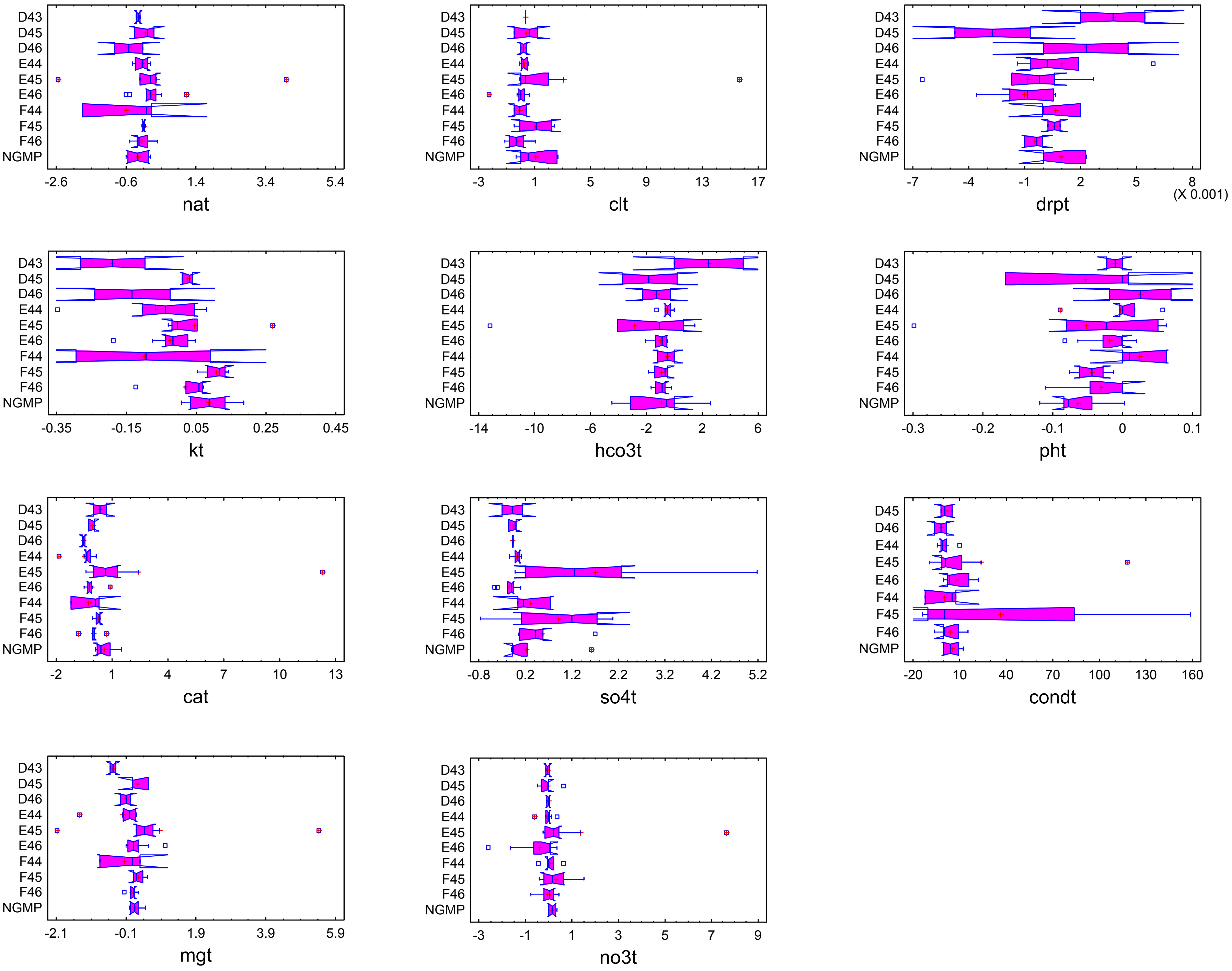


Figure 7. Box-Whisker plots showing differences in trends of selected monitored parameters by map sheet. For each category, the rectangular part of the plot extends from the lower quartile to the upper quartile, covering the centre half of each sample. The centre lines within each box show the location of the sample medians. The plus signs indicate the location of the sample means. The whiskers extend from the box to the minimum and maximum values in each sample, except for any outside or far outside points, which are plotted separately. Outside points are points which lie more than 1.5 times the interquartile range above or below the box and are shown as small squares. Far outside points are points which lie more than 3.0 times the interquartile range above or below the box and are shown as small squares with plus signs through them. Also included on the plots are notches covering a distance above and below each median. If the two notches for any pair of medians overlap, there is not a statistically significant difference between the medians at the 95% confidence level. If the two notches for any pair of medians do not overlap, there is a statistically significant difference between the medians at the 95% confidence level.

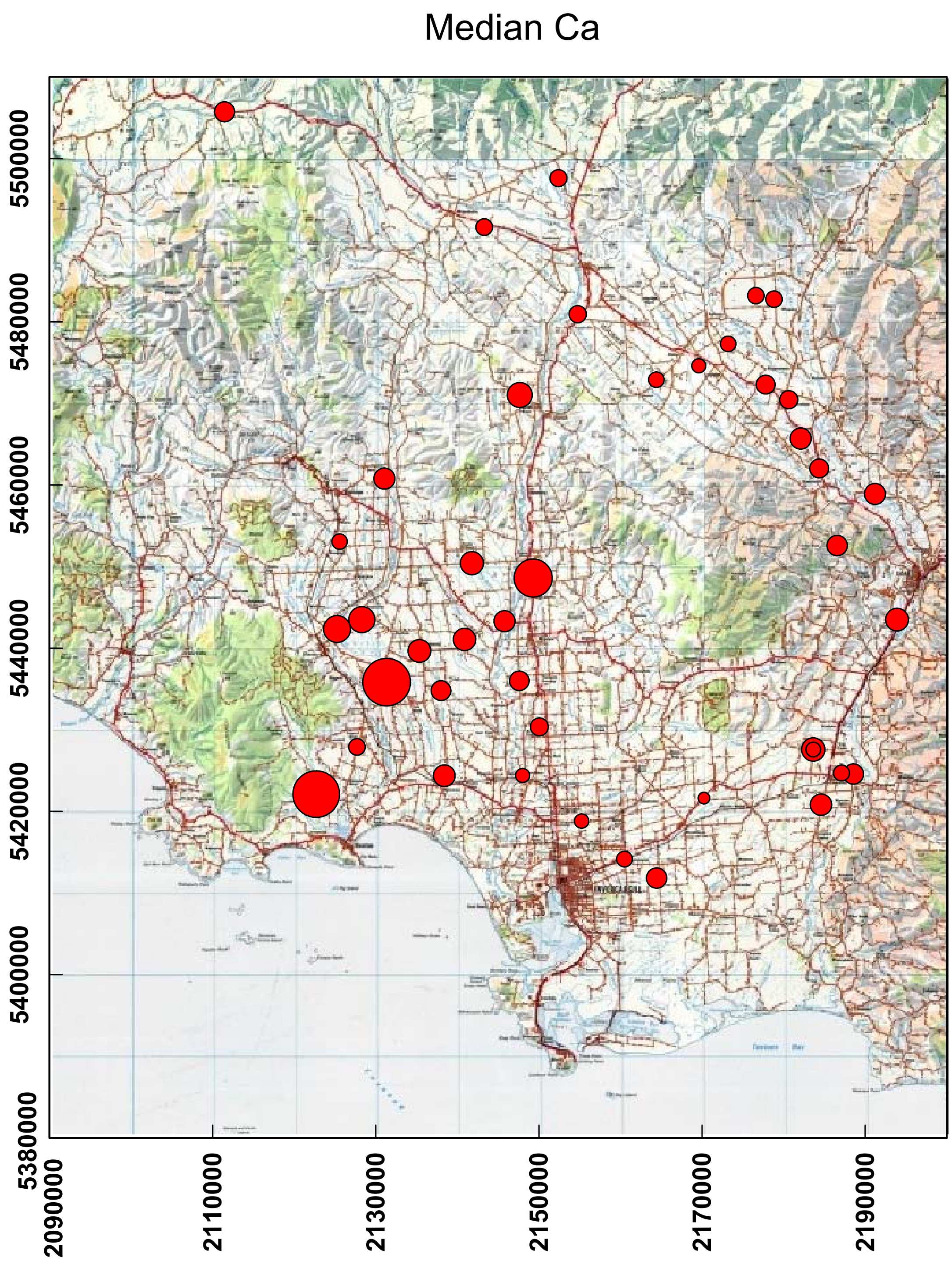
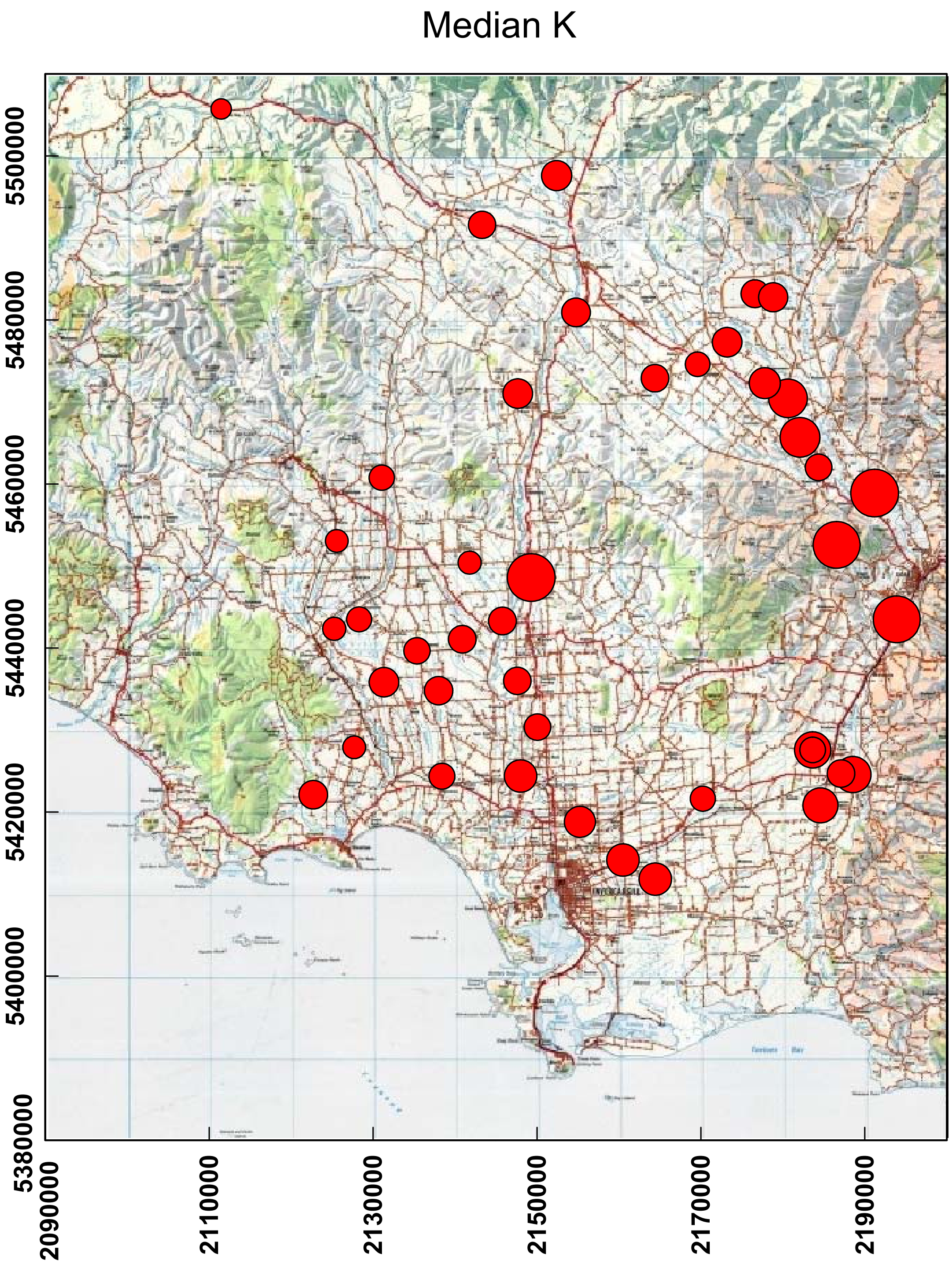


Figure 8. Bubble plots showing values of selected monitored parameters by site location. The diameter of the bubble is linearly proportional to the value of the parameter in question. For clarity of presentation, sites are not labelled (refer to Figure 1).



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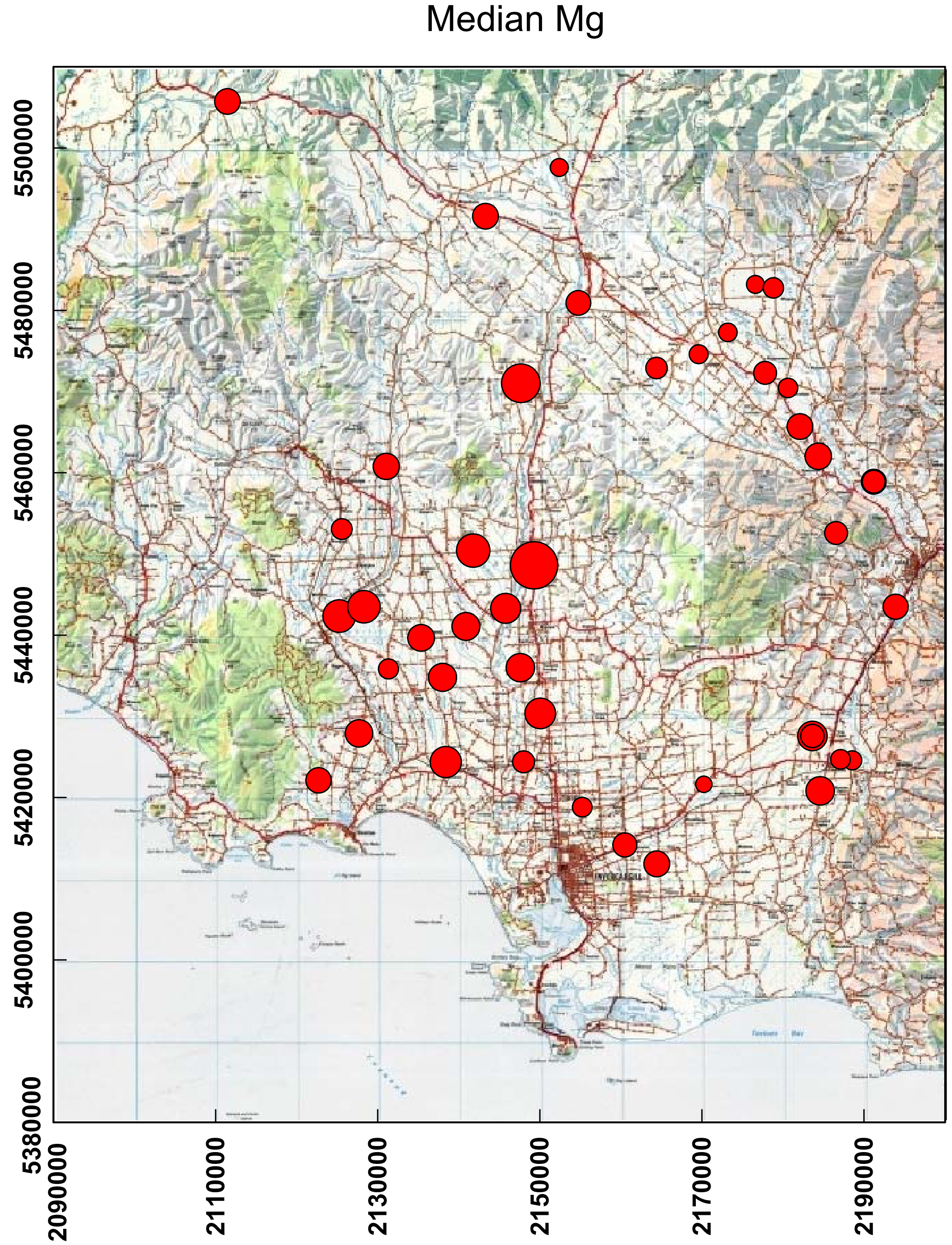

