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A Groundwater Quality Assessment of the Fractured Rock Aquifers of the Piccadilly Valley, South Australia

K. M. IVKOVIC, K. L. WATKINS, R. G. CRESSWELL & J. BAULD

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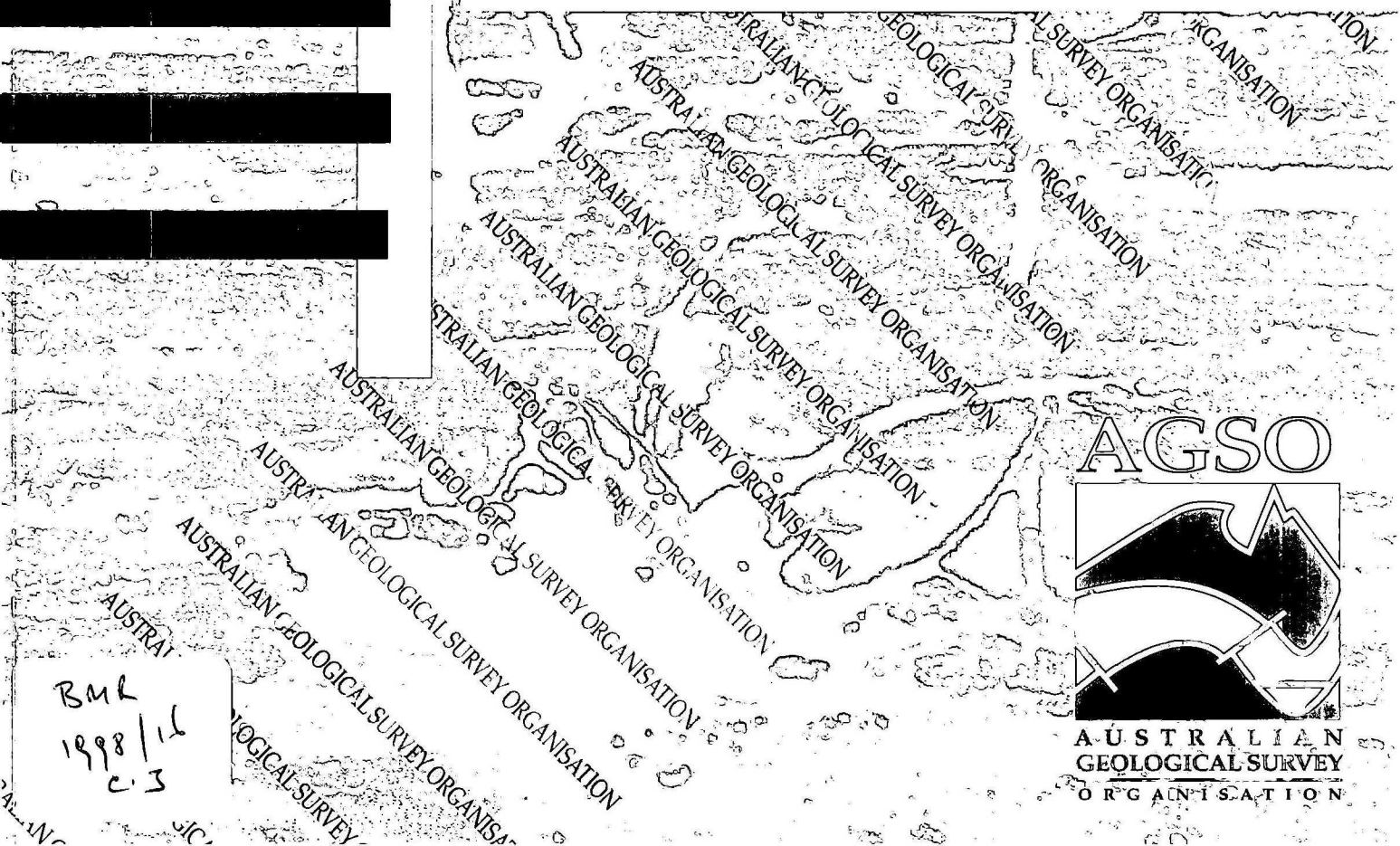

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Australian Groundwater Quality Assessment Project Report No. 2

A Groundwater Quality Assessment of the Fractured Rock Aquifers of the Piccadilly Valley, South Australia

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We thank Dr Santo Raguso (CSIRO Division of Water Resources) for the use of his laboratory facilities in order to undertake our microbiological work. We would also like to extend our appreciation to Dr Andrew Herczeg (CSIRO Division of Water Resources) for his assistance in stable isotope interpretation.

This study could not have been undertaken without the co-operation received from the land holders in the Piccadilly Valley, and we gratefully acknowledge their assistance.

EXECUTIVE SUMMARY

The Piccadilly Valley lies within the Onkaparinga Catchment in the Mount Lofty Ranges near Adelaide. As the greater Adelaide urban area expands into the Mount Lofty Ranges, the Piccadilly Valley is coming under significant development pressure. At the time this investigation was carried out the Mount Lofty Ranges Catchment was identified as an area significantly lacking in groundwater quality information and, within this large area, the Piccadilly Valley was recommended as having the highest priority. Thus the fractured rock aquifers of the Piccadilly Valley were the focus of a groundwater quality assessment by the Australian Geological Survey Organisation (AGSO) during April and May 1994. Groundwater samples recovered from 42 supply bores were analysed for environmental isotopes, physical parameters, inorganic constituents, nutrients, pesticides and contaminant and indigenous microbes.

Intermingled with the rural residential development now encroaching into the Piccadilly Valley, and penetrating beyond it into adjacent grazing lands, are intensive agricultural industries such as market gardens, orchards and viticulture, together with increasing extraction of groundwater for bottled mineral waters. Thus far, the overall impact of these land uses on groundwater quality appears to have been limited. However, several classes of contaminants, including pesticides, nitrate and faecal indicator bacteria, were found in Piccadilly Valley groundwaters. Their presence, in the context of our current understanding of the hydrogeological processes taking place within the Piccadilly Valley, suggests that groundwater resources occurring in the fractured rock aquifers may be vulnerable to increasing land use intensity.

Groundwater nitrate concentrations were generally low and appear similar to those documented in 1979; median concentrations are comparable, having risen slightly from 0.38 to 0.67 mg/L of nitrate-N. On the other hand, about two-thirds of groundwater samples showed slight to substantial increases above apparent background concentrations, although only one sample (15 mg/L) exceeded the drinking water guideline value of 11.3 mg/L nitrate-N. The isotopic signatures of nitrate-N were consistent with derivation from human and/or animal wastes and with leaking septic tanks as the most probable sources.

Faecal indicator bacteria were detected in 19% of samples, suggesting that there is some potential for transmission of gastrointestinal pathogens if untreated groundwater is used for drinking purposes. While grazing livestock cannot be precluded in some instances, leaking septic tanks are again the most probable sources of contamination.

Pesticides were detected in only 5% of samples, at low concentrations. The compounds found were: atrazine, a triazine herbicide; desethylatrazine, a degradation product of atrazine; and vinclozolin, a dichloroanilide fungicide. While the Australian Drinking Water Guidelines state that pesticides should not be detected in drinking water, the concentration of atrazine is well below that considered to be of health concern.

The contrast with earlier data, which demonstrated the frequent occurrence of pesticides in surface waters, is striking and suggests that the relatively steep topography of the Piccadilly Valley may promote rapid surface runoff into creeks and streams concomitantly diminishing the opportunity for transport of contaminants into the underlying aquifers. The detection of both the parent compound (atrazine) and its degradation product suggests that, while movement through the fractured rock aquifer may be relatively rapid, the movement of contaminants with the chemical properties of atrazine through the overlying soil layer may be sufficiently slow in some areas for substantial breakdown to occur.

Some naturally occurring elements were elevated above drinking water guideline values on aesthetic or health criteria. Health drinking water guideline values were exceeded for 4 elements: aluminium, iodide and nickel in one sample each; manganese in a further three samples. Approximately two-thirds of samples contained iron concentrations which exceeded the aesthetic guideline value.

Hydrochemical and environmental isotopic data acquired at the same time enable the contamination documented to be understood in the context of the hydrological processes taking place in the Piccadilly Valley. Tritium data suggests that groundwater recharge and groundwater movement occurs primarily via preferential flow paths and that the maximum residence time for Piccadilly Valley Groundwaters is of the order of 50 years. Recharge appears to be generally greatest around the margins of the Piccadilly Valley, with the exception of the northern margin.

Consideration of chemically distinguishable water types indicate that the recharge waters evolve from a relatively simple composition/facies-type (Na-Cl) to more complex compositions (eg Na-Mg-Cl-HCO_3) as dissolution of minerals takes place along the flow paths. Deuterium, oxygen-18 and chlorine-36 isotope data confirm that mixing is the dominant process. They also suggest the possibility that the groundwaters contain paleowaters which have been mixed with modern recharge waters, although this remains conjectural at present.

Anthropogenic contamination was directly correlated with tritium concentration, and hence aquifer recharge. Rural residential development is occurring preferentially on the higher elevations around the margins of the Piccadilly Valley, thus coinciding with those areas of greatest recharge which appear to be most vulnerable to groundwater contamination from leaking septic tanks and other sources. The recommendations arising from this investigation emphasize the need not only to benchmark and monitor groundwater quality but also the concomitant need to understand the influences of natural hydrogeolgical and geochemical processes, especially recharge, in order to protect groundwater resources from anthropogenic contamination arising from various land use and management regimes.

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1.0 INTRODUCTION

Groundwater is an important resource in rural and urban Australia where increasingly it is extracted for drinking, industrial and agricultural purposes. About 20% of the nation's total water requirements are presently met by groundwater (DPIE 1987), though this proportion may be as high as 50-100% in large areas of inland, arid-zone Australia or transiently higher in areas subject to extended drought conditions.