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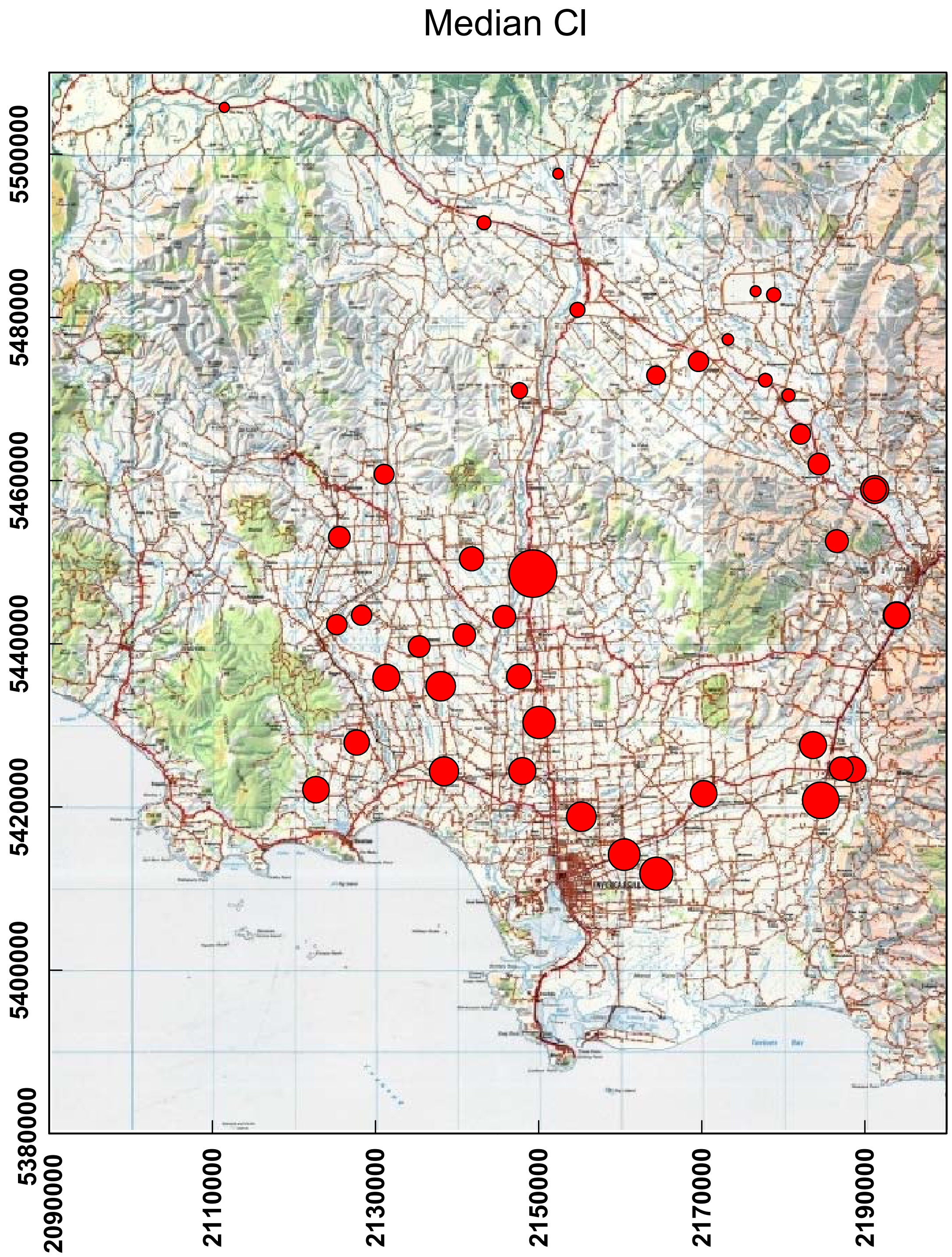

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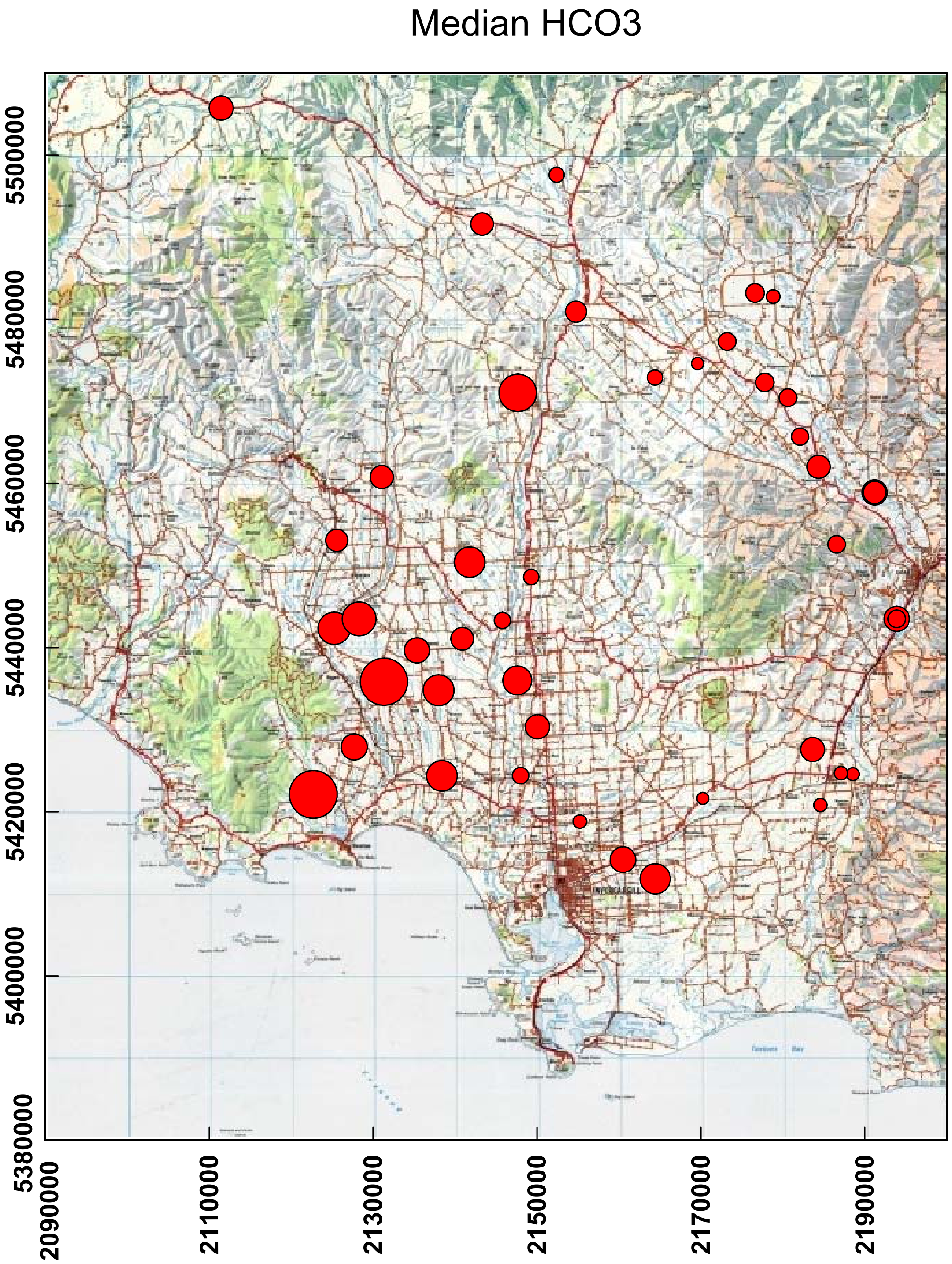

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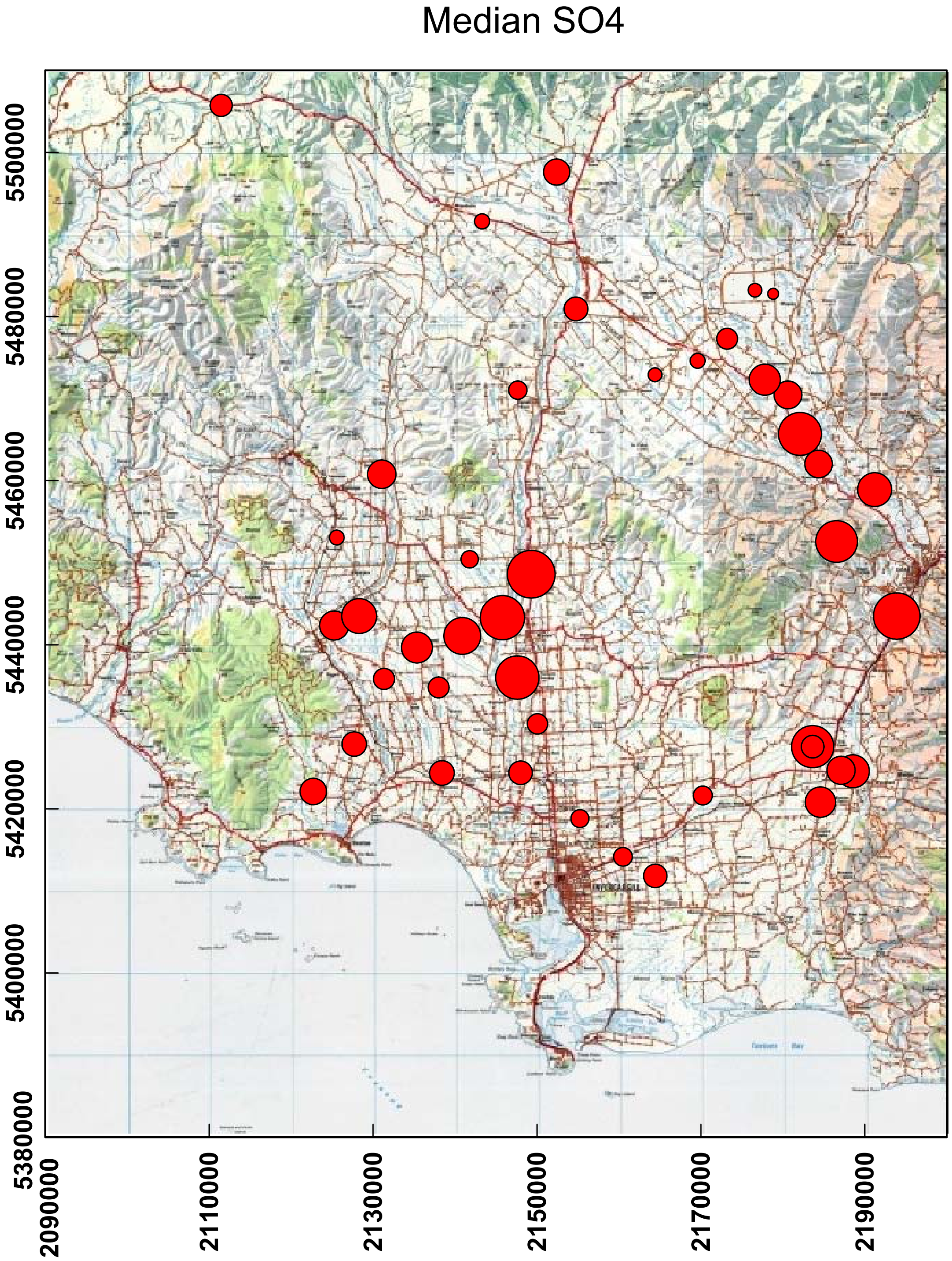


Figure 8. Continued.

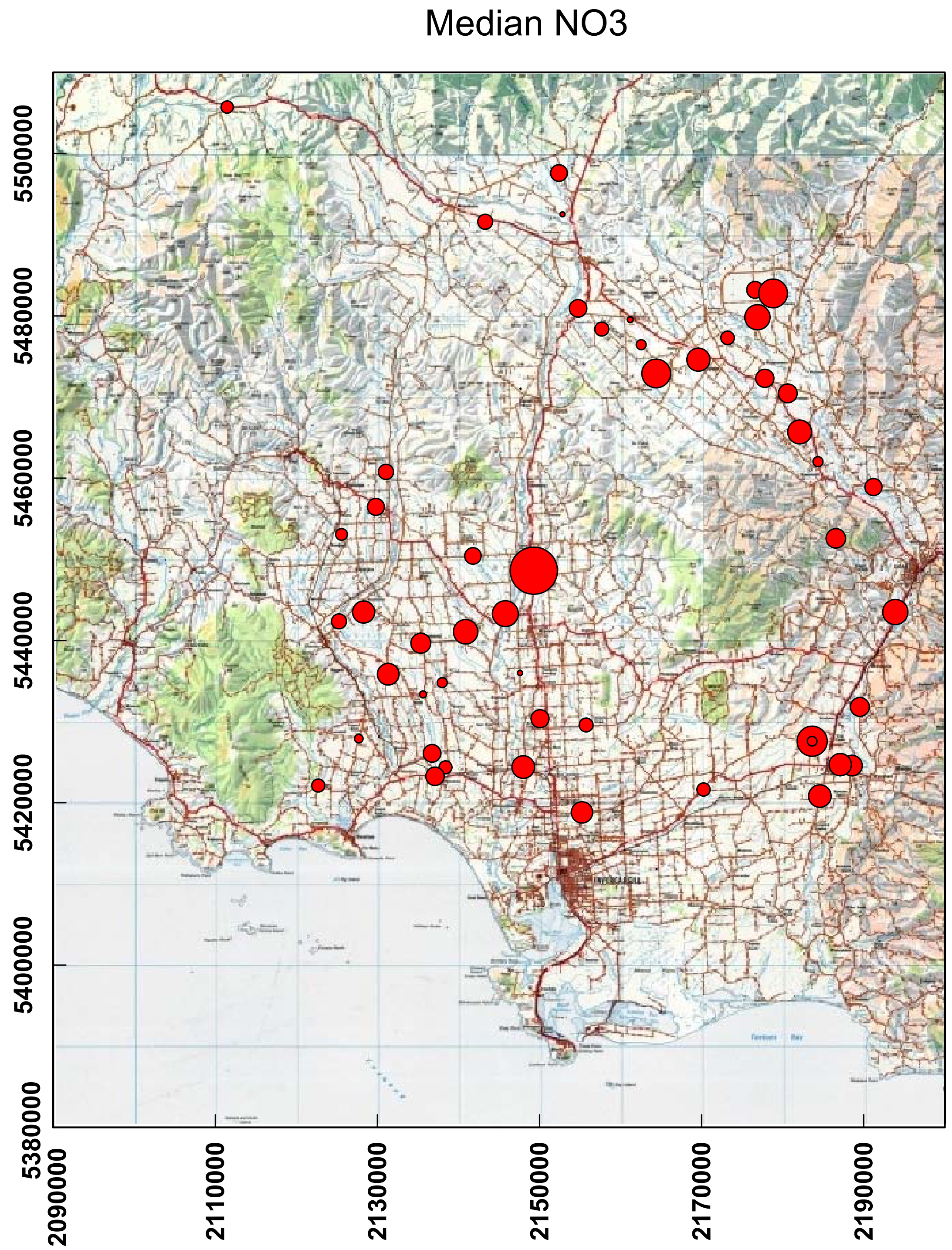


Figure 8. Continued.

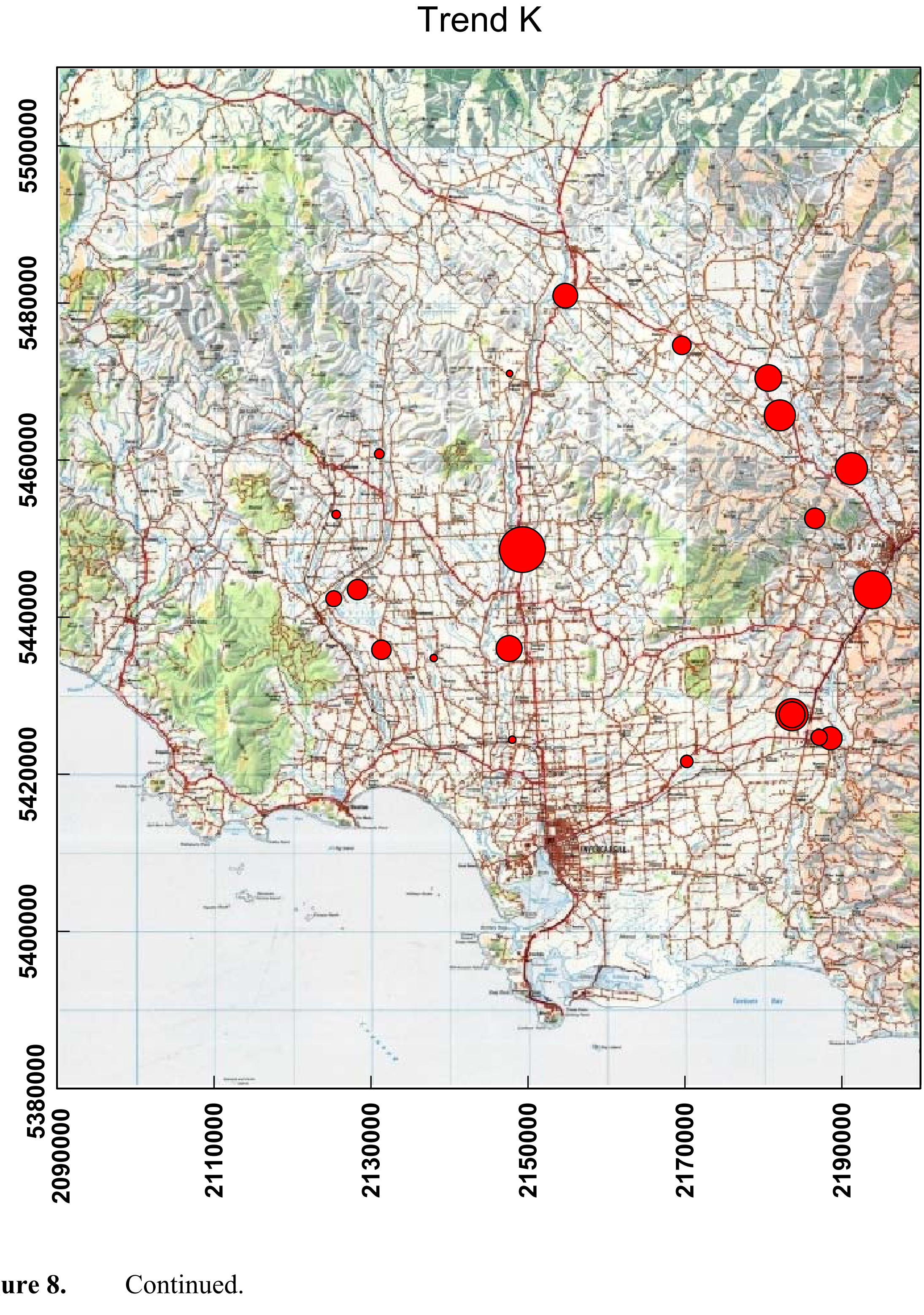


Figure 8. Continued.

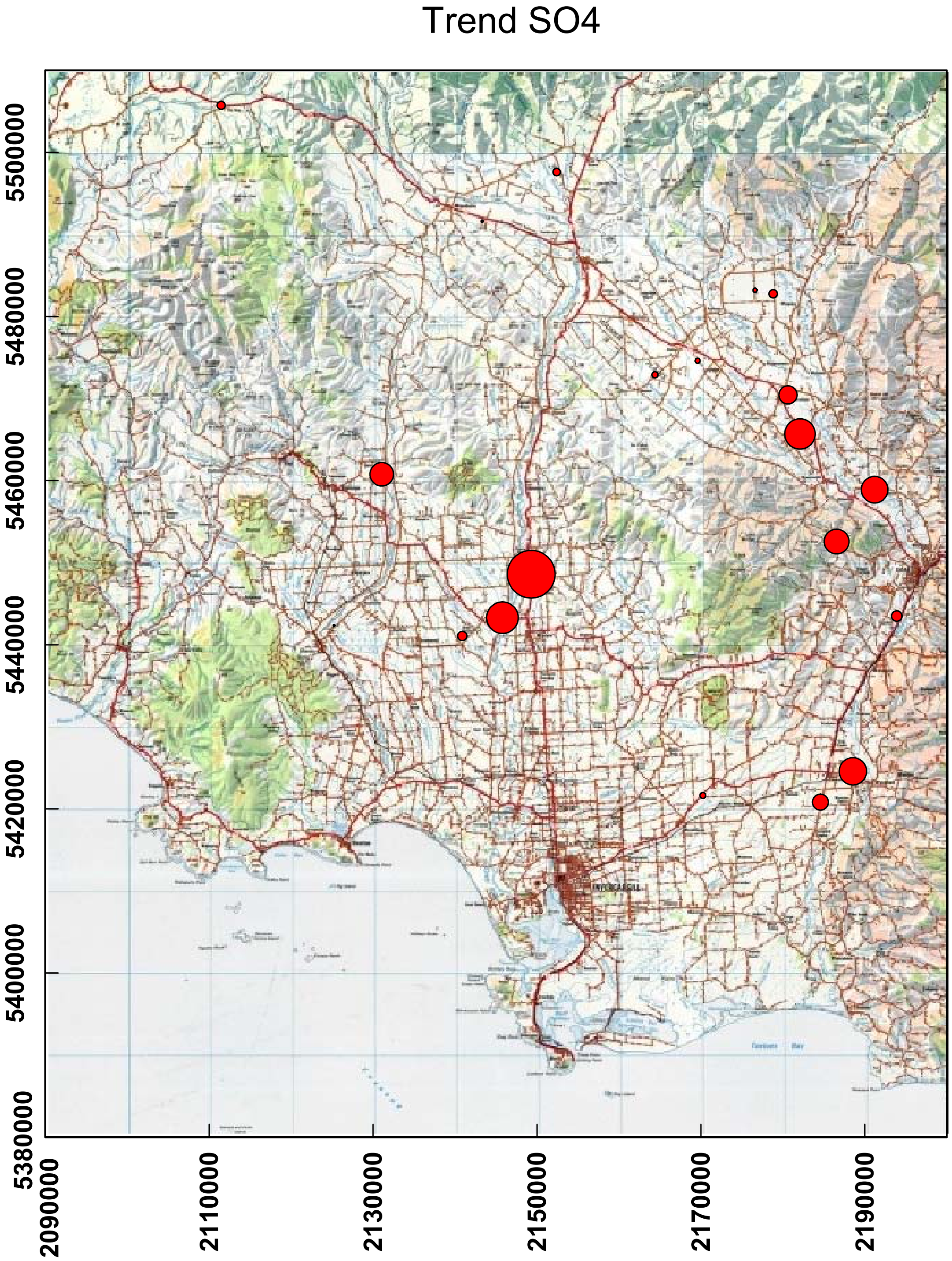
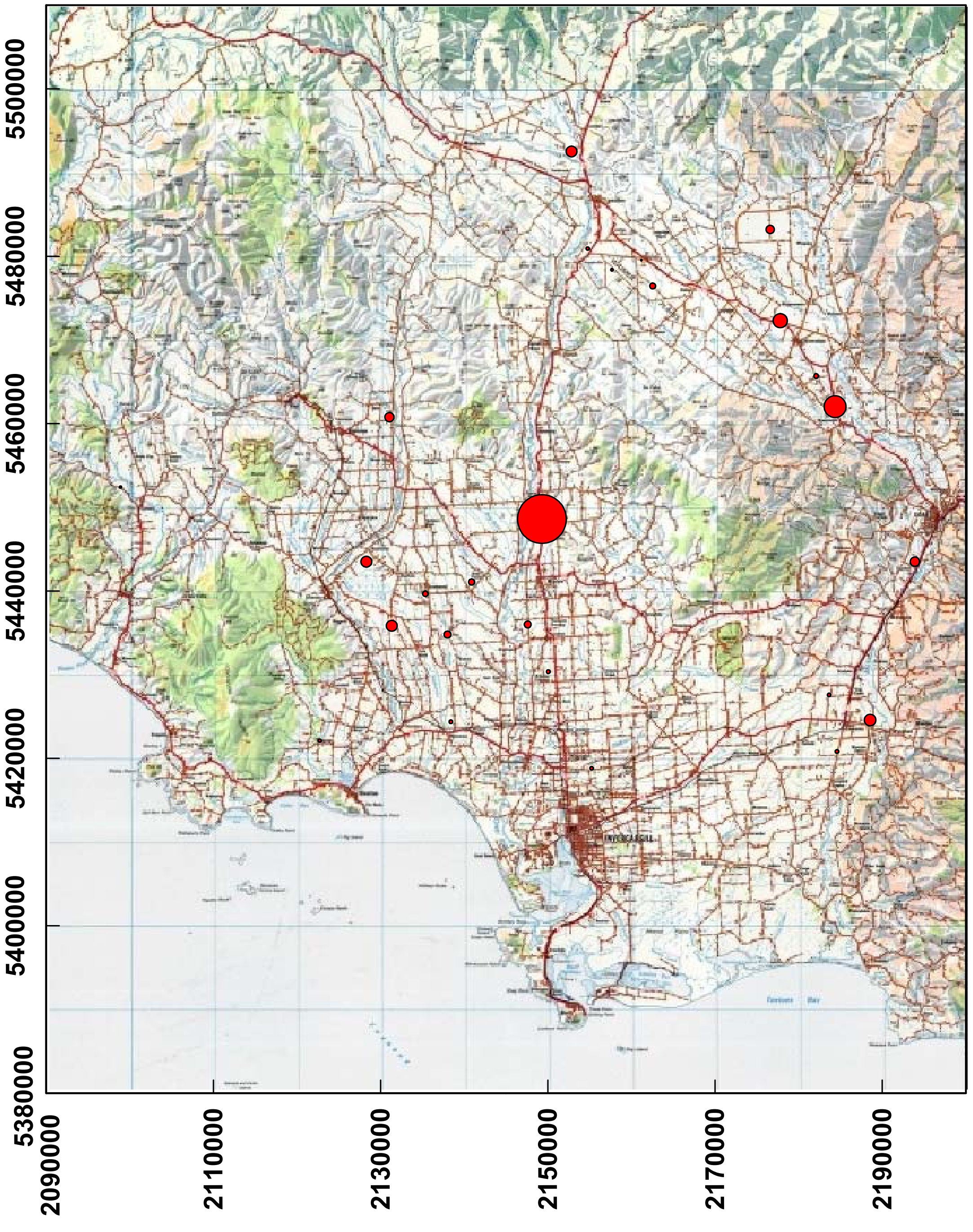


Figure 8. Continued.



Trend NO3

Figure 8. Continued.

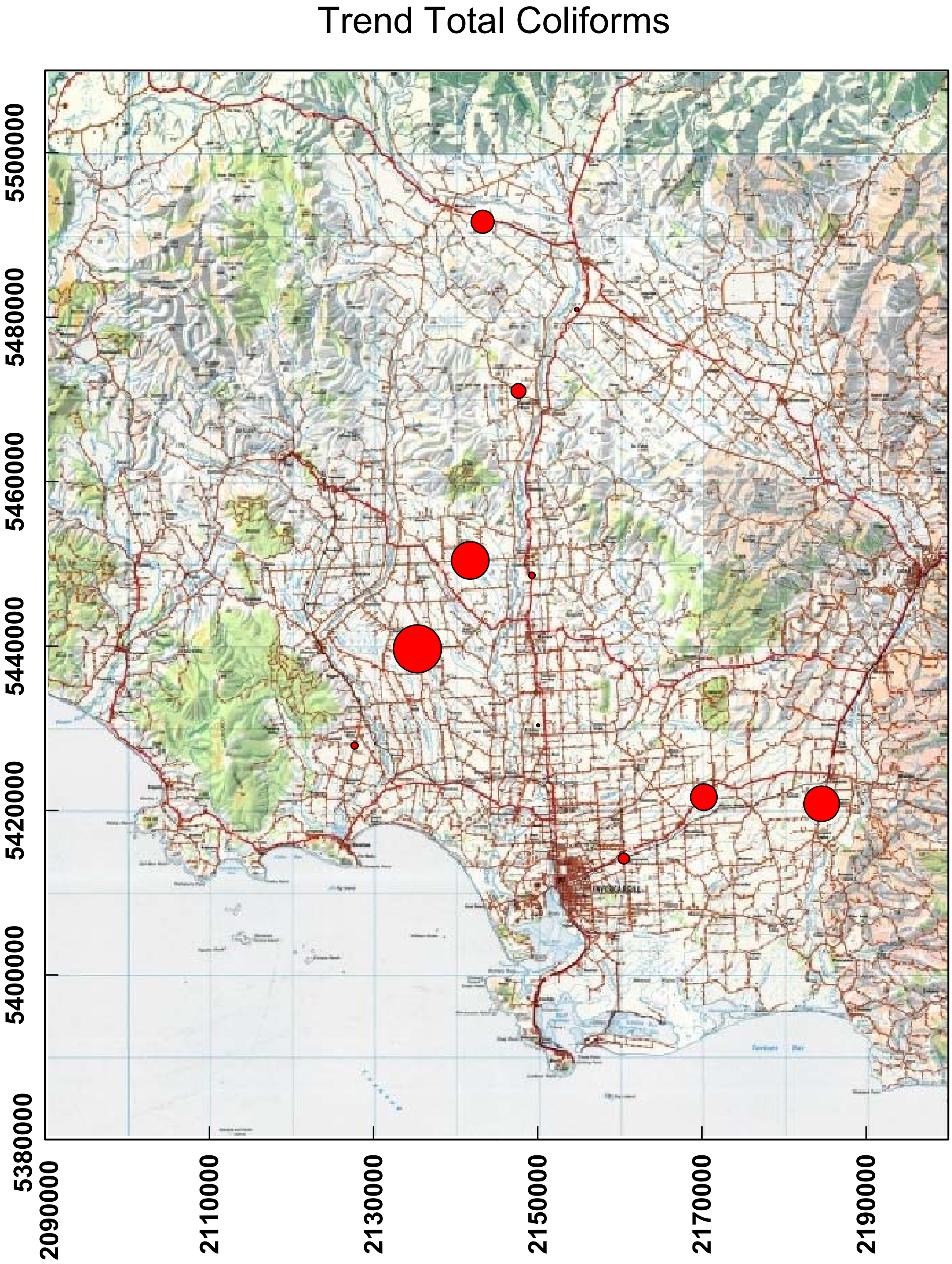


Figure 8. Continued.

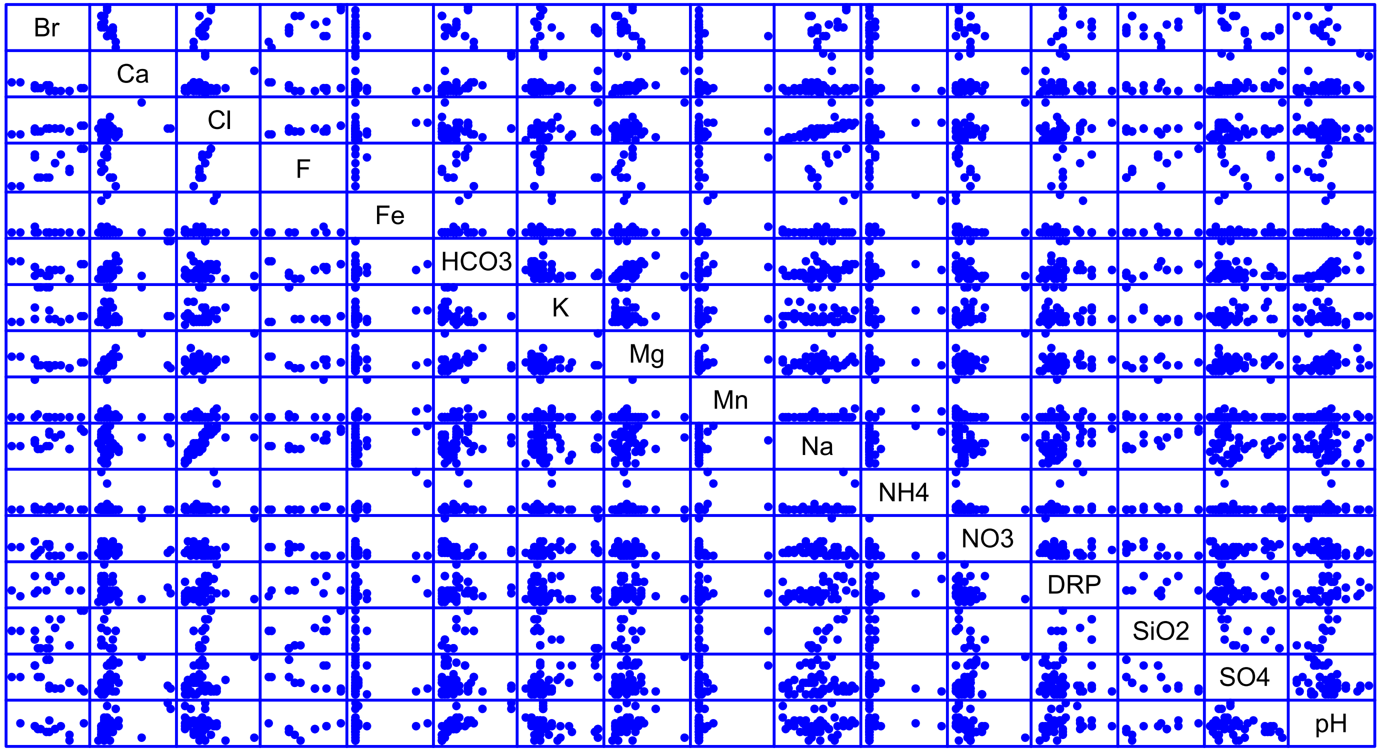


Figure 9. Tiered scatterplots showing relationships between the medians of selected monitored parameters. Concentrations expressed in mg/L for all variables except pH, which is in pH units. Each pair of variables is plotted twice, once with the first variable on the X-axis and once with it on the Y-axis. This is the graphical equivalent of the correlation matrix and is useful for helping determine which variables are most strongly correlated with which others (see also Appendix 11).

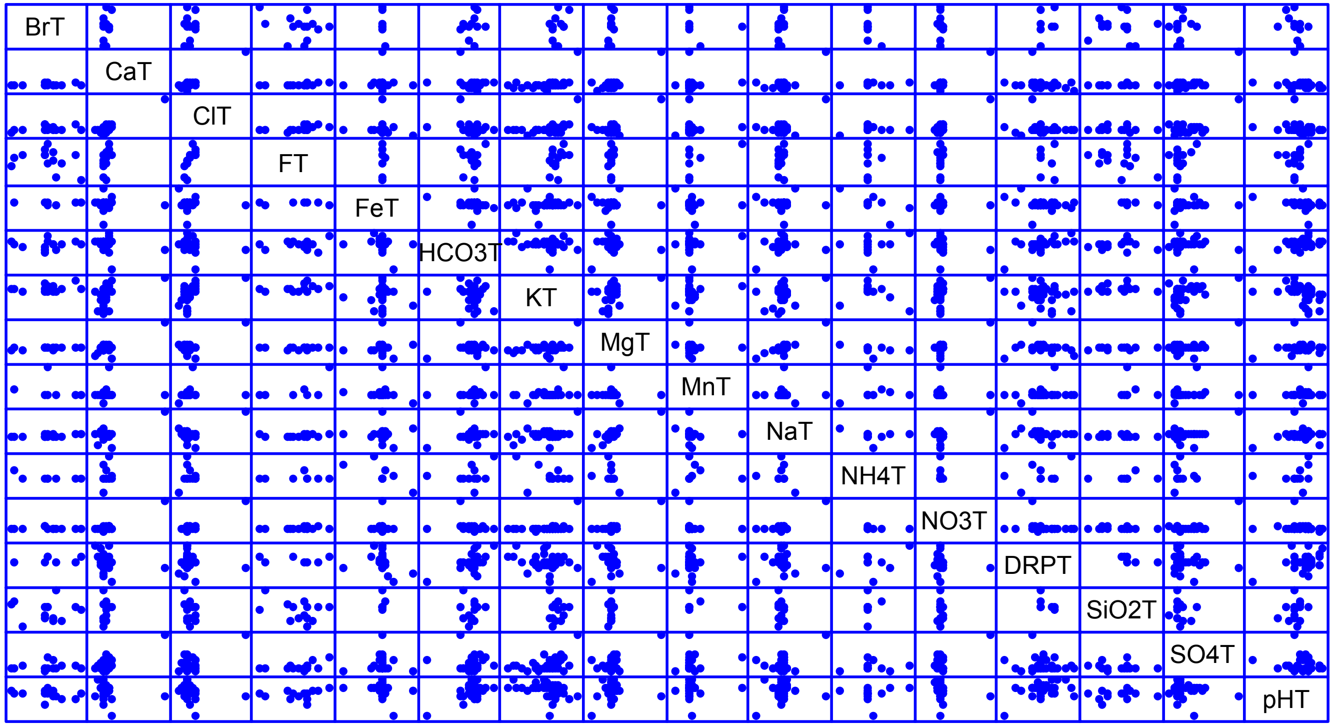


Figure 10. Tiered scatterplots showing relationships between the trends of selected monitored parameters. Trends are expressed in mg/L per year for all variables except pH, which is in pH units per year. Each pair of variables is plotted twice, once with the first variable on the X-axis and once with it on the Y-axis. This is the graphical equivalent of the correlation matrix and is useful for helping determine which variables are most strongly correlated with which others (see also Appendix 13).