Consequently, the quality of the nation's groundwater resources is of growing concern to water managers in all States. Groundwater quality (ie, its acceptability as judged by domestic, industrial, agricultural or environmental criteria) is determined by both natural processes and human activities. Even contaminant-free groundwater may be unusable as a consequence of toxic levels of naturally occurring components such as cadmium, fluoride or arsenic. Historically, in Australia, resource assessment has dominated groundwater investigations and groundwater quality has been synonymous with salinity and its relationship to irrigation-induced land salinisation. However, during the past decade groundwater quality has increasingly come to be assessed by additional factors such as nutrient, toxic chemical and microbiological loads, concomitant with increasing awareness of the vulnerability of groundwater resources to contamination.

Knowledge of the present status of groundwater quality and its improvement or degradation with time, together with a clear understanding of the determinative biogeochemical processes and hydrogeological framework, are essential prerequisites to managing one of our nation's essential natural resources. There is, however, a disquieting lack of information about the quality of Australia's groundwater resources. For example, the application of agrochemicals (eg insecticides, herbicides, fungicides and fertilisers) continues to be extensive and widespread in areas of irrigated agricultural production throughout the nation. Groundwater resources underlying these areas are commonly exploited for domestic and town water supplies, as well as for irrigation, and/or pumped to adjacent surface waters for disposal. The impact of these human activities on Australia's groundwater resources is essentially unknown yet potentially of far-reaching health, environmental and economic significance to resource management.

It was in response to this situation that AGSO (then the BMR) commenced investigations in 1990 which evolved into the Australian Groundwater Quality Assessment Project. Reconnaissance studies were carried out in four States (New South Wales, Queensland, South Australia, and Victoria) in cooperation with the relevant State water management agencies during the period 1990-1992 (Bauld, 1994).

Following these reconnaissance studies AGSO received support through the Prime Minister's 1992 Statement on the Environment. Funds were provided during 1993-1996 for AGSO to assess groundwater quality "in key areas of national priority".

Such areas were identified in consultation with State water resource management agencies and their groundwater quality assessed through baseline measurements conducted by AGSO and the State agencies.

Between July 1993 and June 1996 groundwater samples were acquired from 553 bores in nine catchments during 15 field operations around the country. Three of the nine catchments and 39% of the groundwater samples acquired were from within the Murray-Darling Basin. The aquifers within the catchments investigated were generally both shallow and associated with irrigated agricultural production (Bauld, 1996). All States and the Northern Territory were represented, with the exception of the ACT.

During discussions with staff from Primary Industries and Resources, South Australia and the Department of Environment and Natural Resources, the Mount Lofty Ranges Catchment near Adelaide was identified as an area significantly lacking in groundwater quality information. Within this large area, the Piccadilly Valley region of the Onkaparinga Catchment was recommended as having the highest priority. The Piccadilly Valley is presently subject to significant development pressure as the greater Adelaide urban area expands into the Mount Lofty Ranges. Intermingled with the rural residential developments in the Piccadilly Valley, are intensive agricultural industries such as market gardens, orchards and viticulture, together with increasing extraction of groundwater for bottled mineral waters. This report deals specifically with groundwater quality in the Piccadilly Valley, as determined from sampling 42 bores in the Piccadilly Valley during April and May 1994.

The objectives of Project activities in the fractured rock aquifers of the Piccadilly Valley Catchment, as in other field areas, was to establish comprehensive benchmark groundwater quality conditions for subsequent monitoring, to identify and understand processes impacting on groundwater quality in the aquifers, and to integrate information obtained and provide advice to the responsible natural resource managers.

2.0 PHYSICAL CHARACTERISTICS OF THE PICCADILLY VALLEY

2.1 LOCATION, PHYSIOGRAPHY AND CLIMATE

The Piccadilly Valley is located approximately 10 km to the southeast of Adelaide, South Australia and lies within the Adelaide metropolitan water supply catchment of Onkaparinga in the Mount Lofty Ranges. The surrounding land use is characterised by highly productive irrigated horticulture, grazing and urban expansion. The underlying fractured rock aquifers provide a source of water for domestic and irrigation purposes, as well as for bottling by spring water companies. Prior to this study, little information was available on the groundwater quality of the Piccadilly Valley, other than a nitrate study which indicated a few elevated nitrate concentrations (Harvey, 1979).

The study area, comprising the Piccadilly Valley and adjacent areas, occupies an area of approximately 16 km^2 (Fig 2.1). The Piccadilly Valley is bounded by the upper-reaches of the Cox Creek Catchment, which lies within the greater Onkaparinga Catchment. The northern boundary of the Piccadilly Valley extends from approximately 2 km west of the town of Summertown to Uraidla in the northeast of the study area. The valley continues in a southwesterly direction from Uraidla towards the towns of Piccadilly and Crafers. The western extent of the Piccadilly Valley is bounded by Mt Lofty and Mt Bonython and the eastern extent by smaller ridges. The elevation ranges from 700m at Mt Lofty to 420m at the catchment exit. Cox Creek and several of its tributaries flow through the valley. The soils are closely related to the geology and are classified as podzols with a loamy texture overlying clay subsoils.

The climate is Mediterranean, with cool wet winters and warm dry summers. The mean annual rainfall is 1100 mm, which predominantly falls during the winter months from May to September. Thunderstorms with high rainfall intensities frequently occur in spring and early summer and lead to significant runoff events at the beginning of the growing seasons when the plant roots and canopy have not developed sufficiently to protect soil surfaces (Thoma, 1988).

2.2 GEOLOGY AND HYDROGEOLOGY

The stratigraphic and tectonic history of the Mount Lofty Ranges is complex; a detailed account may be found in Preiss (1987). Little published information exists on the hydrogeology of the Piccadilly Valley. A basic introduction to the geology (which

is currently undergoing revision) and hydrogeology of the Piccadilly Valley are discussed in Wake-Dyster (1974) and Edwards (1980) and is summarised below.

The predominant rock units of hydrogeological importance in the Piccadilly Valley are the slates (Woolshed Flat Shale) and sandstones (Aldgate Sandstone) of the Proterozoic, Adelaidean System (Torrensian Series) on the western side of the northeaserly striking Crafers Fault (Fig 2.2). The sandstones and slates have been folded into a southwest plunging anticline which rests unconformably on basement schists and gneisses (Barossa Complex). This major structure produces general north-south strikes and moderate easterly dips, but numerous local variations of these trends exist. The Barossa Complex outcrops on the eastern side of the Crafers Fault. In the southwest corner of the study area, the Torrensian rocks form a minor anticline plunging southwest. Quartzites (Stonyfell Quartzite) overlie the slates and sandstones towards Mt Lofty and Mt Bonython. The lack of geological logs for existing bores makes it difficult to establish an accurate three-dimensional perspective of the geological/hydrogeological setting; a schematic cross-section is presented in Figure 2.3 (after Forbes, 1980).

The characteristics of the aquifer formations in the study area are discussed below. The flow and storage of water within these rock units primarily occurs within the fracture system. The fractures represent avenues of high permeability within an otherwise relatively low-permeability matrix.

Barossa Complex: This formation is composed of micaceous schist and granitic gneiss. These rocks are high-grade metamorphic sediments of Archaean (Lower Proterozoic) age and comprise some of the oldest rocks in the Mt Lofty Ranges. In the Piccadilly Valley area the Barossa Complex forms the core of the ranges over which all other rocks are draped. This formation is a poor aquifer. The fine grain-size and rapid decomposition of some schistic rock minerals are factors which considerably reduce permeability in the weathered zone, and due to mineral dissolution, may lead to some deterioration in the quality of the water.

Aldgate Sandstone: This formation is characterised by alternating medium to coarse grained sandstones, quartzite and sandy slates. In some areas the Aldgate Sandstone is deeply weathered and kaolinized, and is associated with remnant ferricrete (ironstone) (Maschmedt, 1993). The Aldgate Sandstone generally conforms in strike and dip with the major anticlinal structure, and lies at the base of the Torrensian Series of the Adelaide System (Upper Proterozoic). The Aldgate Sandstone has a primary permeability which is of less importance than the secondary joint system for water storage. Moderate supplies of good quality water are obtained from these rocks. This aquifer is considered to be the best in the area and is extensively used for irrigation purposes.

Woolshed Flat Shale: This formation is characterised by siltstone, slates and phyllite with some dolomitic lenses. The Woolshed Flat Shale generally conforms in strike and dip with the major anticlinal structure and overlies the Aldgate Sandstone in the Torrensian Series. The storage capacity of this formation is mainly a function of cleavage and joint development as the general permeability of the rocks are low. Although the siltstones, phyllites and slates tend to be relatively impervious, their

generally fissile nature permits the entry of water along cleavage planes and results in storage of limited groundwater supplies. Due to the incompetent nature of these rocks, joint systems have developed in those areas which have been subjected to major stresses. The fine grain-size and ready decomposition of slate minerals to clays are factors which considerably reduce permeability in the weathered zone and may lead to some deterioration in the quality of the water.

Stoneyfell Quartzite: This formation is predominantly characterised by quartzite with some minor sandstone and siltstone beds. The Stonyfell Quartzite lies above the Woolshed Flat Shale in the Torrensian Series and is the youngest formation in the study area. The Woolshed Flat Shale-Stoneyfell Quartzite transition is a coarsening-upward sequence that may represent deltaic progradation eastwards into a marine basin (Preiss, 1987; p. 107). Quartzite, being more resistant to erosion than most rock-types, outcrops along the ridges, while the softer sandstone and slates underlie the areas of lower topographic relief in the Piccadilly Valley. The competent nature of quartzites leads to pronounced fracturing under stress. The coarser grain-size and more stable mineral assemblage minimises the aquifer sealing to which the slates and schists are prone, and the high permeability of well-jointed quartzites produces a significant groundwater storage.