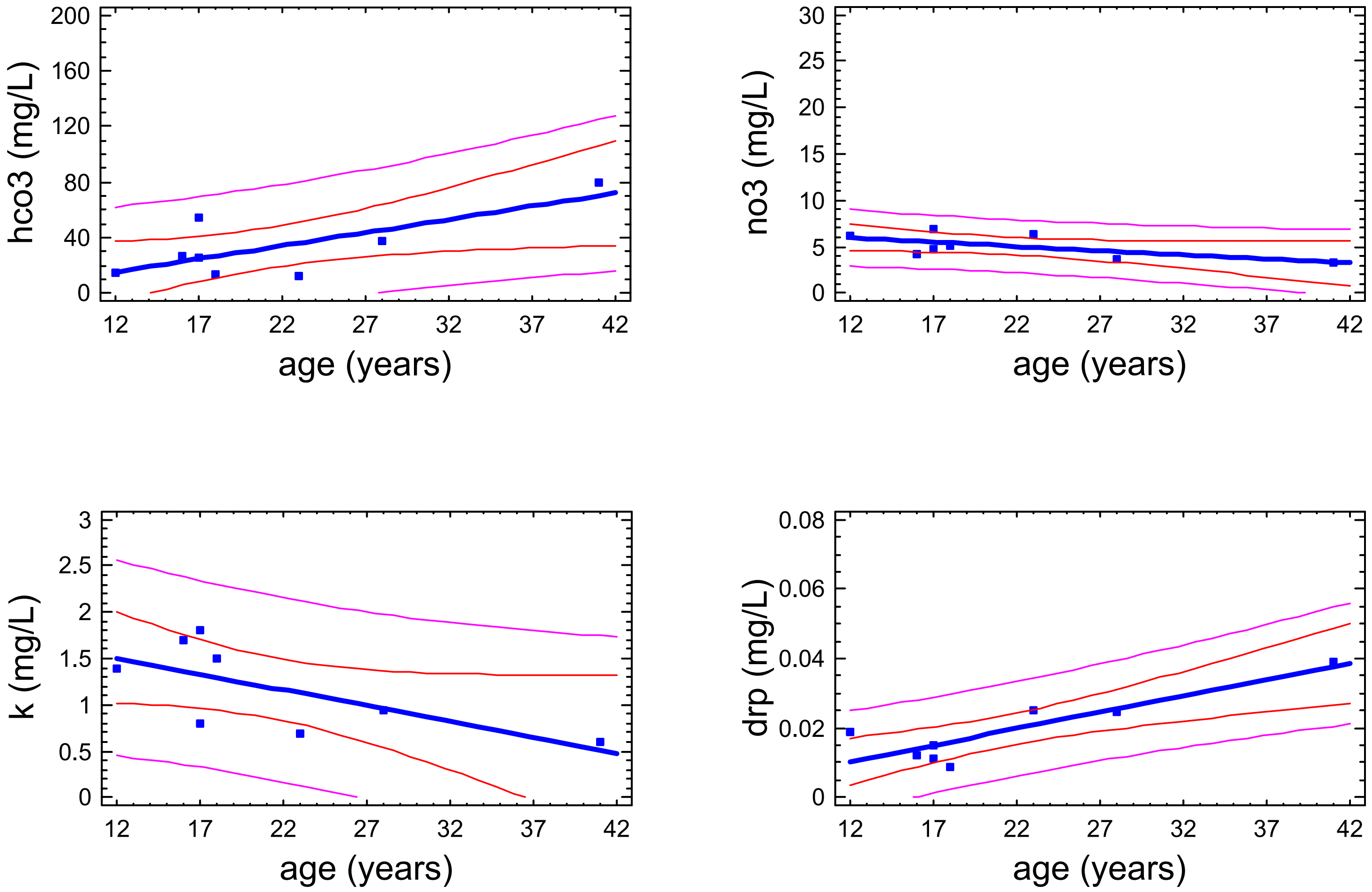


Figure 11. Linear relationships between age and the median values of parameters to which it is most highly correlated (see also Appendix 18). The inner bounds show 95.0% confidence limits for the mean lab measurement at given values of the field measurement. The outer bounds show 95.0% prediction limits for new observations.

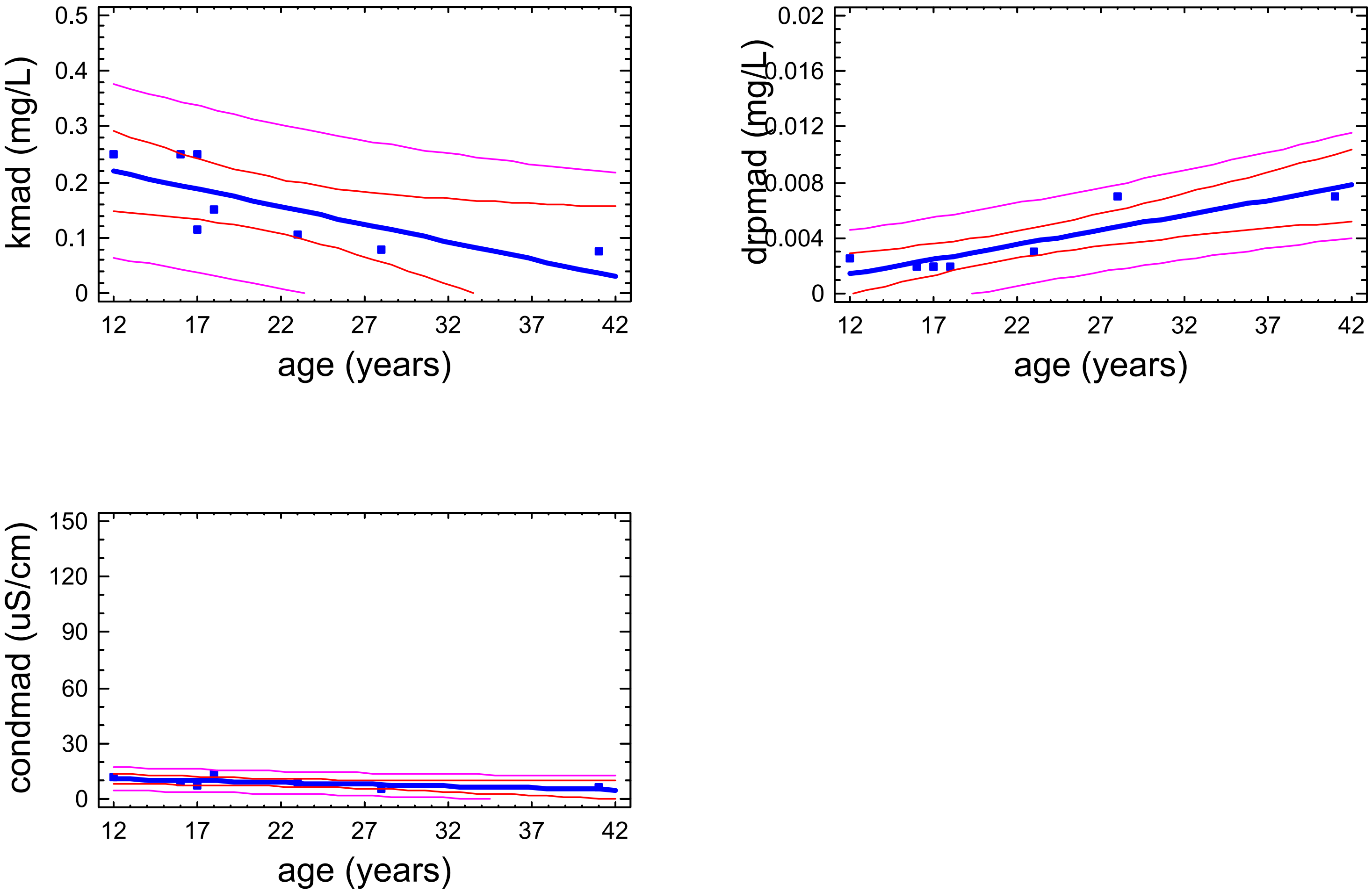


Figure 12. Linear relationships between age and the MADs of parameters to which it is most highly correlated (see also Appendix 18). The inner bounds show 95.0% confidence limits for the mean lab measurement at given values of the field measurement. The outer bounds show 95.0% prediction limits for new observations.

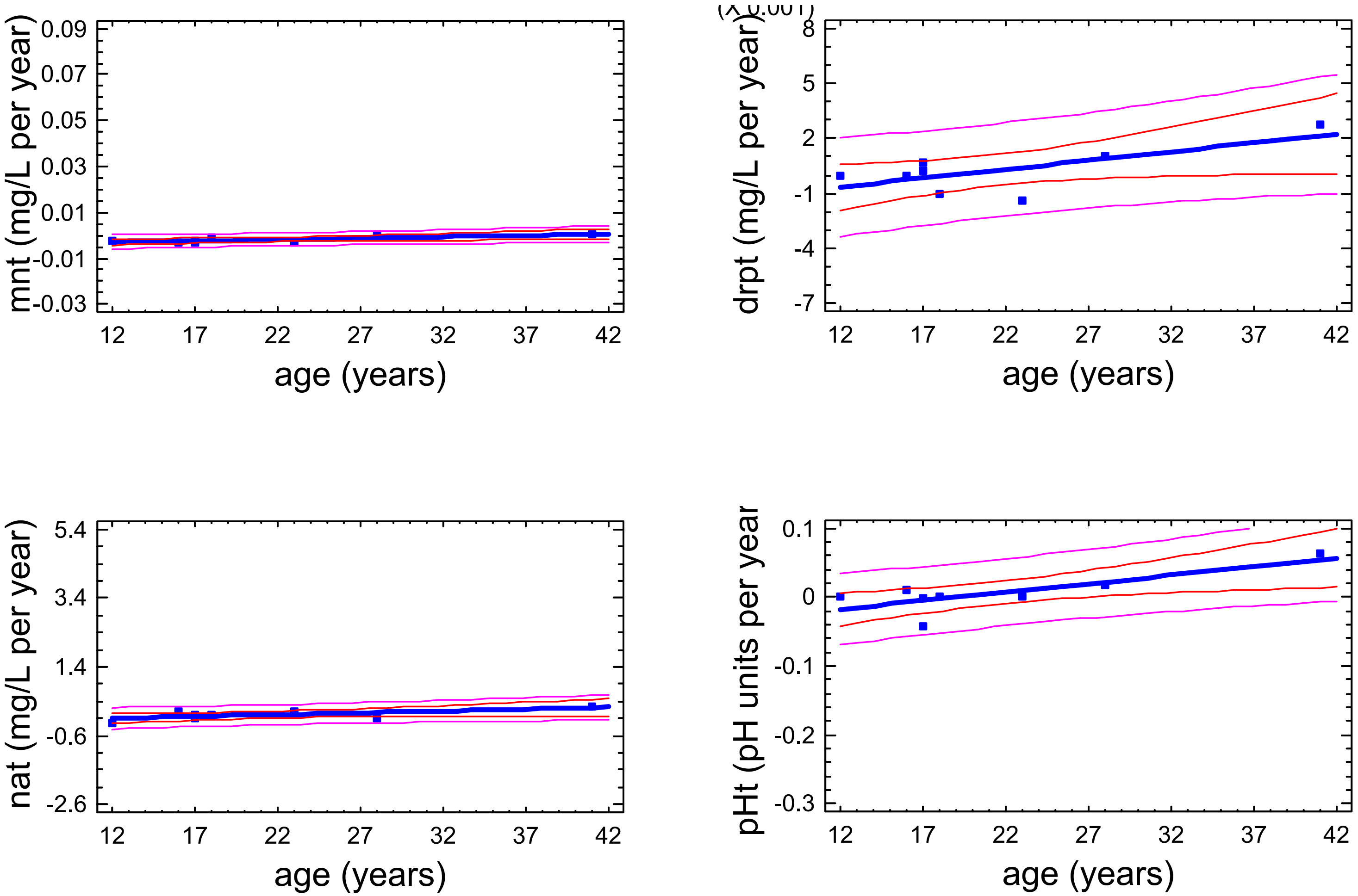


Figure 13. Linear relationships between age and the trends of parameters to which it is most highly correlated (see also Appendix 18). The inner bounds show 95.0% confidence limits for the mean lab measurement at given values of the field measurement. The outer bounds show 95.0% prediction limits for new observations.

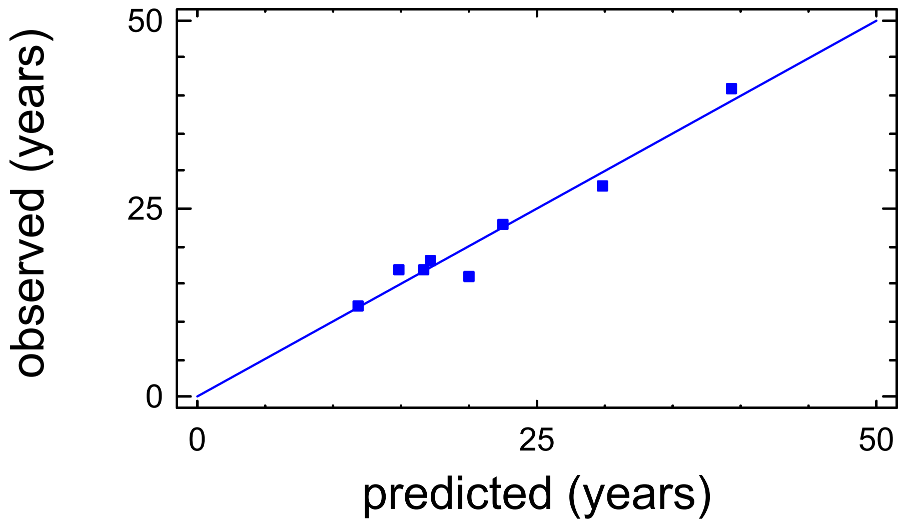


Figure 14. Multiple linear regression showing estimates of groundwater age based on the MAD of DRP and trend of Na (see also Appendix 19). The closer the points lie to the diagonal line, the better the model at predicting the observed data (R^2 = 93%).

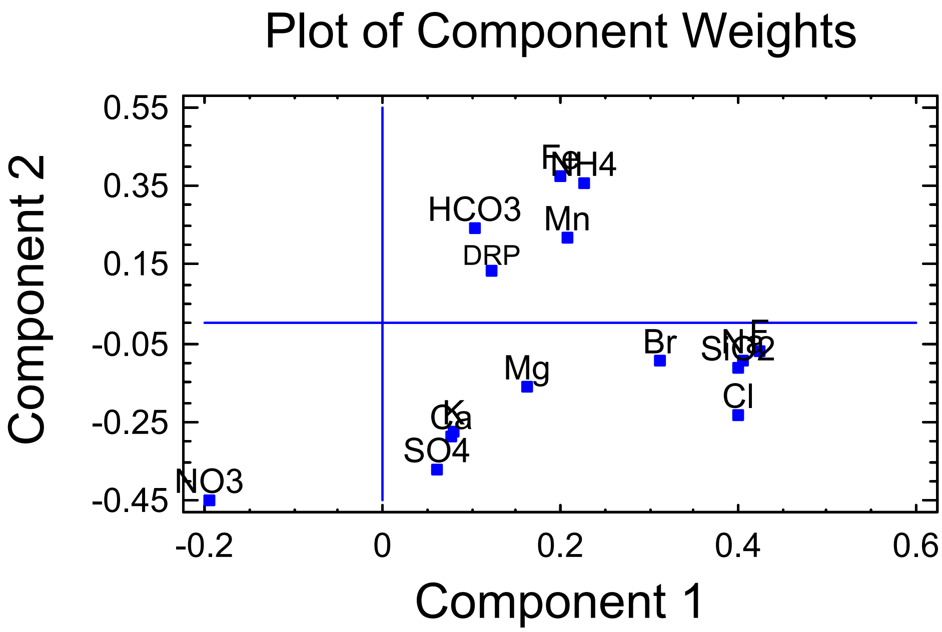


Figure 15. Component bi-plot based on Principal Components Analysis using scaled log-transformed medians of selected parameters (see Appendix 20). This plot shows the weights for selected the two dominant components. Reference lines have also been drawn at 0.0 in each dimension. A weight close to 0.0 indicates little contribution of the variable to that component.