Edwards (1980) delineated the configuration of the groundwater potentiometric surface and flow directions using water levels obtained from eighteen wells at the end of the irrigation season during the period April to May 1979 (Fig 2.4, after Edwards 1980). Groundwater recharge occurs in the surrounding hills and moves from the edges of the valley towards the topographically lower, central area where it discharges into Cox Creek (Fig 2.4). Cox Creek is a perennial stream (although it was nearly dry during our sampling in April-May 1994) and receives base flow from groundwater discharging from the aquifers in the catchment, although some of the tritium data obtained from this study suggests that Cox Creek also recharges the groundwater system in some areas. The proportions of recharge from the aquifers to the Cox Creek as base flow are not well understood as there is little detailed information on the potentiometric configuration, transmissivities and storage coefficients of the aquifers and their hydraulic connection to the creek (Ramamurthy, 1983).

Water levels were not obtained from the bores sampled in this study since their headworks precluded such measurements. The wells in the area surveyed were overgrown with blackberries and weeds and thus waterlevels could not obtained from them. Historical potentiometric data suggests that the aquifer systems are unconfined through to semi-confined.

The isotopic and hydrochemical data collected in this study proved to be invaluable in evaluating the hydrogeological processes occurring within the Piccadilly Valley and are discussed in Chapters 4 and 5 of this report.

2.3 LAND AND WATER USE

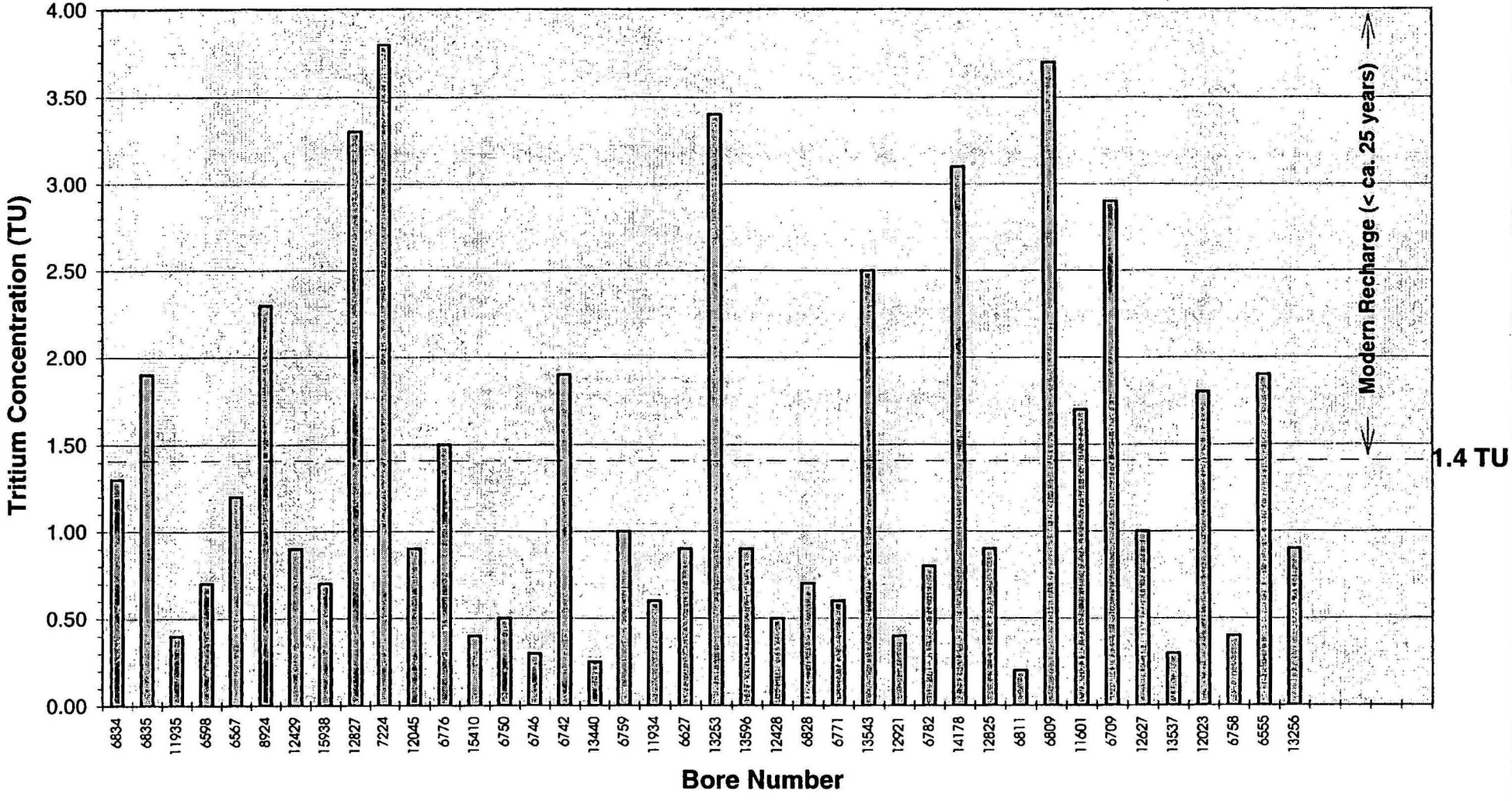
The main land uses in the Piccadilly Valley are market gardens, orchards, viticulture, grazing pastures and residential developments, many of which use septic tanks (Figure 2.5; *N.B.* The digital data of this 1994 land use coverage has been enlarged beyond the data capture scale of 1:50,000 to a scale of 1:40,000. This figure should be used as a general guide to the land uses in the area and is not definitive.).

Land use is presently undergoing considerable change in the Piccadilly Valley. The townships of Crafers, Uraidla, Summertown and Piccadilly are expanding due to their close proximity to Adelaide. Several land uses, in particular market gardens and orchards, are declining. The underlying economic factors, such as high land prices, small properties, a build up of plant disease and little opportunity for expansion are forcing the farming community to diversify into higher return crops such as viticulture or shift entirely to areas with lower land values (Thoma, 1988).

The groundwater resources in the Piccadilly Valley are extracted for irrigated agriculture, domestic purposes and bottled mineral water. The land uses tends to reflect the geology and associated groundwater yields. Market gardens tend to be located on Aldgate sandstone where the groundwater yields are high. Orchards are generally located in areas with lower groundwater yields such as on hillslopes. In areas with poor groundwater yields e.g., areas overlying the Barossa Complex, surface water is collected in large dams and the land is predominantly used for grazing; the dam water is used to supply beef cattle and other livestock with drinking water.

Native vegetation, not cleared for pasture or other land uses, survives either in reserves or in areas which have no other economic purpose. Thus native vegetation tends to be located in rugged terrains or on hill tops to prevent severe erosion of the soils.