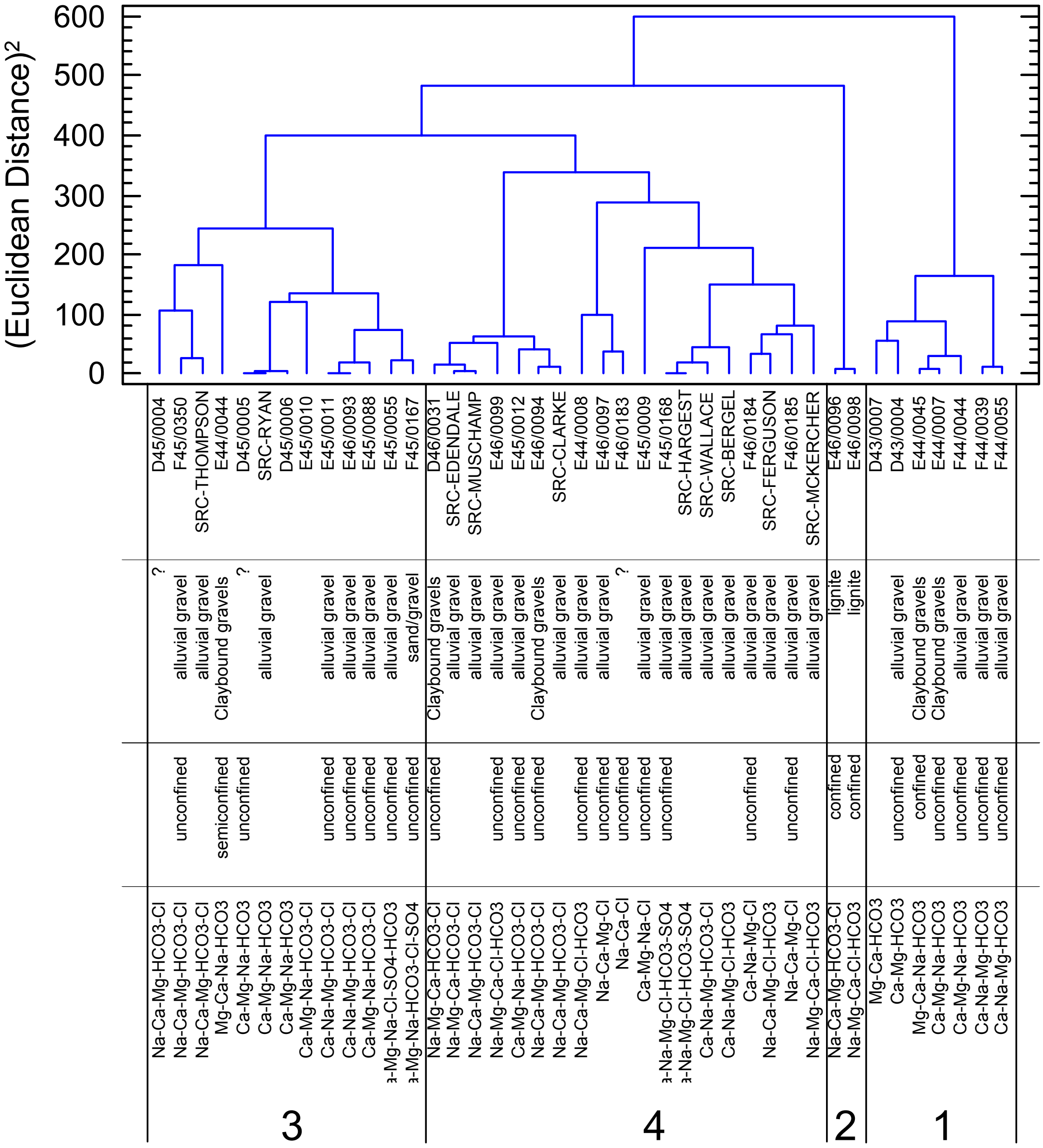


Figure 16. Dendrogram based on Hierarchical Cluster Analysis conducted with scaled log-transformed medians of selected parameters. The Y-axis is a measure of similarity (small values) or dissimilarity (large values) between two sites or two clusters of sites. The site names, aquifer lithologies, aquifer confinement and water types are given along the X axis. The results indicate that the Southland monitoring sites can be divided into 4 clusters, with characteristics as follows: 1) relatively young, unimpacted, river-recharged groundwaters, 2) anoxic, more evolved groundwaters representative of confined or organic-rich aquifers, 3) rainfall-recharged groundwaters of intermediate age and predominant Ca-HCO_3 character, showing some evidence of human/agricultural impact, and 4) rainfall-recharged groundwaters of intermediate age with slightly more Na-Cl character and a similar level of human/agricultural impact.

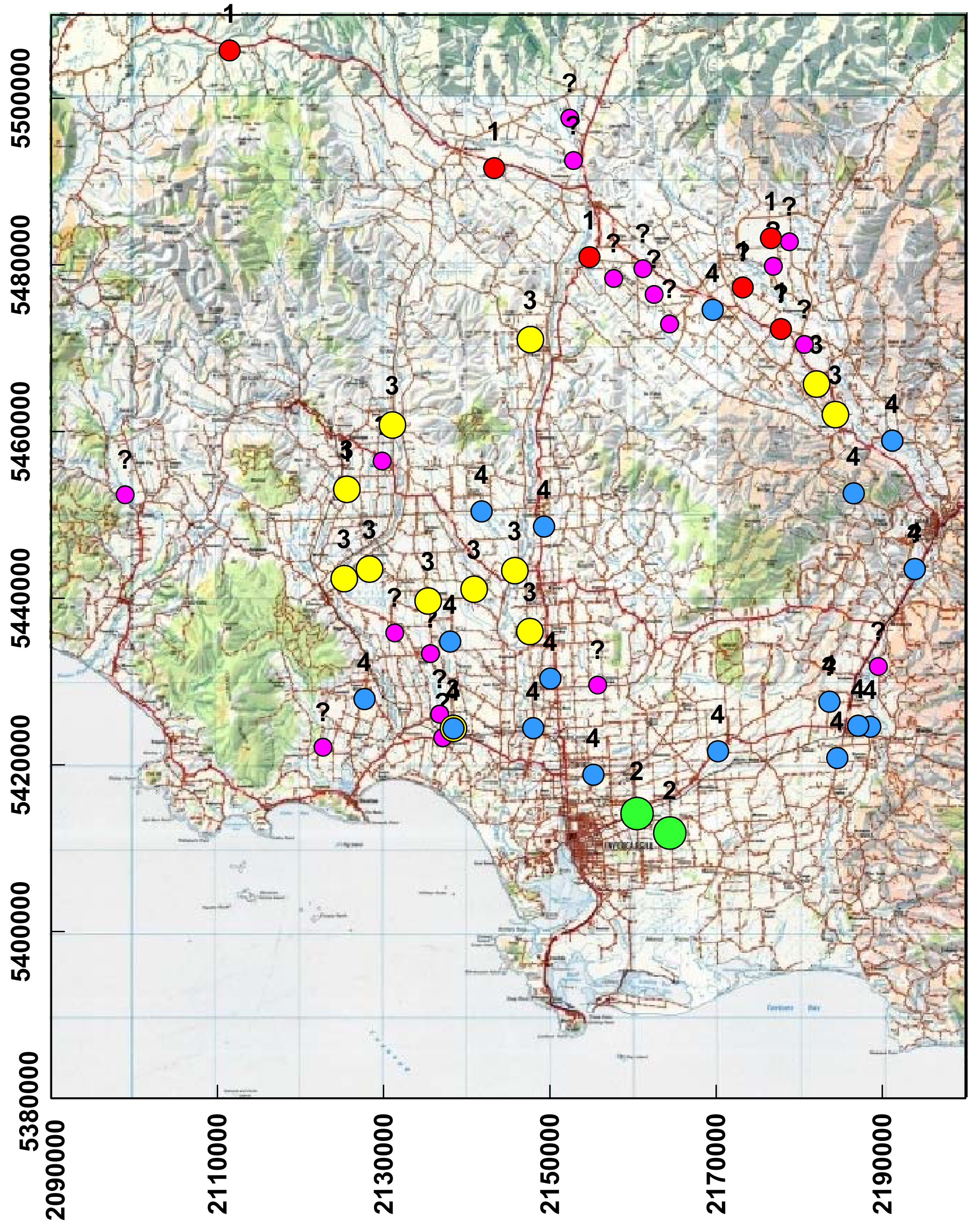


Figure 17. Map showing spatial distribution of the four categories of groundwater defined using Hierarchical Cluster Analysis: 1) relatively young, unimpacted, river-recharged groundwaters, 2) anoxic, more evolved groundwaters representative of confined or organic-rich aquifers, 3) rainfall-recharged groundwaters of intermediate age and predominant Ca-HCO_3 character, showing some evidence of human/agricultural impact, and 4) rainfall-recharged groundwaters of intermediate age with slightly more Na-Cl character and a similar level of human/agricultural impact. Some sites could not be assigned to one of these four categories because some analytical data were not available; these are shown by the symbol "?"

Table 1. Summary table showing site details, monitoring history, cluster assignments, and median, MAD and trends by analyte. Details about methodology, nomenclature and table formatting are provided in the associated legend.

Site Details													Monitoring History					Cluster			
ID	Name	Program	Easting	Northing	Depth	Lithology	Confinement	Use	WHP1	WHP2	WHP3	WHP4	From	To	#	CBE Calc	CBE OK	Water Type	Med(1)	Med(2)	Trend(A)
1	D45/0004	SOE	2125572	5453063	12			dom	Y	Y	Y	Y	04/00	12/03	14	13	4	Na-Ca-Mg-HCO3-Cl	3	*1B-2*	*P*
2	D43/0007	SOE											03/02	12/03	8	5	0	Mg-Ca-HCO3	1	*1B-2*	*P*
3	D43/0004	SOE	2111467	5505727	13	gravel	unconfined	other	Y	?	N	N	03/02	12/03	9	2	0	Ca-Mg-HCO3	1	*1B-1*	*P*
4	D45/0005	SOE	2125259	5442350	5		unconfined	stock	Y	Y	Y	Y	04/00	12/03	16	16	2	Ca-Mg-Na-HCO3	3	*1A-1*	*WR2*
5	D46/0003	SOE	2122706	5422119	24		semiconfined	stock	Y	Y	Y	Y	04/00	12/03	13	13	2	Ca-HCO3	?	*1A-1*	*WR1*
6	D46/0031	SOE	2127700	5427900	19	claybound gravel	unconfined	stock	N	Y	N	N	12/01	12/03	9	7	3	Na-Mg-Ca-HCO3-Cl	4	*1A-1*	*P*
7	E44/0008	SOE	2169600	5474600	5.6	alluvial gravel	unconfined	dom/stock	Y	Y	Y	Y	04/00	12/03	16	16	10	Na-Ca-Mg-Cl-HCO3	4	*1A-2*	*WR2*
8	E44/0036	SOE	2164400	5472900	7.2	alluvial gravel	unconfined	dom/stock	Y	Y	Y	Y	03/01	12/03	12	12	8	Na-Ca-Mg-Cl-HCO3	?	*1A-2*	*P*
9	E44/0044	SOE	2147660	5471028	25.2	claybound gravel	semiconfined	stock	Y	Y	N	N	03/02	12/03	6	5	0	Mg-Ca-Na-HCO3	3	*2A*	*WR1*
10	E44/0045	SOE	2143300	5491600	29.1	claybound gravel	confined	stock	Y	Y	Y	?	04/01	12/03	7	6	0	Mg-Ca-Na-HCO3	1	*1B-2*	
11	E44/0173	SOE	2152400	5497600	6	alluvial gravel	unconfined	dom	Y	Y	Y	Y	09/01	12/03	10	10	4	Ca-Mg-Na-HCO3	?	*1B-2*	*P*
12	E45/0009	SOE	2149299	5448598	6	alluvial gravel	unconfined	dom	Y	?	?	?	04/00	12/03	17	17	13	Ca-Mg-Na-Cl	4	*1A-2*	*I*
13	E45/0010	SOE											04/00	12/03	14	14	5	Ca-Mg-Na-HCO3-Cl	3	*1A-1*	*WR1*
14	E45/0011	SOE	2140886	5441073	7.5	alluvial gravel	unconfined	dom	?	?	?	?	04/00	12/03	16	16	10	Ca-Na-Mg-HCO3-Cl	3	*1A-2*	*WR2*
15	E45/0012	SOE	2141785	5450414	12	alluvial gravel	unconfined	dom/stock	?	Y	?	?	04/00	12/03	16	14	5	Ca-Mg-Na-HCO3-Cl	4	*1A-2*	*WR1*
16	E46/0092	SOE	2131333	5435840	20	limestone	unconfined	stock	Y	Y	N	N	04/00	12/03	16	16	4	Ca-HCO3	?	*1A-1*	*WR2*
17	E46/0093	SOE	2135355	5439663	7	gravel	unconfined	dom	Y	?	?	?	04/00	12/03	16	15	6	Ca-Na-Mg-HCO3-Cl	3	*1A-2*	*WR1*
18	E46/0094	SOE	2138404	5424372	13.5	claybound gravel	unconfined	dom/stock	N	?	?	?	04/00	12/03	16	15	6	Na-Ca-Mg-HCO3-Cl	4	*1A-2*	*P*
19	E46/0096	SOE	2164434	5411830	65	lignite	confined	stock	Y	Y	N	?	06/00	12/03	9	8	6	Na-Ca-Mg-HCO3-Cl	2	*2A*	*P*
20	E45/0055	SOE	2145786	5443302	7.2	alluvial gravel	unconfined	dom	N	Y	Y	?	03/01	12/03	10	10	9	Ca-Mg-Na-Cl-SO4-HCO3	3	*1A-2*	*I*
21	E46/0097	SOE	2155237	5418813	8	alluvial gravels	unconfined	other	N	Y	Y	?	04/00	12/03	16	16	14	Na-Ca-Mg-Cl	4	*1A-2*	*P*
22	E46/0098	SOE	2160493	5414157	22	lignite	confined	stock	N	Y	Y	?	09/00	12/03	7	7	4	Na-Mg-Ca-Cl-HCO3	2	*2A*	*P*
23	E46/0099	SOE	2150061	5430360	10	alluvial gravels	unconfined	dom/stock	Y	Y	Y	Y	04/00	12/03	16	16	10	Na-Mg-Ca-Cl-HCO3	4	*1A-2*	*P*
24	F44/0005	SOE	2180628	5470446	6		unconfined	dom	N	Y	Y	?	04/00	12/03	16	15	10	Ca-Mg-Na-HCO3	?	*1B-2*	*WR1*
25	F44/0039	SOE	2176600	5483200	35	alluvial gravels	unconfined	stock	Y	Y	Y	Y	04/01	12/03	10	10	5	Ca-Na-Mg-HCO3	1	*1B-1*	*P*
26	F44/0139	SOE	2178822	5482766	27	alluvial gravels	unconfined	dom/stock	Y	?	?	?	10/02	12/03	5	5	2	Na-Ca-Mg-HCO3-Cl	?	*1A-2*	
27	F45/0167	SOE	2182092	5465690	5	alluvial gravels	unconfined	dom	Y	?	?	?	09/00	12/03	14	14	12	Ca-Mg-Na-HCO3-Cl-SO4	3	*1A-2*	*I*
28	F45/0168	SOE	2186560	5452580	6	alluvial gravels	unconfined	dom/stock	Y	?	?	?	06/00	12/03	15	15	11	Ca-Na-Mg-Cl-HCO3-SO4	4	*1A-2*	*WR1*
29	F46/0183	SOE	2170235	5421630	20		unconfined	stock	Y	Y	?	?	04/00	12/03	11	11	8	Na-Ca-Cl	4	*1B-2*	*WR1*
30	F46/0184	SOE	2188547	5424579	4.2	alluvial gravel	unconfined	dom	?	Y	Y	Y	04/00	12/03	16	16	11	Ca-Na-Mg-Cl	4	*1A-2*	*I*
31	F46/0185	SOE	2184586	5420822	14	alluvial gravel	unconfined	dom/stock	?	Y	Y	Y	04/00	12/03	16	16	15	Na-Ca-Mg-Cl	4	*1A-2*	*P*
32	E44/0007	SOE	2154762	5480924	9.3	claybound gravel	unconfined	dom/stock	Y	Y	Y	Y	04/00	12/03	16	14	6	Ca-Mg-Na-HCO3	1	*1A-2*	*WR1*
41	D45/0029	NO3	2129813	5456461	11	claybound gravel	unconfined	stock	Y	Y	N	N	03/02	12/03	10	0	0		?		
42	D45/0036	NO3	2098892	5452411	12	lignite	semiconfined	stock	Y	Y	N	N	03/02	12/03	7	0	0		?		
43	E44/0010	NO3	2162544	5476445	6.7	alluvial gravel	unconfined	dom/stock	N	Y	N	N	03/02	12/03	8	0	0		?		
44	E44/0035	NO3	2161194	5479535	11.5	claybound gravel	unconfined	dom	Y	Y	N	N	03/02	12/03	8	0	0		?		
45	E44/0087	NO3	2152840	5492519	3.2	alluvial gravel	unconfined	stock	N	Y	N	N	03/02	12/03	8	0	0		?		
46	E44/0172	NO3	2157679	5478371	6	claybound gravel	unconfined	dom	Y	Y	Y	Y	03/02	12/03	8	0	0		?		
47	E46/0013	NO3	2155753	5429578	7.5	claybound gravel	unconfined	stock	Y	Y	N	N	03/02	12/03	8	0	0		?		
48	E46/0110	NO3	2135624	5433348	4.6	alluvial gravel	unconfined	stock	N	N	N	N	03/02	12/03	8	0	0		?		
49	E46/0146	NO3	2137106	5423261	6	alluvial gravel	unconfined	dom/stock	Y	N	N	N	07/02	07/02	1	0	0		?		
50	E46/0156	NO3	2136741	5426088	6.5	alluvial gravel	unconfined	dom/stock	N	N	N	Y	03/02	12/03	8	0	0		?		
51	F44/0040	NO3	2176886	5479828	9.2	alluvial gravel	unconfined	dom/stock	N	Y	Y	Y	03/02	12/03	8	0	0		?		
52	F44/0044	NO3	2177800	5472300	6	alluvial gravel	unconfined	dom	Y	Y	N	N	11/97	12/03	8	1	0	Ca-Mg-Na-HCO3	1	*1A-2*	
53	F44/0055	NO3	2173205	5477288	3.1	alluvial gravel	unconfined	dom/stock	N	Y	Y	Y	03/02	12/03	9	1	0	Ca-Na-Mg-HCO3	1	*1B-1*	
54	F45/0175	NO3											03/02	03/03	5	0	0		?		
55	F45/0350	NO3	2184361	5462028	5	alluvial gravel	unconfined	dom	N	Y	Y	Y	02/03	09/03	3	1	0	Na-Ca-Mg-HCO3-Cl	3	*1A-1*	
56	F46/0003	NO3	2189523	5431807	9	alluvial gravel	unconfined	dom/stock	Y	Y	N	N	03/02	12/03	7	0	0		?		
57	Home Creek	NO3											03/02	09/03	7	0	0		?		
58	E45/0088	SOE	2131060	5460777	6	alluvial gravel	unconfined	dom/stock	Y	Y	N	?	03/02	12/03	8	5	2	Ca-Mg-Na-HCO3-Cl	3	*1A-2*	*P*
386	SRC-MCKERCHER	NGMP	2148000	5424400	5	alluvial gravel							09/98	09/98	1	1	1	Na-Mg-Ca-Cl-HCO3	4	*1A-2*	
387	SRC-CLARKE	NGMP	2138000	5434800	33	alluvial gravel							09/98	06/03	20	19	19	Na-Ca-Mg-HCO3-Cl	4	1A-2	WR1
388	SRC-RYAN	NGMP	2128300	5443500	5	alluvial gravel							09/98	06/03	20	17	17	Ca-Mg-Na-HCO3	3	*1A-2*	*I*
389	SRC-FERGUSON	NGMP	2187100	5424700		alluvial gravel							09/98	06/03	20	18	18	Na-Ca-Mg-Cl-HCO3	4	*1A-2*	*I*
390	SRC-THOMPSON	NGMP	2147600	5436000		alluvial gravel							09/98	06/03	19	17	17	Na-Ca-Mg-HCO3-Cl	3	1A-1	WR2
391	SRC-EDENDALE	NGMP	2191200	5458900		alluvial gravel							09/98	06/99	4	4	4	Na-Mg-Ca-HCO3-Cl	4	*1A-2*	*P*
392	SRC-MUSCHAMP	NGMP	2193900	5443500	17.6	alluvial gravel							09/98	09/98	1	1	1	Na-Ca-Mg-HCO3-Cl	4	*1A-2*	
393	SRC-BERGEL	NGMP	2183637	5427583		alluvial gravel							09/98	09/98	1	1	1	Ca-Na-Mg-Cl-HCO3	4	*1A-2*	
394	SRC-WALLACE	NGMP	2191200	5458900	3.2	alluvial gravel							09/98	06/03	20	17	17	Ca-Na-Mg-HCO3-Cl	4	1A-1	P
395	SRC-HARGEST	NGMP	2193900	5443500		alluvial gravel							09/98	06/03	20	18	17	Ca-Na-Mg-Cl-HCO3-SO4	4	*1A-2*	*I*
455	SRC-9091501	NGMP	2183637	5427583									09/99	03/03	15	14	14	Na-Mg-Ca-HCO3-Cl	?	*1A-2*	*WR2*