Fig 4.1 Piccadilly Valley April-May 1994: Tritium Concentrations in Groundwater



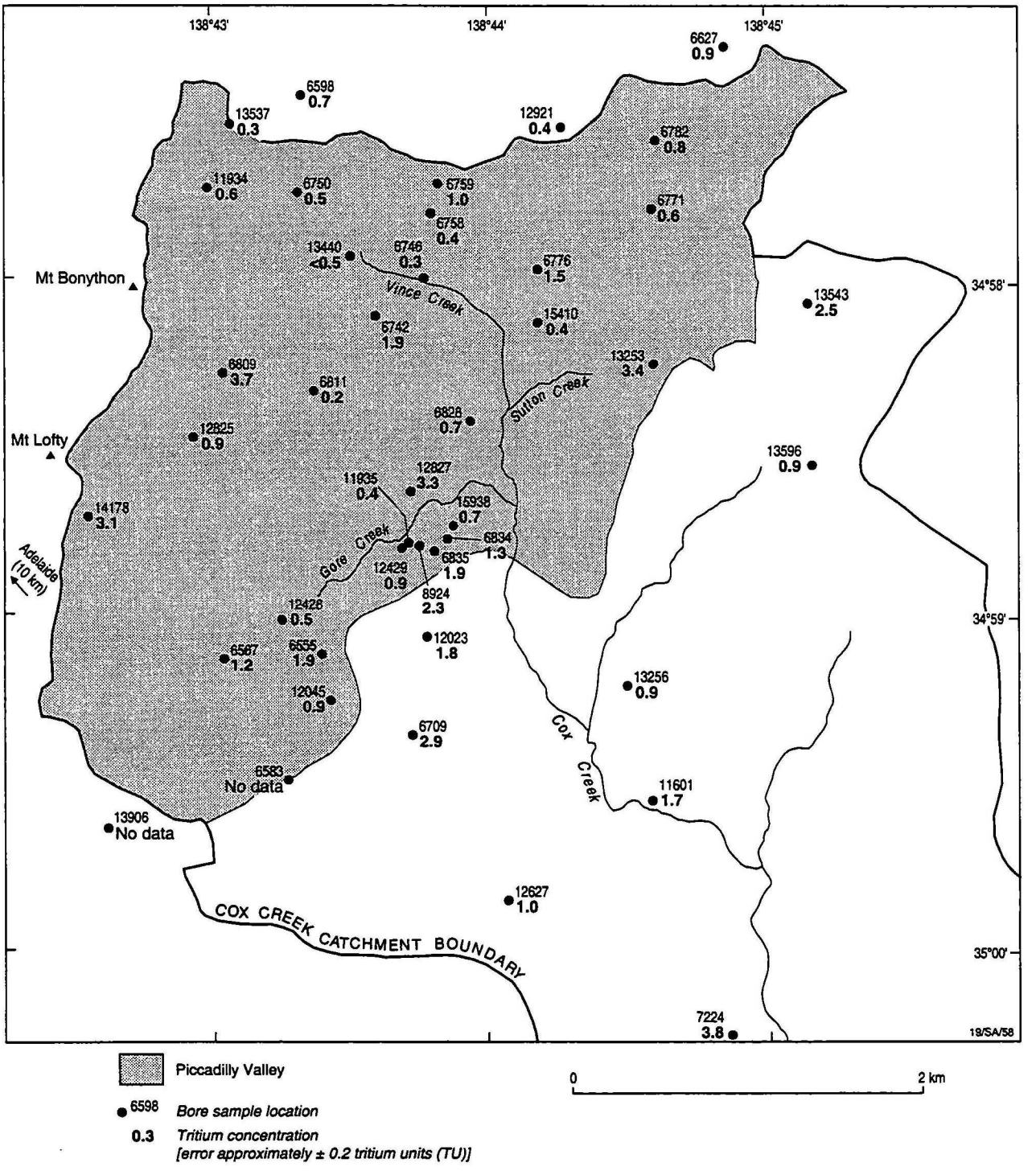


Figure 4.2 Plan view of tritium concentrations in Piccadilly Valley Groundwaters

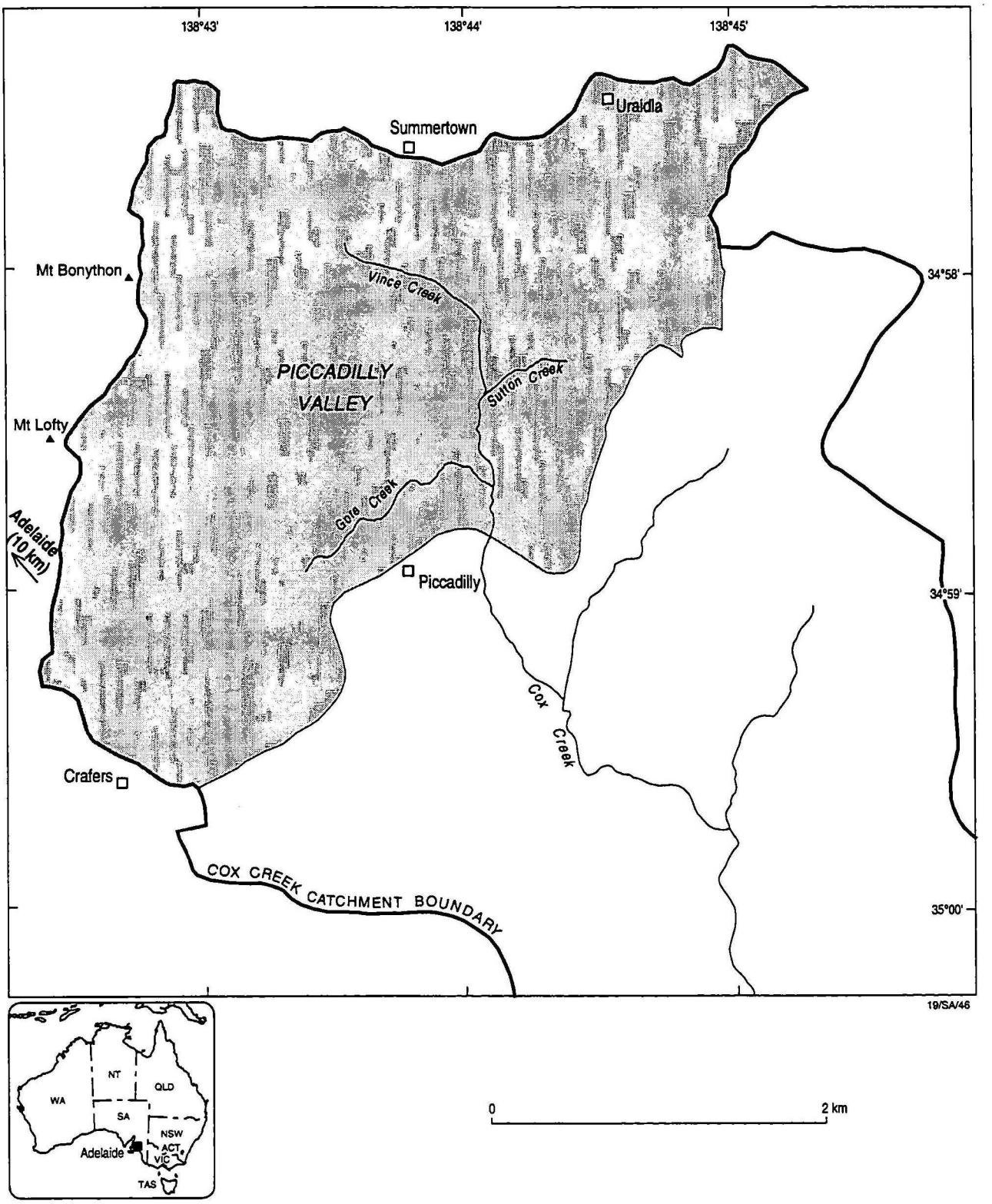


Figure 2.1 Location of the Piccadilly Valley study area

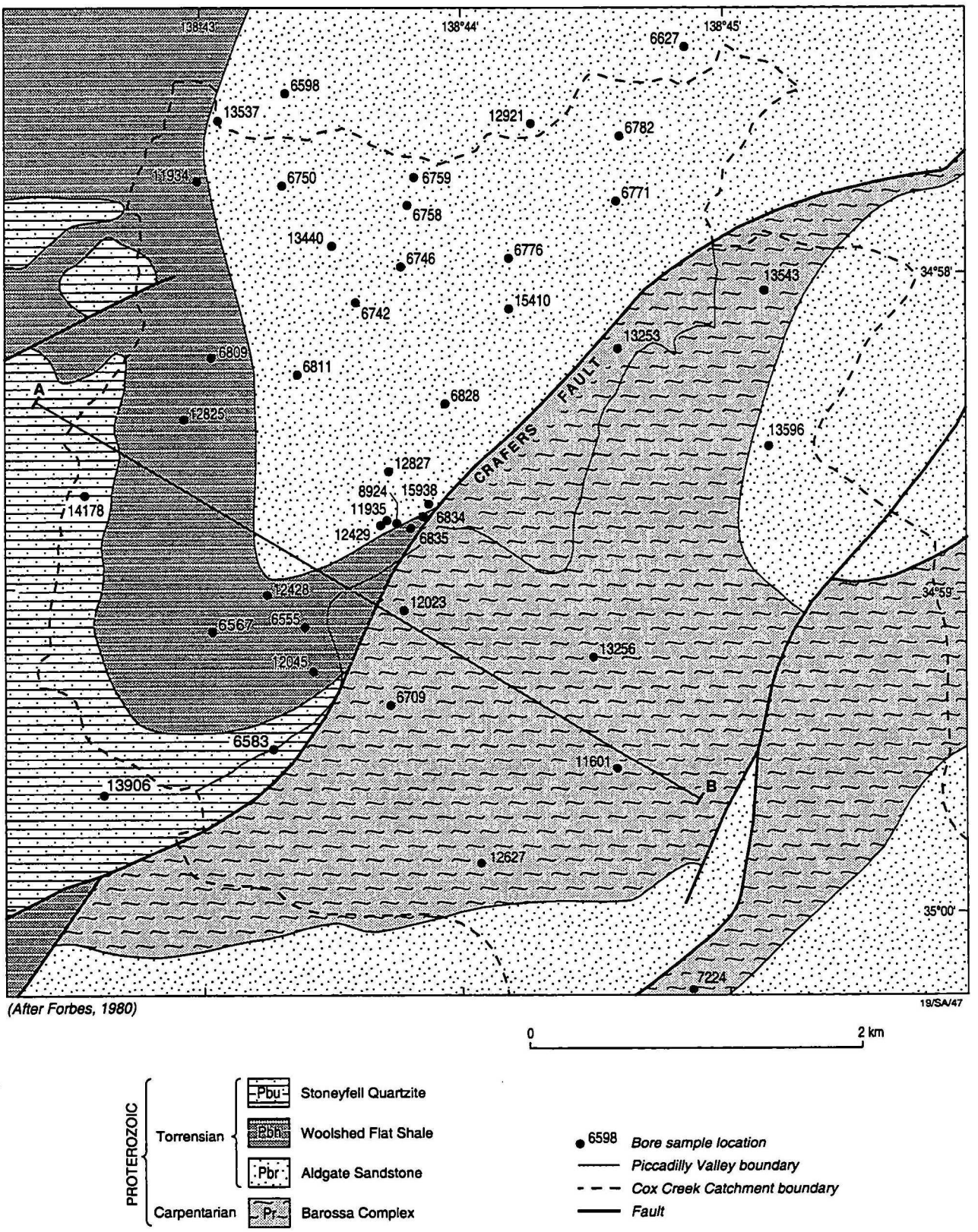


Figure 2.2 Geology of the Piccadilly Valley

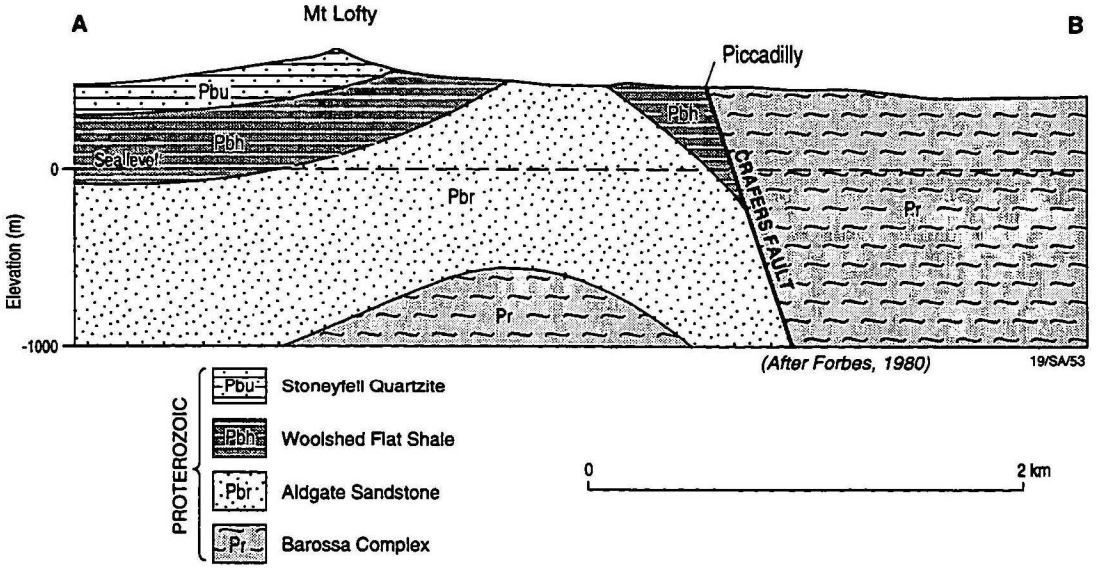


Fig 2.3 Schematic geological cross-section of the Piccadilly Valley

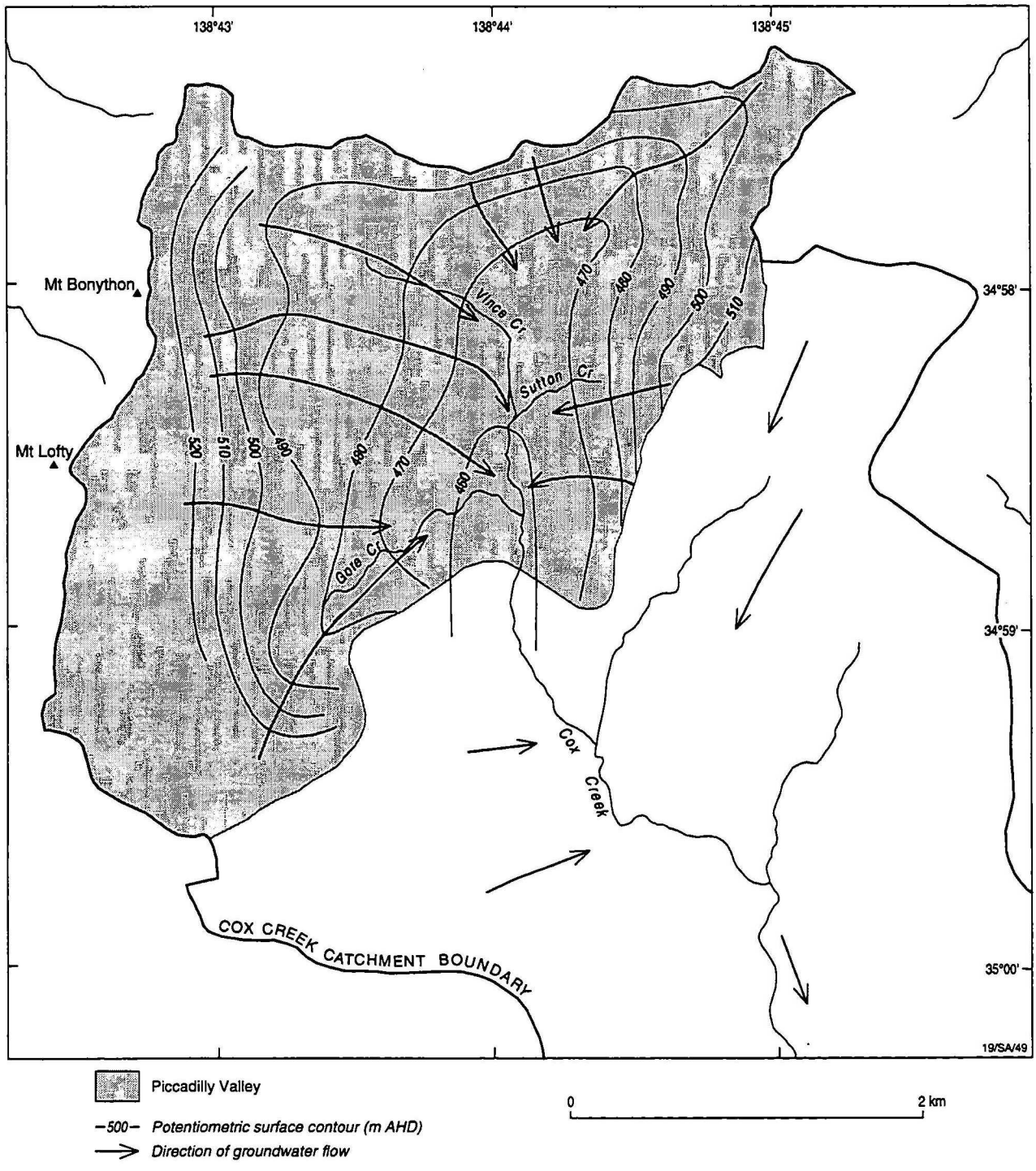
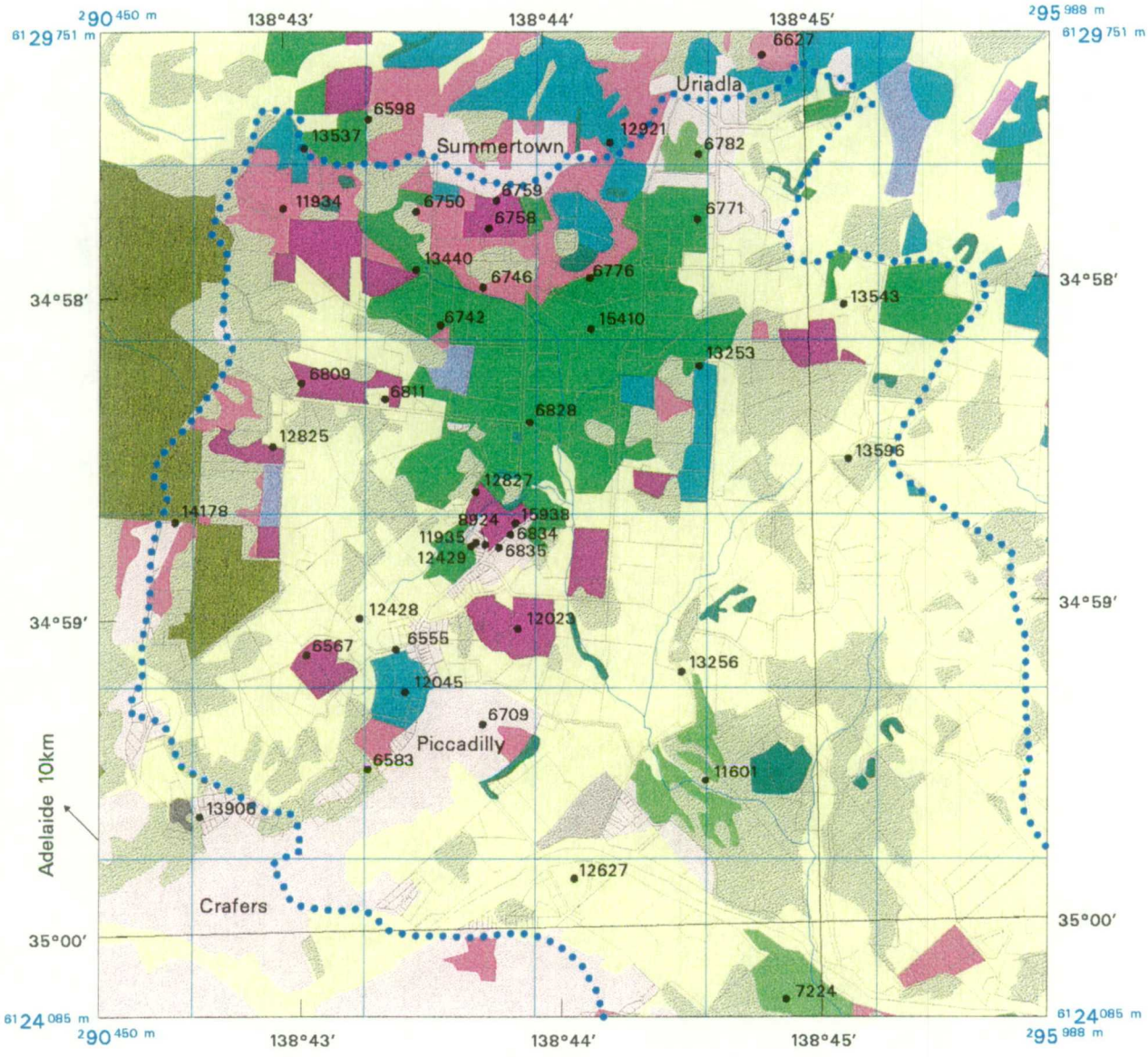


Figure 2.4 Potentiometric surface and flow directions in the Piccadilly Valley (after Edwards, 1980)

Fig. 2.5 Regional Land Use of the Piccadilly Valley, South Australia



SCALE 1:40 000

1 0 1 2 Kilometres

UNIVERSAL TRANSVERSE MERCATOR PROJECTION
LATITUDE OF ORIGIN: 0°, LONGITUDE OF ORIGIN: 141°
AUSTRALIAN GEODETIC DATUM 1966

- Berry
- Flori/Berry/Horticulture
- Grazing
- Horse
- Intensive Vegetables
- Mine/Quarry
- Native Vegetation
- National Parks & Wildlife Service
- Orchards
- Plantation Forest
- Recreational
- Rural Living
- Urban
- Vineyards
- 6709 Bore Location
- Cox Creek Catchment

Compiled by: K. Ivkovic, AGSO
Cartography by: R.S. Hill, AGSO

Digital Landuse Data supplied by:
Department of Primary Industries, South Australia (PISA)

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3.0 SAMPLING STRATEGY AND DATA MANAGEMENT

In April and May 1994 the Australian Geological Survey Organisation (AGSO) sampled 42 bores in the Piccadilly Valley (Figure 3.1; Table 3.1). The bores sampled were private bores which were fitted with either turbine or submersible pumps. The selection of bores was based on landowner co-operation with the aim of obtaining spatial coverage representing the different geological types (Fig 2.2), land uses (Fig 2.5 and Table 3.1) and bore depths (Table 5.1) in the study area. The bores were primarily constructed with a slotted casing, but in a few instances were open hole bores. A summary of the bore records obtained from the Department of Mines and Energy, SA is provided in Appendix B.