Site Details		Tracers			As			Br			Ca			Cl			F			Fe			HCO3			K		
		Age	18O	15N	mg/L			mg/L			mg/L			mg/L			mg/L			Total, mg/L			mg/L			mg/L		
ID	Name	years	per mil	per mil	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend
1	D45/0004		-7.7		ND	ND	ND	ND	ND	ND	7.95	0.20	0.00	16.00	1.00	0.00	ND	ND	ND	1.18	**0.51**	0.00	42.00	1.00	0.00	0.59	0.05	0.00
2	D43/0007				ND	ND	ND	ND	ND	ND	12.00	0.00	0.00	2.75	**0.45**	0.00	ND	ND	ND	0.34	**0.05**	0.00	54.00	0.00	0.00	0.97	**0.15**	0.00
3	D43/0004		-9.6		ND	ND	ND	ND	ND	ND	13.50	0.50	0.00	3.50	**0.90**	0.00	ND	ND	ND	0.03	**0.02**	**-0.08**	50.00	2.00	0.00	0.47	**0.08**	0.00
4	D45/0005		-8.0		ND	ND	ND	ND	ND	ND	24.55	0.55	0.00	14.00	1.00	1.20	ND	ND	ND	0.06	**0.01**	0.00	89.00	3.00	-2.00	0.61	0.06	0.00
5	D46/0003				ND	ND	ND	ND	ND	ND	73.50	1.65	0.00	24.00	1.00	0.00	ND	ND	ND	0.00	**0.00**	0.00	195.00	5.00	0.00	0.93	**0.14**	0.00
6	D46/0031				ND	ND	ND	ND	ND	ND	9.20	0.30	-0.44	22.00	0.00	0.00	ND	ND	ND	0.01	**0.01**	0.00	58.00	2.00	-2.30	0.59	**0.21**	0.00
7	E44/0008	23	-8.3		ND	ND	ND	ND	ND	ND	6.60	0.60	0.00	14.00	1.00	0.00	ND	ND	ND	0.01	**0.01**	0.00	13.00	1.00	0.00	0.69	**0.11**	0.00
8	E44/0036		-8.4		ND	ND	ND	ND	ND	ND	8.13	0.45	0.00	12.00	0.00	0.00	ND	ND	ND	0.01	**0.00**	**-0.01**	20.00	2.00	0.00	0.87	**0.10**	0.00
9	E44/0044				ND	ND	ND	ND	ND	ND	21.00	1.00	0.00	8.80	0.50	0.00	ND	ND	ND	0.10	0.01	0.00	120.00	0.00	0.00	1.00	0.10	0.00
10	E44/0045				ND	ND	ND	ND	ND	ND	9.40	0.22	0.00	6.60	0.10	0.00	ND	ND	ND	0.01	0.00	0.00	43.00	1.00	0.00	0.85	**0.25**	**-0.39**
11	E44/0173		-8.9	3.5	ND	ND	ND	ND	ND	ND	9.70	**1.55**	0.00	4.00	**0.50**	0.00	ND	ND	ND	0.01	**0.01**	0.00	19.50	**2.00**	0.00	1.04	0.10	0.00
12	E45/0009			4.0	ND	ND	ND	ND	ND	ND	49.00	**18.00**	**14.18**	78.00	**13.00**	**16.51**	ND	ND	ND	0.01	**0.00**	**-0.01**	20.00	**4.00**	**-3.99**	2.60	**0.50**	**0.51**
13	E45/0010				ND	ND	ND	ND	ND	ND	26.00	2.00	0.00	18.00	1.50	0.00	ND	ND	ND	0.00	**0.00**	**-0.01**	53.00	3.00	0.00	0.88	**0.12**	0.00
14	E45/0011		-7.8	4.2	ND	ND	ND	ND	ND	ND	17.00	1.00	0.00	17.50	1.50	0.00	ND	ND	ND	0.02	**0.02**	0.00	44.00	2.00	0.00	0.87	**0.12**	0.00
15	E45/0012	41	-7.9	8.5	ND	ND	ND	ND	ND	ND	18.00	0.70	0.00	20.00	1.00	0.00	ND	ND	ND	0.01	**0.00**	**-0.01**	80.00	2.00	0.00	0.61	**0.08**	0.00
16	E46/0092			8.4	ND	ND	ND	ND	ND	ND	76.50	5.00	0.00	25.00	1.00	0.00	ND	ND	ND	0.00	**0.00**	**-0.01**	190.00	10.00	0.00	1.00	**0.16**	0.00
17	E46/0093	17	-7.9	6.3	ND	ND	ND	ND	ND	ND	17.50	**2.50**	0.00	16.00	1.50	0.00	ND	ND	ND	0.28	**0.17**	0.00	54.00	5.00	0.00	0.79	**0.12**	0.00
18	E46/0094				ND	ND	ND	ND	ND	ND	15.85	0.55	0.00	29.00	1.00	0.00	ND	ND	ND	0.09	**0.04**	0.00	80.00	1.00	-1.01	0.77	**0.15**	0.00
19	E46/0096				ND	ND	ND	ND	ND	ND	14.00	0.70	0.00	37.50	1.00	0.00	ND	ND	ND	7.40	0.15	0.00	78.00	1.50	0.00	1.20	**0.20**	0.00
20	E45/0055		-7.7		ND	ND	ND	ND	ND	ND	15.00	1.00	0.00	18.00	0.00	0.00	ND	ND	ND	0.04	**0.02**	0.00	22.50	**3.00**	0.00	0.88	0.07	0.00
21	E46/0097			4.1	ND	ND	ND	ND	ND	ND	6.90	0.10	0.00	30.00	0.00	0.00	ND	ND	ND	0.01	**0.00**	0.00	15.50	1.50	**-1.60**	1.10	**0.14**	0.00
22	E46/0098				ND	ND	ND	ND	ND	ND	8.30	0.40	0.00	34.50	1.00	0.00	ND	ND	ND	6.20	0.60	-0.60	56.00	1.00	0.00	1.20	**0.20**	0.00
23	E46/0099		-7.5	6.9	ND	ND	ND	ND	ND	ND	10.70	0.70	0.00	36.00	3.00	0.00	ND	ND	ND	0.00	**0.00**	**-0.01**	50.00	3.00	0.00	0.80	**0.11**	0.00
24	F44/0005	16	-9.7	5.2	ND	ND	ND	ND	ND	ND	11.00	1.00	0.00	5.90	**2.00**	0.00	ND	ND	ND	0.01	**0.01**	0.00	27.00	1.00	0.00	1.70	**0.25**	0.00
25	F44/0039		-9.7		ND	ND	ND	ND	ND	ND	9.05	0.20	0.00	4.00	0.25	0.00	ND	ND	ND	<0.005	ND	ND	29.50	1.50	-1.35	0.89	**0.10**	0.00
26	F44/0139		-8.5		ND	ND	ND	ND	ND	ND	9.10	0.20	**-1.11**	7.00	0.10	0.00	ND	ND	ND	0.01	**0.00**	0.00	16.00	0.00	0.00	0.97	**0.12**	0.00
27	F45/0167	17	-8.3	5.2	ND	ND	ND	ND	ND	ND	15.00	1.00	0.00	14.00	1.00	0.00	ND	ND	ND	0.02	**0.02**	0.00	25.00	2.00	0.00	1.80	**0.25**	0.00
28	F45/0168		-7.7	4.3	ND	ND	ND	ND	ND	ND	14.00	1.00	0.00	18.00	1.00	0.00	ND	ND	ND	0.01	**0.01**	0.00	26.00	1.00	0.00	2.50	0.20	0.00
29	F46/0183				ND	ND	ND	ND	ND	ND	4.60	0.10	0.00	24.00	1.00	0.00	ND	ND	ND	0.08	**0.04**	0.00	12.00	1.00	0.00	0.72	**0.08**	0.00
30	F46/0184	18	-7.2	6.4	ND	ND	ND	ND	ND	ND	14.00	1.00	0.00	23.00	1.00	1.21	ND	ND	ND	0.03	**0.02**	0.00	14.00	**2.00**	-1.35	1.50	0.15	0.00
31	F46/0185	12	-7.3	8.0	ND	ND	ND	ND	ND	ND	15.50	1.50	0.00	46.00	4.00	0.00	ND	ND	ND	0.02	**0.01**	0.00	15.00	**2.00**	-1.26	1.40	**0.25**	**-0.17**
32	E44/0007	28	-9.4		ND	ND	ND	ND	ND	ND	10.00	0.90	0.00	7.65	**1.25**	0.00	ND	ND	ND	0.04	**0.03**	0.00	38.00	3.00	0.00	0.94	0.08	0.00
41	D45/0029				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
42	D45/0036				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
43	E44/0010		-8.4	20.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
44	E44/0035				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
45	E44/0087		-9.5		ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
46	E44/0172				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
47	E46/0013				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
48	E46/0110				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
49	E46/0146				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
50	E46/0156			23.0	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
51	F44/0040			4.3	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
52	F44/0044		-9.1		ND	ND	ND	ND	ND	ND	12.00	ND	ND	6.40	ND	ND	ND	ND	ND	0.02	ND	ND	29.00	ND	ND	1.10	ND	ND
53	F44/0055				ND	ND	ND	ND	ND	ND	8.10	ND	ND	4.50	ND	ND	ND	ND	ND	<0.005	ND	ND	27.00	ND	ND	1.00	ND	ND
54	F45/0175				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
55	F45/0350		-7.4		ND	ND	ND	ND	ND	ND	12.00	ND	ND	16.00	ND	ND	ND	ND	ND	0.16	ND	ND	46.00	ND	ND	0.81	ND	ND
56	F46/0003		-7.1	6.7	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
57	Home Creek				ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
58	E45/0088		-8.0		ND	ND	ND	ND	ND	ND	15.00	0.50	0.00	13.50	1.00	0.00	ND	ND	ND	0.20	**0.18**	0.00	45.50	**6.50**	0.00	0.73	**0.09**	0.00
386	SRC-MCKERCHER				ND	ND	ND	0.09	ND	ND	6.70	ND	ND	25.00	ND	ND	ND	ND	ND	0.04	ND	ND	23.00	ND	ND	1.20	ND	ND
387	SRC-CLARKE				**2.32**	ND	ND	0.14	**0.02**	0.00	13.10	0.60	-0.28	30.00	1.00	0.00	0.13	**0.02**	0.00	0.11	**0.04**	0.00	81.50	5.50	0.00	0.92	0.08	0.00
388	SRC-RYAN				**2.70**	ND	ND	0.04	**0.01**	0.00	23.00	1.00	0.00	13.90	0.25	0.39	0.03	**0.01**	0.00	<0.02	ND	ND	97.50	5.50	-4.79	0.71	0.06	0.05
389	SRC-FERGUSON				ND	ND	ND	0.12	0.01	0.00	8.50	0.20	0.00	19.00	0.20	0.15	0.06	0.00	0.00	<0.02	ND	ND	15.10	0.70	-0.61	0.87	**0.10**	0.06
390	SRC-THOMPSON				**2.10**	ND	0.00	0.07	**0.02**	**-0.01**	12.85	0.65	0.00	21.00	1.00	0.59	0.11	0.01	0.00	1.10	**0.37**	0.00	71.00	3.00	-2.33	0.86	**0.11**	0.00
391	SRC-EDENDALE				ND	ND	ND	0.11	0.01	0.00	8.75	0.30	**-1.23**	27.00	2.00	0.00	0.11	ND	ND	<0.02	ND	ND	54.00	1.50	0.00	0.69	0.05	0.00
392	SRC-MUSCHAMP				ND	ND	ND	0.09	ND	ND	9.30	ND	ND	25.00	ND	ND	ND	ND	ND	0.04	ND	ND	54.00	ND	ND	0.80	ND	ND
393	SRC-BERGEL				ND	ND	ND	0.07	ND	ND	18.40	ND	ND	24.00	ND	ND	ND	ND	ND	<0.01	ND	ND	25.00	ND	ND	1.50	ND	ND
394	SRC-WALLACE				**1.81**	ND	ND	0.08	**0.02**	0.00	14.85	**1.80**	0.00	18.20	**2.30**	**1.85**	0.05	**0.01**	0.00	0.01	ND	0.00	43.00	3.50	0.00	2.60	0.20	0.09
395	SRC-HARGEST				**2.32**	ND	ND	0.09	**0.02**	0.00	17.50	1.00	0.00	23.00	**3.00**	**2.42**	0.05	**0.01**	0.00	<0.02	ND	ND	26.50	1.50	-1.82	2.50	0.20	0.12
455	SRC-9091501				**1.37**	ND	ND	0.10	**0.02**	0.00	7.30	0.40	0.00	25.00	1.00	0.00	0.09	**0.01**	0.00	<0.02	ND	ND	49.00	1.00	0.00	0.75	**0.09**	0.00

Site Details		Mg			Mn			Na			NH4			NO2			NO3			DRP			SiO2			SO4		
		mg/L			mg/L			mg/L			mg/L as N			mg/L as N			mg/L as N			mg/L as P			mg/L			mg/L		
ID	Name	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend
1	D45/0004	4.05	0.30	0.00	0.04	0.01	0.00	15.00	0.00	0.00	<0.01	ND	ND	ND	ND	ND	1.65	0.35	-0.34	0.01	0.01	0.00	ND	ND	ND	2.00	0.10	0.00
2	D43/0007	8.25	0.25	0.00	0.01	0.00	0.00	4.55	0.20	0.00	<0.01	ND	ND	ND	ND	ND	1.70	0.00	0.00	0.04	0.00	0.00	ND	ND	ND	6.45	0.30	0.00
3	D43/0004	6.15	0.15	0.00	0.00	ND	0.00	4.55	0.20	0.00	0.01	0.00	0.01	ND	ND	ND	1.80	0.30	0.00	0.01	0.00	0.00	ND	ND	ND	4.50	0.15	0.00
4	D45/0005	10.00	0.80	0.49	0.01	0.00	0.00	12.00	0.50	0.00	<0.01	ND	ND	ND	ND	ND	2.70	0.10	0.00	0.02	0.00	0.00	ND	ND	ND	7.80	0.20	0.00
5	D46/0003	6.00	0.20	0.00	0.00	0.00	0.00	20.00	1.00	0.00	<0.01	ND	ND	ND	ND	ND	2.05	0.05	0.00	0.03	0.01	0.00	ND	ND	ND	6.45	0.20	0.00
6	D46/0031	7.05	0.17	-0.27	<0.001	ND	ND	21.00	1.00	0.00	<0.01	ND	ND	ND	ND	ND	0.88	0.07	0.00	0.03	0.00	0.00	ND	ND	ND	5.50	0.10	0.00
7	E44/0008	3.35	0.15	0.00	0.00	0.00	0.00	13.00	1.00	0.00	<0.01	ND	ND	ND	ND	ND	6.45	0.95	0.00	0.03	0.00	0.00	ND	ND	ND	2.05	0.15	0.00
8	E44/0036	4.33	0.22	0.00	<0.001	ND	ND	16.50	0.50	0.00	<0.01	ND	ND	ND	ND	ND	10.00	0.00	0.00	0.02	0.00	0.00	ND	ND	ND	1.75	0.10	0.00
9	E44/0044	14.00	1.00	0.00	0.11	0.00	0.00	14.00	0.00	0.00	<0.01	ND	ND	ND	ND	ND	0.01	0.00	0.00	0.02	0.00	0.00	ND	ND	ND	3.10	0.10	0.00
10	E44/0045	6.20	0.20	0.00	<0.001	ND	ND	8.30	0.40	-0.55	<0.01	ND	ND	ND	ND	ND	2.70	0.10	0.00	0.02	0.01	0.00	ND	ND	ND	2.10	0.10	0.00
11	E44/0173	3.00	0.41	0.00	<0.001	ND	ND	5.05	0.40	0.00	<0.01	ND	ND	ND	ND	ND	3.35	1.45	0.00	0.01	0.00	0.00	ND	ND	ND	6.30	0.50	0.00
12	E45/0009	21.00	7.00	6.04	0.01	0.00	0.00	20.00	4.00	4.06	<0.01	ND	ND	ND	ND	ND	27.00	13.00	10.66	0.01	0.00	0.00	ND	ND	ND	21.00	6.00	7.66
13	E45/0010	8.90	1.00	0.86	0.00	0.00	0.00	13.50	0.50	0.00	<0.01	ND	ND	ND	ND	ND	6.20	1.60	0.00	0.01	0.00	0.00	ND	ND	ND	18.50	0.50	0.00
14	E45/0011	7.30	0.50	0.00	0.00	0.00	0.00	16.00	1.00	0.00	<0.01	ND	ND	ND	ND	ND	7.25	0.80	0.00	0.02	0.00	0.00	ND	ND	ND	12.50	0.50	0.00
15	E45/0012	10.50	0.50	0.00	0.00	0.00	0.00	17.00	1.00	0.00	<0.01	ND	ND	ND	ND	ND	3.30	0.50	0.00	0.04	0.01	0.00	ND	ND	ND	2.75	0.25	0.00
16	E46/0092	3.75	0.35	0.00	0.00	0.00	0.00	17.00	1.00	0.00	<0.01	ND	ND	ND	ND	ND	5.65	0.65	0.00	0.02	0.01	0.00	ND	ND	ND	4.10	0.10	0.00
17	E46/0093	6.70	0.85	0.00	0.00	0.00	0.00	17.00	1.00	0.00	<0.01	ND	ND	ND	ND	ND	4.75	0.70	0.00	0.02	0.00	0.00	ND	ND	ND	8.80	1.20	0.00
18	E46/0094	9.10	0.63	0.40	0.00	0.00	0.00	26.00	0.00	0.00	<0.01	ND	ND	ND	ND	ND	2.00	0.15	0.00	0.04	0.00	0.00	ND	ND	ND	5.60	0.20	0.00
19	E46/0096	6.25	0.30	0.71	0.20	0.05	0.00	27.00	1.00	0.00	0.05	0.01	0.00	ND	ND	ND	<0.01	ND	ND	0.02	0.02	0.00	ND	ND	ND	5.05	0.30	0.00
20	E45/0055	8.45	0.80	0.00	0.01	0.01	0.00	12.00	1.00	0.00	<0.01	ND	ND	ND	ND	ND	8.10	0.50	0.00	0.01	0.00	0.00	ND	ND	ND	18.00	2.00	2.01
21	E46/0097	3.60	0.15	0.00	0.00	0.00	0.00	22.00	1.00	0.00	<0.01	ND	ND	ND	ND	ND	5.50	0.30	0.00	0.01	0.00	0.00	ND	ND	ND	2.95	0.15	0.00
22	E46/0098	5.40	0.10	0.00	0.15	0.01	0.00	23.00	1.00	0.00	0.07	0.01	0.00	ND	ND	ND	<0.01	ND	ND	0.04	0.02	0.00	ND	ND	ND	3.20	0.60	0.00
23	E46/0099	8.80	0.50	0.00	0.00	0.00	0.00	25.00	1.00	0.00	<0.01	ND	ND	ND	ND	ND	3.90	1.10	0.00	0.07	0.00	0.00	ND	ND	ND	3.80	0.15	0.00
24	F44/0005	3.54	0.34	0.28	0.00	0.00	0.00	6.30	0.10	0.00	<0.01	ND	ND	ND	ND	ND	4.25	0.30	0.00	0.01	0.00	0.00	ND	ND	ND	7.10	0.60	0.00
25	F44/0039	3.00	0.11	0.00	<0.001	ND	ND	6.50	0.30	0.00	<0.01	ND	ND	ND	ND	ND	3.40	0.25	0.00	0.02	0.00	0.00	ND	ND	ND	1.70	0.00	0.00
26	F44/0139	3.90	0.40	-0.91	0.00	0.00	0.00	12.00	1.00	-1.90	<0.01	ND	ND	ND	ND	ND	10.00	0.00	0.00	0.02	0.00	0.00	ND	ND	ND	1.10	0.10	0.00
27	F45/0167	6.20	0.50	0.61	0.00	0.00	0.00	9.80	0.40	0.00	<0.01	ND	ND	ND	ND	ND	6.90	0.30	0.00	0.01	0.00	0.00	ND	ND	ND	17.00	2.00	2.00
28	F45/0168	4.90	0.40	0.00	0.00	0.00	0.00	13.00	1.00	0.00	<0.01	ND	ND	ND	ND	ND	4.60	0.45	-0.45	0.02	0.00	0.00	ND	ND	ND	16.00	2.00	1.01
29	F46/0183	2.50	0.10	0.10	0.00	0.00	0.00	16.00	1.00	0.00	<0.01	ND	ND	ND	ND	ND	2.10	0.20	-0.20	0.01	0.00	0.00	ND	ND	ND	3.30	0.20	0.00
30	F46/0184	3.40	0.45	0.29	0.01	0.00	0.00	13.00	1.00	0.00	<0.01	ND	ND	ND	ND	ND	5.15	0.80	0.00	0.01	0.00	0.00	ND	ND	ND	10.00	0.95	1.55
31	F46/0185	7.60	0.80	0.00	0.00	0.00	0.00	20.50	1.00	0.00	<0.01	ND	ND	ND	ND	ND	6.15	0.15	0.00	0.02	0.00	0.00	ND	ND	ND	8.50	0.40	0.63
32	E44/0007	5.70	0.30	0.00	0.01	0.00	0.00	9.50	0.50	0.00	<0.01	ND	ND	ND	ND	ND	3.70	0.40	0.00	0.02	0.01	0.00	ND	ND	ND	5.20	1.20	0.00
41	D45/0029	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.45	0.25	-0.49	ND	ND	ND	ND	ND	ND	ND	ND	ND
42	D45/0036	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.01	0.01	0.01	ND	ND	ND	ND	ND	ND	ND	ND	ND
43	E44/0010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.20	0.40	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND
44	E44/0035	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.42	0.04	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND
45	E44/0087	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.29	0.11	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND
46	E44/0172	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.35	0.25	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND
47	E46/0013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	2.30	0.80	-2.03	ND	ND	ND	ND	ND	ND	ND	ND	ND
48	E46/0110	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.58	0.44	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND
49	E46/0146	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.10	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
50	E46/0156	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	3.75	1.05	-1.78	ND	ND	ND	ND	ND	ND	ND	ND	ND
51	F44/0040	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	7.70	0.30	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND
52	F44/0044	4.90	ND	ND	0.00	ND	ND	7.90	ND	ND	<0.01	ND	ND	ND	ND	ND	4.00	1.00	0.00	0.02	ND	ND	ND	ND	ND	8.90	ND	ND
53	F44/0055	3.20	ND	ND	<0.001	ND	ND	6.10	ND	ND	<0.01	ND	ND	ND	ND	ND	2.20	0.50	0.00	0.02	ND	ND	ND	ND	ND	4.00	ND	ND
54	F45/0175	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	1.60	0.30	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND
55	F45/0350	6.60	ND	ND	0.14	ND	ND	14.00	ND	ND	0.02	ND	ND	ND	ND	ND	1.20	0.55	0.00	0.02	ND	ND	ND	ND	ND	7.00	ND	ND
56	F46/0003	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	4.30	0.50	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND
57	Home Creek	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.52	0.05	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND
58	E45/0088	6.45	0.95	0.00	0.00	0.00	0.00	10.25	1.15	0.00	0.01	0.00	0.00	ND	ND	ND	2.80	0.30	0.00	0.01	0.00	0.00	ND	ND	ND	7.45	0.60	0.00
386	SRC-MCKERCHER	4.50	ND	ND	<0.01	ND	ND	22.00	ND	ND	0.01	ND	ND	ND	ND	ND	6.20	ND	ND	<0.1	ND	ND	19.50	ND	ND	5.10	ND	ND
387	SRC-CLARKE	7.40	0.30	0.00	0.02	0.01	0.00	24.50	0.50	-0.67	<0.01	ND	ND	ND	ND	ND	1.20	0.29	0.00	<0.05	ND	ND	41.00	2.50	0.00	4.00	0.30	0.00
388	SRC-RYAN	9.90	0.20	0.00	<0.005	ND	ND	15.40	0.60	-0.37	<0.01	ND	ND	ND	ND	ND	5.90	0.85	0.72	<0.05	ND	ND	27.00	1.00	0.00	11.20	0.20	-0.17
389	SRC-FERGUSON	3.60	0.10	0.00	0.01	0.00	0.00	13.60	0.35	-0.28	<0.01	ND	ND	ND	ND	ND	6.00	0.20	0.14	<0.05	ND	ND	15.10	0.50	-0.28	7.30	0.60	0.40
390	SRC-THOMPSON	7.55	0.30	-0.20	0.98	0.13	-0.04	18.20	0.50	-0.41	0.01	0.00	0.00	ND	ND	ND	0.31	0.18	0.14	<0.04	ND	ND	26.00	2.00	0.00	17.30	1.00	0.00
391	SRC-EDENDALE	5.75	0.05	-0.32	<0.01	ND	ND	22.00	0.00	0.00	0.01	0.01	0.00	ND	ND	ND	1.20	0.15	0.00	<0.1	ND	ND	34.00	1.00	0.00	4.20	0.00	0.00
392	SRC-MUSCHAMP	4.90	ND	ND	<0.01	ND	ND	23.00	ND	ND	<0.01	ND	ND	ND	ND	ND	1.50	ND	ND	<0.1	ND	ND	34.00	ND	ND	5.60	ND	ND
393	SRC-BERGEL	8.20	ND	ND	<0.01	ND	ND	17.10	ND	ND	<0.01	ND	ND	ND	ND	ND	11.00	ND	ND	<0.1	ND	ND	19.70	ND	ND	16.40	ND	ND
394	SRC-WALLACE	4.90	0.50	0.00	0.10	0.08	0.00	13.50	0.20	0.00	<0.01	ND	ND	ND	ND	ND	3.50	1.00	0.00	<0.05	ND	ND	13.70	0.90	0.00	10.60	1.00	0.81
395	SRC-HARGEST	5.90	0.50	0.00	<0.005	ND	ND	15.50	0.40	0.00	<0.01	ND	ND	ND	ND	ND	7.70	1.30	0.58	<0.05	ND	ND	13.00	0.40	0.00	19.85	1.15	0.00
455	SRC-9091501	5.10	0.30	0.00	<0.005	ND	ND	19.20	0.60	-0.60	ND	ND	ND	ND	ND	ND	1.10	0.10	0.00	0.04	ND	0.00	29.00	1.00	0.00	4.70	0.20	0.00