Groundwater samples were analysed for physical characteristics, major and minor inorganic chemical constituents, some stable and radioactive isotopes, nutrients, pesticides, faecal indicator bacteria and other microbes. The raw and manipulated data from this report are contained in ®EXCEL tables, which are contained on diskette in the back pocket of this report (see also Appendix A).

A minimum of three casing volumes of water were pumped from each bore and samples were collected after field readings had stabilised. All samples, with exception of those obtained for isotope analysis, were filtered with a 0.45µm filter. Samples obtained for cation, nutrient, trace metals, iodide and chlorine-36 analysis were acidified to a pH <2. Chlorine-36 samples were filtered with a GF/C filter prior to acidification; the chloride was then precipitated with silver nitrate in the field and the bottle (without an air gap) sealed with wax for later analysis. Samples obtained for deuterium and oxygen -18 isotopes were collected in McCartney bottles to which a few grains of mercuric chloride were added; the bottles were completely filled (without an air gap) and sealed with tape. Samples obtained for microbiological analysis were analysed immediately by AGSO technical staff at a microbiological laboratory belonging to the CSIRO Division of Land and Water Resources in Adelaide. Samples obtained for pesticide extraction were processed in the field. Samples collected for nutrient analysis were frozen and all other sample bottles were kept under ambient temperatures until they were sent to laboratories for analysis.

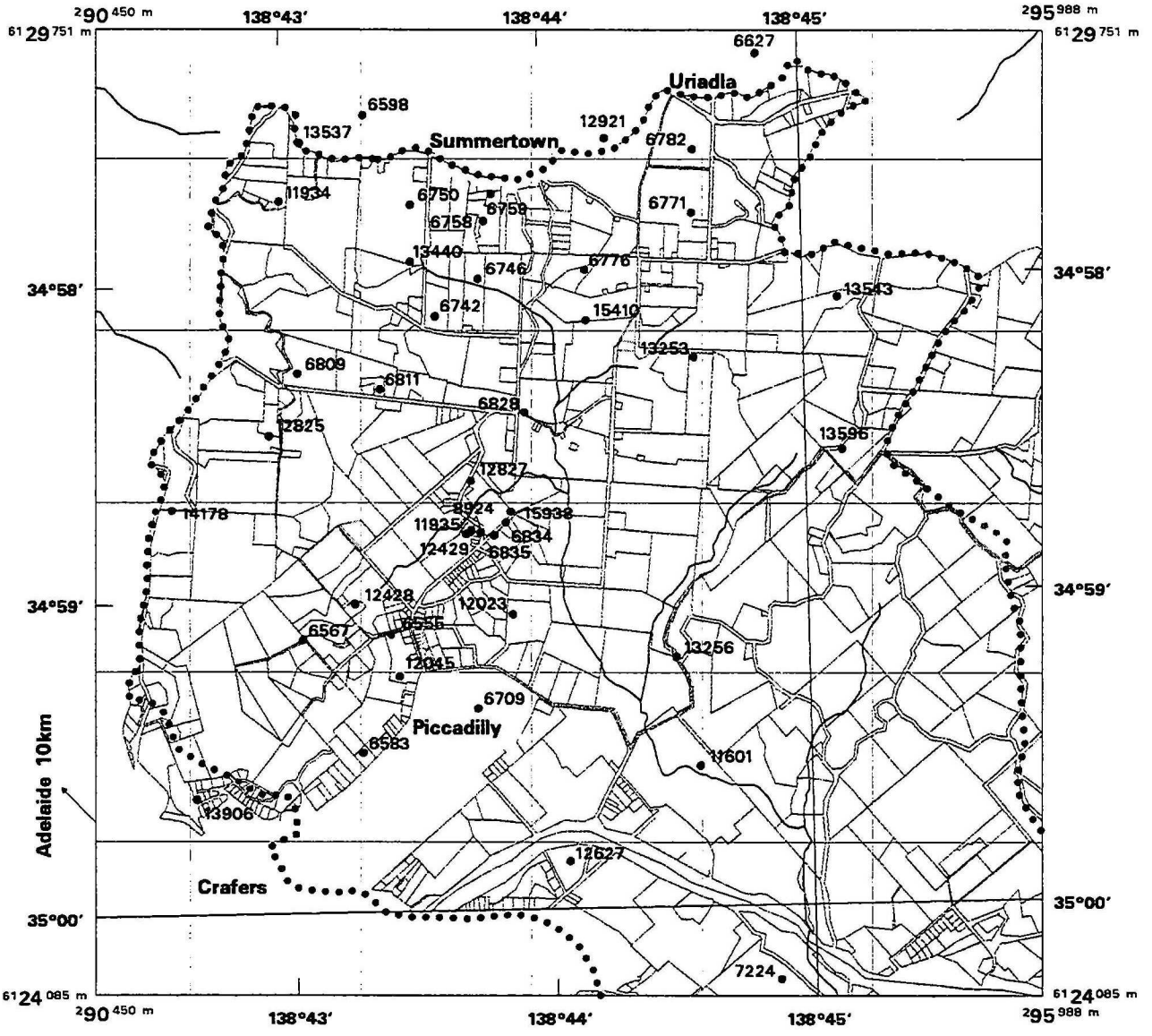
Duplicate samples were obtained for a minimum of every fifteenth sample in order to assess the reproducibility of the data. The average value of the duplicates were used for data interpretation. Duplicate results are typically compared as relative percent difference and are discussed in Appendix C.

Spiked samples were included in order to assess the accuracy of the data. A spiked sample is a sample in which the compound being analysed is actually added (or spiked) into the sample to determine the accuracy of the analytical system. The results of a spike are expressed in terms of the percent recovery with regard to the amount added and are also discussed in Appendix C.

Table 3.1: Piccadilly Valley Bore Location and Land Use Data

10:000 Mapsheet	Bore Number	Latitude	Longitude	Latitude (Decimal Degrees)	Longitude (Decimal Degrees)	Landuse
6628-48	6555	34 59.111	138 43.389	34.98518	138.72315	Orchard, Spring water , adjacent grazing
6628-48	6567	34 59.122	138 43.047	34.98537	138.71745	Botanic garden
6628-48	6583	34 59.483	138 43.271	34.99138	138.72118	Domestic garden, residential, adjacent native vegetation
6628-48	6598	34 57.470	138 43.323	34.95783	138.72205	Market garden
6628-48	6627	34 57.329	138 44.840	34.95500	138.74733	Orchard, residential
6628-48	6709	34 59.351	138 43.718	34.98918	138.72863	Domestic, residential
6628-48	6742	34 57.993	138 43.752	34.96655	138.72920	Market garden
6628-48	6746	34 58.107	138 43.585	34.96845	138.72642	Market garden
6628-48	6750	34 57.755	138 43.314	34.96258	138.72190	Market garden
6628-48	6758	34 57.812	138 43.779	34.96353	138.72965	Viticulture, garden, residential
6628-48	6759	34 57.726	138 43.811	34.96210	138.73018	Domestic, residential
6628-48	6771	34 57.799	138 44.582	34.96332	138.74303	Market garden, water supply for Uraidla
6628-48	6776	34 57.972	138 44.165	34.96620	138.73608	Market garden, adjacent orchard
6628-48	6782	34 57.599	138 44.591	34.95998	138.74318	Uriadla P.S., adjacent toilets
6628-48	6809	34 58.278	138 43.049	34.97130	138.71748	Viticulture, domestic, adjacent native vegetation
6628-48	6811	34 58.332	138 43.366	34.97220	138.72277	Nursury, adjacent grazng, viticulture and native vegetation
6628-48	6828	34 58.414	138 43.922	34.97357	138.73203	Market garden
6628-48	6834	34 58.761	138 43.840	34.97935	138.73067	Flowers,domestic,residential
6628-48	6835	34 58.801	138 43.794	34.98002	138.72990	Domestic, residential, paddock
6627-03	7224	35 00.238	138 44.862	35.00397	138.74770	Arbury Park Outdoor School
6628-48	8924	34 58.791	138 43.741	34.97985	138.72902	Residential area; adjacent market gardens
6628-48	11601	34 59.545	138 44.571	34.99242	138.74285	Golf course, domestic
6628-48	11934	34 57.736	138 42.992	34.96227	138.71653	Domestic, residential
6628-48	11935	34 58.783	138 43.705	34.97972	138.72842	Residential area; adjacent market gardens
6628-48	12023	34 59.054	138 43.487	34.98423	138.72500	Viticulture
6628-48	12045	34 59.244	138 43.420	34.98740	138.72367	Domestic
6628-48	12428	34 59.011	138 43.252	34.98352	138.72087	Domestic,horses/grazing
6628-48	12429	34 58.794	138 43.686	34.97990	138.72810	Residential area; adjacent market gardens
6628-48	12627	34 59.845	138 44.059	34.99742	138.73432	Domestic garden
6628-48	12825	34 58.472	138 42.935	34.97453	138.71558	Viticulture, domestic
6628-48	12827	34 58.624	138 43.708	34.97707	138.72847	Viticulture
6628-48	12921	34 57.558	138 44.251	34.95930	138.73752	Orchards, market Gardens, residential
6628-48	13253	34 58.253	138 44.578	34.97088	138.74297	Orchards, adjacent grazing
6628-48	13256	34 59.200	138 44.487	34.98667	138.74145	Domestic, adjacent golf course and native vegetation
6628-48	13440	34 57.934	138 43.495	34.96557	138.72492	Viticulture
6628-48	13537	34 57.553	138 43.075	34.95922	138.71792	Market gardens, orchard, flowers, strawberries and domestic
6628-48	13543	34 58.071	138 45.136	34.96785	138.75227	Viticulture
6628-48	13596	34 58.549	138 45.142	34.97582	138.75237	Protea, domestic, adjacent grazing and native vegetation
6628-48	13906	34 59.626	138 42.627	34.99377	138.71045	Domestic, residential adjacent native vegetation
6628-48	14178	34 58.701	138 42.556	34.97835	138.70927	Domestic, private gardens, residential
6628-48	15410	34 58.130	138 44.165	34.96883	138.73608	Market gardens
6628-48	15938	34 58.727	138 43.860	34.97878	138.73100	Viticulture, grazing

Fig. 3.1 Bore Sample Locations in the Piccadilly Valley, South Australia



SCALE 1:40 000

1 0 1 2 Kilometres

UNIVERSAL TRANSVERSE MERCATOR PROJECTION
LATITUDE OF ORIGIN: 0°, LONGITUDE OF ORIGIN: 141°
AUSTRALIAN GEODETIC DATUM 1966

6709 Bore Location

Crafers Urban locality

River, Stream

Cox Creek Catchment

Road

Compiled by: K. Ivkovic, AGSO
Cartography by: R.S. Hill, AGSO

Digital Landuse Data supplied by:
Department of Primary Industries, South Australia (PISA)

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4.0 ENVIRONMENTAL ISOTOPES

Environmental isotopes occur naturally in the hydrological cycle (Lloyd and Heathcote, 1985). They are suited to providing information on the type, origin and age of water, as well as some of the processes which may be operative. Their usefulness is maximised by correlating isotope data with other hydrogeological and hydrochemical data, as well as by using multiple isotopes.

The environmental isotopes used for this investigation were tritium, deuterium, oxygen-18 and chlorine-36.

4.1 TRITIUM

Tritium (^3H) is a radioactive isotope of hydrogen and has a half-life of 12.43 years. It is measured in Tritium Units (TU), where one TU is equivalent to one atom of ^3H in 10^{18} atoms of hydrogen. Tritium is naturally produced in the atmosphere by cosmic ray bombardment of nitrogen and oxygen. The tritium atoms are oxidised to form water and become mixed with precipitation which may then enter groundwater via recharge (Mazor, 1991).

During 1952 - 1963, tritium concentrations in precipitation increased by up to three orders of magnitude over natural levels as a result of the nuclear weapons testing. Peak tritium levels, or 'bomb pulses', mark the occurrence of particular events such as the 1962-63 atmospheric tests. International agreement in the 1960's put a voluntary moratorium on atmospheric testing of nuclear weapons and the radioactive decay of bomb tritium has since been declining towards its natural background levels. The application of tritium as an environmental isotope in the southern hemisphere is becoming less useful as the bomb pulse tritium levels are falling to the pre-1952 level (between 4 to 10 TU) in Australian precipitation. Southern hemisphere peaks ranged from 50 to 100 TU whereas the northern hemisphere peaks were 500 to 10,000 TU. As a result the application of tritium as an environmental tracer in the northern hemisphere will be useful into the 2030's (Calf, 1988).

4.1.1 Tritium and Groundwater Dating

When anthropogenic tritium was detected, it was hoped that the specific tritium 'pulses' contributed by the individual tests would provide a means of accurate dating of groundwater. However, it turned out that the input values in precipitation varied considerably from one location to another, and during the seasons and years within each location. In addition, complicated mixing takes place in each aquifer, and the mode and extent of mixing of each year's recharge with that of previous years'

recharge is unknown. Tritium concentrations in precipitation are affected by latitude, distance from the ocean and the season, and these factors must be taken into consideration when determining a realistic tritium input. Hence, age determinations accurate to the year are impossible with groundwater studies. However, semi-quantitative dating is possible and can be very informative (Mazor, 1991).

Calf (1988) determined a semi-quantitative rule for dating Australian groundwaters. Table 4.1 (after Calf, 1988) gives an interpretation of the age of the groundwater based on its tritium activity. The tritium activity values in the table have been altered from Calf's original report and recalculated to account for tritium decay during 1988 to 1994, when the samples from this study were obtained.

Table 4.1: ***Interpretation of Tritium Activity in Australian Groundwaters***
(Mixing within aquifers is assumed to be negligible; adapted from Calf, 1988)

Activity (TU)	Interpretation
Less than 0.2	Water is older than approximately 50 years
Less than 1.4	Water is older than approximately 25 years
Between 1.4 and 7.2	Interpretation is difficult; water is probably modern
Between 7.2 and 14.3	Water is approximately 15 to 25 years old
More than 14.3	Water is probably related to water from peak fall-out period 1960-64

The yearly 1986 weighted mean for tritium in Adelaide rainfall was 5.8 TU (Calf, 1988). If this value is used to calculate tritium decay from 1986 to 1994 (8 years) then 1994 Adelaide rainfall would contain a tritium activity of about 4 TU, which is about the estimated pre-1952 level.

Tritium concentrations (Table 4.2 and Fig 4.1) for Piccadilly Valley groundwater samples ranged from <0.5 to 3.8 TU with a median value of 0.9 TU suggesting that the groundwaters in the Piccadilly Valley contain both modern (less than 25 years old) and older waters, as indicated in Table 4.1 above. About one third (15/40) of the bores were considered to contain measurable quantities of modern water as they had tritium concentrations greater than 1.4 TU. Tritium was not detectable in one bore (13440), which may indicate the water from this bore is older than 50 years. A further seven bores (11935, 15410, 6746, 12921, 6811, 13537 and 6758) had tritium concentrations around 0.2 TU (between 0.2 to 0.4 +/- 0.2 TU), which could potentially make the water from these bores older than approximately 50 years. The remaining bores had tritium concentrations between 1.4 and 0.2 TU and assuming that the mixing of waters is negligible, contain water probably between 25 and 50 years old.

It is important to consider that the intermixing of old (containing no or low tritium) waters with recent (higher tritium) waters will give rise to an intermediate tritium activity that does not reflect the semi-quantitative ages indicated in Table 4.1. The mixing of older and younger waters could occur through modern groundwater recharge to older groundwaters by the infiltration of rain and/or surface waters and/or through the mixing of high and low tritium waters from interconnected fractures and different fractures within an open-hole section, below the casing, of a bore during pumping.

Table 4.2 Piccadilly Valley: April-May 1994 Groundwater Tritium Concentrations

Bore Number	Tritium Units
6834	1.3 +/- 0.2
6835	1.9 +/- 0.2
11935	0.4 +/- 0.2
6598	0.7 +/- 0.2
6567	1.2 +/- 0.2
8924	2.3 +/- 0.2
12429	0.9 +/- 0.2
15938	0.7 +/- 0.2
12827	3.3 +/- 0.3
7224	3.8 +/- 0.4
12045	0.9 +/- 0.2
6776	1.5 +/- 0.2
15410	0.4 +/- 0.2
6750	0.5 +/- 0.2
6746	0.3 +/- 0.2
6742	1.9 +/- 0.2
13440	<0.5
6759	1.0 +/- 0.2
11934	0.6 +/- 0.2
6627	0.9 +/- 0.2
13253	3.4 +/- 0.3
13596	0.9 +/- 0.2
12428	0.5 +/- 0.2
6828	0.7 +/- 0.2
6771	0.6 +/- 0.2
13543	2.5 +/- 0.3
12921	0.4 +/- 0.2
6782	0.8 +/- 0.2
14178	3.1 +/- 0.3
12825	0.9 +/- 0.2
6811	0.2 +/- 0.2
6809	3.7 +/- 0.4
11601	1.7 +/- 0.2
6709	2.9 +/- 0.3
12627	1.0 +/- 0.2
13537	0.3 +/- 0.2
12023	1.8 +/- 0.2
6758	0.4 +/- 0.2
6555	1.9 +/- 0.2
13256	0.9 +/- 0.2

4.1.2 Tritium and Recharge/Discharge Estimation

The tritium concentrations, plotted on a map of the study area in Fig 4.2, give an indication of where measurable quantities of recharge are occurring. These data suggest that recharge is mainly occurring on the western, eastern and southeastern margins of the Piccadilly Valley, as well as in some (but not all) of the bores in the vicinity of Cox Creek and its tributaries. Bores 12827, 7224, 13253, 14178 and 6809 had total depths ranging from 49m to 190 and each had tritium concentrations greater than 3 TU, which approaches that of recent rainfall (estimated to be about 4 TU), suggesting a rapid rate of recharge to considerable depths in these areas. The bores in the northwest of the catchment, where the Aldgate Sandstone is thought to be confined by a shale layer, had the lowest tritium values which suggests that little recharge is occurring in this area. Bores 8924, 11935 and 12429 are all within about 50 m of each other and had markedly different tritium concentrations, perhaps due to preferential flow paths and the lack of hydraulic connection between fractures.

Tritium concentrations showed no correlation with the total depth of the bore (Fig 4.3), the depth to the aquifer (as defined by the "first water cut" in the drillers logs; Appendix A) (Fig 4.4) or dissolved oxygen concentration (R^2 = 0.08) (Fig 4.5). Tritium concentrations above 1.4 TU are found in bores as deep as 200m and in aquifers (ie., first water cuts after which the casing becomes slotted) at depths of up to 70m.