Site Details		pH lab			Cond Field			Temp Field			Total Coliforms			Faecal Coliform			Escherischia coli		
		pH units			uS/cm			deg C			cfu/100 ml			cfu/100 ml			cfu/100 ml		
ID	Name	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend
1	D45/0004	6.40	0.00	0.00	160.85	1.50	0.00	11.30	0.30	0.00	<1	ND	ND	**7.00**	ND	0.00	<1	ND	ND
2	D43/0007	7.50	0.00	0.00	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1	ND	ND
3	D43/0004	7.00	0.00	0.00	ND	ND	ND	ND	ND	ND	<1	ND	ND	ND	ND	ND	<1	ND	ND
4	D45/0005	6.80	0.10	0.00	265.35	6.35	4.39	11.15	0.35	0.00	**4.00**	**3.51**	0.00	<1	ND	ND	<1	ND	ND
5	D46/0003	7.70	0.10	0.07	499.10	10.10	0.00	11.30	**2.30**	0.00	**62.00**	**57.00**	0.00	<1	ND	ND	<1	ND	ND
6	D46/0031	7.00	0.20	0.00	214.05	1.70	-4.22	11.75	**1.45**	0.00	**2.00**	**1.47**	0.00	ND	ND	ND	<1	ND	ND
7	E44/0008	6.00	0.00	0.00	141.00	9.00	0.00	11.40	0.40	0.00	<1	ND	ND	<1	ND	ND	<1	ND	ND
8	E44/0036	6.10	0.00	0.00	180.70	5.30	0.00	11.40	0.60	0.00	<1	ND	ND	ND	ND	ND	<1	ND	ND
9	E44/0044	7.40	0.10	0.00	141.70	ND	ND	9.40	ND	ND	1.00	ND	0.00	ND	ND	ND	<1	ND	ND
10	E44/0045	6.70	0.00	0.00	142.30	0.70	0.00	13.70	1.30	0.00	**2.61**	**1.63**	0.00	ND	ND	ND	<1	ND	ND
11	E44/0173	6.25	0.05	0.00	109.00	**19.10**	0.00	11.05	0.40	0.00	<1	ND	ND	ND	ND	ND	<1	ND	ND
12	E45/0009	5.90	0.10	-0.09	634.50	**149.50**	0.00	10.90	0.85	0.00	1.00	**0.53**	0.00	<1	ND	ND	<1	ND	ND
13	E45/0010	6.50	0.10	0.00	294.20	**32.80**	0.00	10.80	0.70	0.00	**9.00**	**8.54**	0.00	<1	ND	ND	0.95	**0.65**	0.00
14	E45/0011	6.80	0.10	0.00	257.00	10.00	0.00	12.10	**2.10**	0.00	<1	ND	ND	<1	ND	ND	<1	ND	ND
15	E45/0012	6.60	0.10	0.00	268.00	6.20	0.00	11.75	0.90	0.00	**17.00**	**14.00**	0.00	<1	ND	ND	<1	ND	ND
16	E46/0092	7.45	0.10	0.00	515.00	22.50	0.00	12.05	**1.30**	0.00	**13.00**	**7.50**	0.00	**3.00**	ND	**-3.59**	1.00	**0.53**	0.00
17	E46/0093	6.60	0.10	0.00	247.40	7.60	0.00	11.50	0.45	0.00	**7.00**	**4.69**	**9.97**	1.00	**0.70**	**-2.16**	0.66	**0.34**	0.00
18	E46/0094	6.70	0.10	0.00	289.00	3.50	0.00	11.70	0.30	0.00	**2.50**	**2.25**	0.00	<1	ND	ND	<1	ND	ND
19	E46/0096	6.60	0.05	0.00	301.50	12.50	0.00	11.20	0.35	0.00	1.00	**0.88**	0.00	<1	ND	ND	<1	ND	ND
20	E45/0055	6.20	0.10	0.00	244.60	13.40	-15.39	11.55	0.85	0.00	<1	ND	ND	ND	ND	ND	<1	ND	ND
21	E46/0097	6.00	0.00	0.00	200.90	3.80	0.00	11.70	0.40	0.00	<1	ND	ND	<1	ND	ND	<1	ND	ND
22	E46/0098	6.40	0.00	0.00	237.20	0.20	0.00	11.90	0.10	0.00	1.00	**0.77**	0.00	<1	ND	ND	<1	ND	ND
23	E46/0099	6.50	0.10	0.00	276.00	11.00	0.00	12.60	0.40	0.00	0.51	**0.30**	0.00	<1	ND	ND	<1	ND	ND
24	F44/0005	6.50	0.10	0.00	137.00	9.40	7.97	10.20	**1.30**	0.00	<1	ND	ND	<1	ND	ND	<1	ND	ND
25	F44/0039	6.60	0.00	0.00	113.60	4.10	0.00	10.95	0.25	0.00	**1.94**	**1.73**	0.00	ND	ND	ND	<1	ND	ND
26	F44/0139	6.50	0.10	0.00	158.80	3.10	-11.83	10.95	0.50	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND
27	F45/0167	6.20	0.05	-0.04	203.95	9.00	0.00	11.20	**1.75**	0.00	1.00	ND	0.00	**4.00**	ND	ND	<1	ND	ND
28	F45/0168	6.10	0.10	0.00	216.00	**23.50**	0.00	10.50	**1.60**	0.00	0.44	**0.29**	0.00	<1	ND	ND	<1	ND	ND
29	F46/0183	5.70	0.00	0.00	143.70	1.30	0.00	11.00	0.20	0.00	**3.41**	**2.43**	0.00	<1	ND	ND	<1	ND	ND
30	F46/0184	5.80	0.00	0.00	200.25	14.25	0.00	11.55	**2.20**	0.00	1.00	**0.48**	0.00	<1	ND	ND	<1	ND	ND
31	F46/0185	5.60	0.00	0.00	283.00	12.00	0.00	10.90	0.50	0.00	**6.50**	**5.00**	0.00	<1	ND	ND	<1	ND	ND
32	E44/0007	6.80	0.20	0.00	147.65	6.15	0.00	11.40	0.70	0.00	1.00	**0.53**	0.00	<1	ND	ND	<1	ND	ND
41	D45/0029	ND	ND	ND	ND	ND	ND	ND	ND	ND	**37.00**	ND	ND	ND	ND	ND	<1	ND	ND
42	D45/0036	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
43	E44/0010	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
44	E44/0035	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
45	E44/0087	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
46	E44/0172	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
47	E46/0013	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
48	E46/0110	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
49	E46/0146	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
50	E46/0156	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
51	F44/0040	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
52	F44/0044	6.40	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
53	F44/0055	6.40	ND	ND	ND	ND	ND	ND	ND	ND	**3.00**	ND	ND	ND	ND	ND	ND	ND	ND
54	F45/0175	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
55	F45/0350	6.50	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
56	F46/0003	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
57	Home Creek	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
58	E45/0088	6.60	0.10	0.00	ND	ND	ND	ND	ND	ND	**1.50**	**0.84**	0.00	ND	ND	ND	<1	ND	ND
386	SRC-MCKERCHER	6.45	ND	ND	180.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
387	SRC-CLARKE	6.55	0.12	-0.09	250.00	5.00	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
388	SRC-RYAN	6.65	0.19	-0.13	270.00	10.00	7.92	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
389	SRC-FERGUSON	5.89	0.11	-0.09	160.00	10.00	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
390	SRC-THOMPSON	6.46	0.08	-0.05	220.00	0.00	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
391	SRC-EDENDALE	6.49	0.10	0.00	185.00	10.00	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
392	SRC-MUSCHAMP	6.77	ND	ND	190.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
393	SRC-BERGEL	6.39	ND	ND	250.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
394	SRC-WALLACE	6.24	0.09	-0.04	200.00	20.00	10.77	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
395	SRC-HARGEST	6.11	0.09	-0.08	230.00	20.00	13.18	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
455	SRC-9091501	6.34	0.10	-0.06	180.00	10.00	0.00	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND

Table 2. Summary of results of Kruskal-Wallis tests assessing differences by analyte related to site location (i.e. map sheet), aquifer lithology, aquifer confinement, groundwater use, and well head protection. Significant differences (95% confidence level) are denoted by the letter “Y” and the orange highlighting. If there are no significant differences by category, the letter “N” is used.

	Lithology			Confinement			Map Sheet			GW Use			Well Head Prot.		
	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend	Med	MAD	Trend
Br															
Ca	N	N	N	N	N	N	N	N	Y	N	Y	N	N	N	N
Cl	N	N	N	N	N	N	Y	N	N	N	N	N	N	N	N
F															
Fe	Y	Y	N	N	N	N	N	N	N	N	N	N	N	N	N
HCO3	N	N	N	N	N	N	Y	N	N	N	N	N	N	N	N
K	N	N	N	N	N	N	N	Y	Y	N	N	N	N	N	N
Mg	N	N	N	N	N	N	Y	N	N	N	Y	N	N	N	N
Mn	N	N	N	N	Y	N	N	N	N	N	N	N	N	N	N
Na	N	N	N	N	N	N	Y	Y	N	N	N	N	N	N	N
NH4	Y	N	N	Y	N	N	N	N	N	N	N	N	N	N	N
NO2															
NO3	Y	Y	N	Y	Y	N	N	N	N	Y	Y	N	N	N	N
DRP	N	N	Y	N	Y	N	Y	N	N	Y	N	N	N	N	N
SiO2															
SO4	N	N	Y	N	N	Y	Y	Y	Y	Y	Y	Y	N	N	N
pH	Y	N	N	N	N	N	Y	N	N	N	N	N	N	N	N
Cond.	N	N	N	N	N	N	Y	N	N	N	N	N	N	N	N
Temp.	N	N	N	N	N	N	N	N	N	N	N	N	N	N	N
Tot. Coli.	N	N	N	N	N	N	N	N	N	Y	N	N	N	N	N

Table 3. Values of the 5th, 25th, 50th (i.e. median), 75th and 95th percentiles in concentration of monitored parameters. The table shows percentiles computed for all of Southland's monitoring sites (including the NGMP), for all NGMP sites (including sites outside of Southland). Also shown are the concentration percentiles for the four categories of groundwater defined for different sub-regions of Southland, as described in Section 5.1: 1) relatively young, unimpacted, river-recharged groundwaters, 2) anoxic, more evolved groundwaters representative of confined or organic-rich aquifers, 3) rainfall-recharged groundwaters of intermediate age and predominant Ca-HCO_3 character, showing some evidence of human/agricultural impact, and 4) rainfall-recharged groundwaters of intermediate age with slightly more Na-Cl character and a similar level of human/agricultural impact.

		1					2					3					4					All Southland					All NGMP				
		5th	25th	50th	75th	95th	5th	25th	50th	75th	95th	5th	25th	50th	75th	95th	5th	25th	50th	75th	95th	5th	25th	50th	75th	95th	5th	25th	50th	75th	95th
Br	mg/L	0.05	0.05	0.05	0.05	0.05	0.13	0.13	0.13	0.13	0.13	0.04	0.05	0.05	0.06	0.07	0.07	0.09	0.09	0.11	0.13	0.05	0.08	0.09	0.12	0.14	0.01	0.04	0.08	0.12	0.44
Ca	mg/L	8.39	9.23	10.00	12.00	13.05	8.59	9.73	11.15	12.58	13.72	10.38	15.00	17.00	23.00	25.13	6.30	8.56	11.90	15.34	18.06	6.81	8.98	12.43	15.13	23.00	4.50	8.35	13.10	30.45	108.05
Cl	mg/L	2.98	3.75	4.50	6.50	7.34	34.65	35.25	36.00	36.75	37.35	11.62	13.90	16.00	17.50	19.20	17.40	20.50	24.00	28.50	37.50	4.00	13.90	18.65	24.75	35.03	3.67	11.30	19.00	30.50	109.70
F	mg/L	0.01	0.01	0.01	0.01	0.02	0.15	0.15	0.16	0.16	0.16	0.02	0.03	0.03	0.03	0.03	0.07	0.08	0.08	0.09	0.11	0.02	0.06	0.06	0.07	0.10	0.02	0.05	0.08	0.13	0.31
Fe	mg/L	<0.01	<0.01	<0.01	0.03	0.04	6.26	6.50	6.80	7.10	7.34	0.00	0.02	0.06	0.13	0.24	0.00	0.00	0.01	0.01	0.02	0.00	0.00	0.01	0.03	0.07	0.00	0.01	0.03	0.27	2.71
HCO3	mg/L	27.60	29.25	38.00	46.50	52.80	57.10	61.50	67.00	72.50	76.90	24.00	44.00	53.00	89.00	106.5	12.90	15.30	26.00	54.00	80.15	14.00	23.00	43.00	54.00	92.00	25.00	39.00	70.00	148.00	415.10
K	mg/L	0.86	0.90	0.95	0.99	1.08	1.20	1.20	1.20	1.20	1.20	0.60	0.72	0.80	0.87	0.93	0.60	0.72	0.87	1.40	2.50	0.60	0.75	0.87	1.00	1.47	0.71	1.05	1.80	3.45	8.19
Mg	mg/L	3.06	4.05	5.70	6.18	7.64	5.44	5.61	5.83	6.04	6.21	5.34	6.60	7.55	9.90	11.60	3.22	3.83	5.33	7.55	9.31	3.13	4.12	5.90	7.51	9.94	1.60	3.45	5.60	8.20	25.90
Mn	mg/L	0.00	0.00	0.00	0.00	0.00	0.15	0.16	0.17	0.18	0.19	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00	0.01	0.00	0.02	0.03	0.11	0.61
Na	mg/L	4.55	5.33	6.50	8.10	9.14	23.20	24.00	25.00	26.00	26.80	10.07	12.00	14.00	15.40	17.48	13.00	14.55	20.00	22.00	25.10	5.79	12.40	15.40	19.60	24.65	7.12	12.35	19.20	29.90	99.60
NH4-N	mg/L	<0.01	<0.01	<0.01	<0.01	<0.01	0.05	0.05	0.06	0.07	0.07	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.00	0.00	0.00	0.06	2.83
NO3-N	mg/L	1.73	2.00	2.70	3.55	3.91	<0.01	<0.01	<0.01	<0.01	<0.01	0.19	1.65	4.75	6.20	7.59	1.15	2.03	4.25	6.11	8.20	0.33	1.20	3.38	5.90	7.96	0.00	0.02	0.67	3.50	9.70
DRP	mg/L	0.01	0.02	0.02	0.02	0.03	0.02	0.03	0.03	0.04	0.04	0.01	0.01	0.01	0.02	0.02	0.00	0.00	0.01	0.02	0.04	0.01	0.01	0.02	0.04	0.04	0.01	0.03	0.08	0.77	6.88
SiO2	mg/L	0.40	0.40	2.83	6.68	8.56	39.64	41.23	43.22	45.22	46.81	9.48	15.70	27.00	28.45	33.73	13.25	14.75	19.60	34.00	38.55	13.00	15.10	25.50	29.00	41.00	10.86	15.53	25.75	37.00	74.33
SO4	mg/L	1.82	3.05	4.50	5.83	8.17	3.29	3.66	4.13	4.59	4.96	2.66	7.45	11.20	17.00	18.20	2.68	3.90	5.60	10.30	19.97	1.93	4.00	6.45	10.60	18.91	0.01	2.83	6.50	11.04	27.00
pH	pH Units	6.40	6.50	6.70	6.90	7.35	6.41	6.45	6.50	6.55	6.59	6.20	6.46	6.60	6.65	7.04	5.69	5.95	6.24	6.53	6.79	5.77	6.20	6.46	6.62	7.42	6.23	6.46	6.78	7.49	8.09
Cond	uS/cm	116	128	142	145	147	240	253	269	285	298	151	212	247	266	282	143	186	207	250	284	138	161	204	250	288	90	165	230	323	901

Table 4. Analyte concentrations (mg/L) for medians of clusters and subclusters defined for the NGMP data by HCA with Ward's linkage rule (Daughney and Reeves, 2003a). NO_3 and NH_4 reported as N, PO_4 reported as P, and all other analytes reported as written. Green cells indicate analytes that vary at the 95% confidence level between clusters at the relevant threshold. Also shown are median concentrations of selected analytes in global average river water and groundwater, after Turekian (1977) and Hem (1985).

Threshold and Cluster[a]		Sites[b]		Centroid Chemistry (mg/L)															
		n	%*n*	Br	Ca	Cl	F	Fe	HCO_3	K	Mg	Mn	Na	NH_4	NO_3	PO_4	SiO_2	SO_4	TDS
1	1	79	74	0.05	13.23	10.41	0.05	0.01	57.17	1.55	4.61	0.00	11.53	0.01	1.36	0.01	21.38	7.49	128.86
	2	28	26	0.11	36.53	26.95	0.16	0.47	216.82	3.50	9.57	0.15	37.96	4.10	0.01	0.04	31.78	2.22	370.37
Global Av. River Water					15	7.8		0.05	58	2.3	4.1	<0.01	6.3				14	3.7	120
Global Av. Groundwater					50	20		0.7	200	3	7	0.03	30				16	30	350
2	1A	45	42	0.08	14.56	19.52	0.05	0.01	62.09	1.86	7.36	0.00	17.40	0.01	2.32	0.01	26.89	10.39	162.54
	1B	34	32	0.02	11.65	4.53	0.06	0.02	51.25	1.22	2.48	0.00	6.68	0.01	0.67	0.01	15.79	4.56	98.95
3	1A-1	28	26	0.07	15.54	16.92	0.07	0.01	69.71	1.36	7.08	0.01	15.60	0.01	1.51	0.00	19.15	11.57	158.60
	1A-2	17	16	0.10	13.09	24.71	0.03	0.02	51.32	3.10	7.84	0.00	20.83	0.01	4.68	0.02	47.03	8.62	181.39
	1B-1	19	18	0.02	18.70	3.11	0.07	0.01	70.60	1.06	2.66	0.00	5.60	0.00	0.62	0.00	11.73	5.18	119.37
	1B-2	15	14	0.04	6.39	7.29	0.04	0.02	34.15	1.46	2.27	0.00	8.36	0.02	0.73	0.02	23.01	3.86	87.68
	2A	16	15	0.07	25.98	17.95	0.13	0.22	153.04	2.36	7.46	0.07	26.84	1.80	0.02	0.03	27.59	5.75	269.31
	2B	12	11	0.20	57.57	46.30	0.21	1.25	344.99	5.91	13.34	0.44	60.29	12.28	0.00	0.05	38.38	0.28	581.51

[a] Cluster descriptions given on Table 5.

[b] Distribution of n sites out of a total of 107 between each cluster.

Table 5. General characteristics of the clusters defined by HCA using medians of analytes from all NGMP sites.

Cluster at Threshold 1	Facies Description	Cluster at Threshold 2	Facies Description	Cluster at Threshold 3	Facies Description
1	Surface-dominated Oxidised Unconfined aquifer Low to moderate TDS Ca-Na-Mg-HCO$_3$ water	1A	Signs of human impact Moderate TDS Na-Ca-Mg-HCO$_3$-Cl water	1A-1	Moderate human impact Carbonate or clastic aquifer Ca-Na-Mg-HCO$_3$-Cl water
				1A-2	Most human Impact Volcanic or volcaniclastic aquifer Na-Ca-Mg-HCO$_3$-Cl water
		1B	Little human impact Low TDS Ca-Na-HCO$_3$ water	1B-1	Carbonate or clastic aquifer Ca-HCO$_3$ water
				1B-2	Volcanic or volcaniclastic aquifer Na-Ca-Mg-HCO$_3$-Cl
2	Groundwater-dominated Reduced Confined aquifer Higher TDS Ca-Na-HCO$_3$ water			2A	Moderately Reduced High TDS
				2B	Highly Reduced Highest TDS

Table 6. General characteristics of the clusters defined by HCA using trends in analytes from all NGMP sites. Also shown are the median rates of change of selected analytes characteristic of each cluster. The category WR can be subdivided into WR1 and WR2 based on subtle differences in the patterns of trends amongst different analytes, but all seem to be representative of natural water-rock interaction.

Median Change (ppm/year)

WR	Water-Rock interaction: Unconfined and confined groundwaters showing no or slow concentration change	Na	-0.40	HCO3	-0.12
		K	0.03	Cl	0.00
		Ca	0.07	SO4	-0.01
		Mg	0.01	SiO2	0.25
D	Dilution: Dilution and oxidation, usually of confined aquifers with reduced groundwater, perhaps indicating a change in flow regime	Na	-1.88		
		Ca	-0.62		
		HCO3	-1.03		
		Cl	-0.84		
I	Impact: Unconfined aquifers with oxidised groundwater, fairly rapidly being becoming more impacted by agricultural runoff	Na	-0.13		
		Cl	1.01		
		NO3	0.27		
		SO4	0.40		
P	Pristine: Oxidised, unconfined groundwater, showing reduced human impact over time	Na	-0.09		
		Cl	-0.25		
		NO3	-0.37		
		SO4	-0.06		