Tritium concentrations were also plotted against the depth to water table (Appendix A, as determined from the drillers logs on the date the bore was drilled) in Fig 4.6. It is apparent from this figure that with the exception of bore 14178, tritium concentrations greater than 1.4 TU occur when the depth to water table is less than about 18 m. (Bore 14178, which had a depth to water table of 52 m, has a relatively thin soil thickness of about 1 m. It may be that once the water has infiltrated through the soil profile to the hard rock, water is transmitted fairly quickly through joints.)

One would expect that with a shallower water table groundwater recharge might occur more rapidly and therefore the water in these areas have greater tritium activities. Nonetheless, some of the lowest tritium concentrations were also found where the water table is shallow, such as in bores 6771, 12428, 15410 where the tritium concentrations are </= 0.6 TU, and the depths to water table less than 3 m. Although no water level data was available for bore 6811, it is recorded as being located in a creek bed in the bore records (presumably with a shallow water table) and had a tritium concentration of 0.2 +/- 0.2 TU. It is most likely that these bores with shallow water tables and low tritium concentrations are located in groundwater discharge areas.

4.1.3 Tritium Concentration and Groundwater Contamination

One would expect the potential for groundwater contamination to be higher in areas where recharge to the aquifer is greatest. The range of contaminants found in this study (discussed in greater detail in chapters 7, 8 and 9) were plotted against the tritium concentrations for each bore (Figure 4.7) in order to determine whether there was a correlation between measurable quantities of recharge, as defined by tritium concentrations greater than 1.4 TU, and groundwater contamination.

The pesticide contaminants atrazine, desethylatrazine and vinclozolin (bores 8924 and 11601) were found only in the samples with tritium concentrations greater than 1.4 TU, suggesting that these contaminants are entering the aquifer via the same flow paths as modern recharge water. The half-life of the herbicide atrazine, reported to be in the range of months to years, is consistent with this interpretation. The presence of the fungicide vinclozolin (reported half-life 1 to 32 days, depending on the application history) is also consistent with this interpretation and suggests quite recent recharge prior to our sampling. Chapter 9.0 provides detailed information on pesticides.

Despite faecal indicator bacteria (FIB) having half-lives on the order of hours to days, only three of the seven FIB-positive samples contained tritium activities greater than 1.4 TU; these three samples contained by far the greatest concentrations of FIB of all the samples. The presence of FIB in water of varying ages, including older waters, may be explained by the mixing of younger (reticulated or bore) water used for domestic purposes (e.g., septic tanks) with older groundwaters and/or through the mixing of recharge waters, carrying FIB, with older waters. Chapter 8.0 provides detailed information on microbiology.

Four of the most elevated nitrate concentrations (bores 6809, 13253, 8924 and 6742) were found in samples containing tritium concentrations greater than 1.4 TU. One might expect that water samples with tritium concentrations less than 1.4 TU would have nitrate concentrations at background concentrations; however, 7/25 bores with tritium concentrations less than 1.4 TU had nitrate concentrations above the reported background concentration of 0.25 mg/L nitrate-N. It is probable that some modern recharge is occurring which is transporting nitrate to these bores, and that mixing is occurring between tritiated and non, or low, tritiated water. Possible mechanisms by which nitrate may be transported to the aquifers are: through the application of nitrogenous fertilisers and rainfall recharge; through the application of fertilisers and irrigation recharge with bore waters of varying ages; and through septic tank leakage. Chapter 7.0 provides detailed information on nutrients.

4.2 DEUTERIUM AND OXYGEN-18

4.2.1 Background

The deuterium (^2H or D) and oxygen (^{18}O) isotopic composition of water is expressed in comparison to an internationally agreed sample of ocean water (SMOW, Standard Mean Ocean Water). The isotopic composition of water is expressed in per mil (‰) deviations from the SMOW standard. These deviations are expressed as δD for the ^2H and $\delta^{18}O$ for ^{18}O. By convention, water with less deuterium than SMOW has a negative δD, and water with more deuterium than SMOW has a positive δD. The same holds true for $\delta^{18}O$ (Mazor, 1991).

The isotopic composition (^{18}O and ^2H) of samples of natural waters collected all over the world falls on a line which yields the following equation : $\delta D = 8\delta\ ^{18}O+10$ (Craig, 1961). This line is called the Global Meteoric Water Line and has been found, with some local variations, to be valid over large parts of the world.

The meteoric line is a convenient reference line for understanding and tracing local groundwater origins and movements. In each hydrochemical investigation the local meteoric water line has to be established from samples of individual rain events, or monthly means of precipitation. The composition of precipitation is reflected, directly or modified, in the composition of groundwater. It is common practice to plot groundwater data on δD -$\delta\ ^{18}O$ diagrams, along with the meteoric line of local precipitation as a reference line, in order to determine if secondary processes have occurred, such as evaporation prior to infiltration, or isotope exchange with aquifer rocks (Mazor, 1991).

There are many interdependent physical processes which can affect the isotopic signature of water. Briefly, these are:

Evaporation: Isotopically light water molecules evaporate more readily than heavy ones. As a result water vapour is enriched in light water molecules (reflected by relatively negative δD and $\delta^{18}O$ values) and the residual water phase becomes enriched in the heavy isotopes (reflected by more positive δD and $\delta^{18}O$ values).

Rainfall intensity: The greater the amount of monthly precipitation, the more negative are the δD and $\delta^{18}O$ values.

Continental effect: The average isotopic composition of precipitation tends to have more negative values further away from the ocean coast.

Altitude effect: The $\delta^{18}O$ values in precipitation become more negative with higher altitudes, whilst the δD values are constant.

Temperature: The isotopic composition of precipitation depends on the temperature at which the oceanic water is evaporated into the air and the temperature of condensation at which clouds and rain are formed. It is difficult to separate temperature effects from altitude effects.

Seasonal effect: Isotopic concentrations change with the season. Winter precipitation is depleted in D and ^{18}O relative to summer rains.

4.2.2 Deuterium and Oxygen-18 in Piccadilly Valley Groundwaters

The δD composition of groundwaters sampled from the Piccadilly Valley (Table 4.3) ranged from -30.2 to -22.6 with a median value of -28.9. The $\delta^{18}O$ ranged from -6.22 to -4.48 with a median value of -5.62. These data are plotted on a map of the study area (Fig 4.8) and on a δD -δ ^{18}O diagram (Fig 4.9). Figure 4.9 indicates that the Piccadilly Valley Groundwaters are isotopically lighter (more negative) than those values which would plot on the Global Meteoric Water Line.

In Fig 4.10 the δD and $\delta^{18}O$ isotopic compositions of the groundwater are plotted along with those of rainwater samples collected during the period 1978 to 1981 by Hughes and Allison (1984) at the Adelaide airport (altitude <10 m AHD; mean annual rainfall 451mm) and at Chain of Ponds in the Adelaide Hills (approximately 15km to the NNE of the Piccadilly Valley; altitude 310 m AHD; mean annual rainfall 859.4 mm). It is evident in Figure 4.10 that the isotopic compositions of the Piccadilly Valley groundwater samples are more similar to those of the Chain of Ponds rainfall data than those of Adelaide rainfall data, with some the groundwater data points overlapping the Chain of Ponds rainfall data. The Chain of Ponds lies at a higher elevation than Adelaide and has a greater annual rainfall, which more closely resembles that of the Piccadilly Valley (altitude 700 to 420 m; mean annual rainfall 1080 mm), and as a result it is not surprising that isotopic data for the Chain of Ponds rainfall more closely resembles that of Piccadilly Valley groundwaters. The generally lighter (more negative) $\delta^{18}O$ isotopic composition of the groundwater samples (relative to the rainfall data), whilst the ^{2}H values remain relatively unaffected, may be due to the greater elevations and rainfall intensity in the Piccadilly Valley catchment area, which may cause some depletion in the isotopic composition.

The δD and $\delta^{18}O$ compositions of the Piccadilly Valley groundwater samples and Chain of Ponds rainfall data were plotted on Fig 4.11 in order to compare the groundwater data with respect to the local meteoric water line (as derived from the best fit through the rainfall data). The $\delta^{18}O$-$\delta^{2}H$ regression line for rainfall has a slope of 6.5 and an intercept of 5.8 (R^2 = 0.9). The slightly flatter slope of the local meteoric water line, in comparison to that of the Global Meteoric Water Line, may be due to the re-evaporation of light summer rains which results in a heavier isotopic signature. The $\delta^{18}O$-$\delta^{2}H$ regression for the groundwater samples has a slope of 3.2 and an intercept of 10.6 (R^2 =0.6) and is much flatter than that obtained for the local meteoric water line.

Table 4.3 Piccadilly Valley: April-May 1994
Groundwater Deuterium and Oxygen-18 Isotopes

Bore Number	δ D $^{0}/_{00}$ SMOW	δ ^{18}O $^{0}/_{00}$ SMOW
6834	-28.4	-5.46
6835	-27.9	-5.33
11935	-28.8	-5.60
6598	-29.3	-5.55
6567	-28.0	-5.48
8924	-27.0	-5.25
12429	-28.8	-5.37
15938	-29.2	-5.73
12827	-28.8	-5.63
7224	-28.7	-5.47
12045	-30.1	-5.70
6776	-28.5	-5.60
15410	-29.2	-5.74
6750	-29.6	-5.84
6746	-29.7	-5.83
6742	-28.0	-5.50
13440	-30.0	-5.80
6759	-29.6	-5.88
11934	-29.4	-6.16
6627	-29.9	-6.22
13253	-27.4	-6.14
13596	-29.6	-5.60
12428	-29.2	-5.86
13906	-29.2	-5.86
6828	-29.4	-5.83
6771	-29.6	-5.65
13543	-29.2	-5.53
12921	-30.0	-5.84
6782	-28.7	-5.67
14178	-27.7	-5.76
12825	-22.6	-4.48
6811	-29.0	-5.77
6809	-27.8	-5.59
11601	-25.2	-5.04
6709	-27.4	-5.43
12627	-27.1	-4.75
6583	-28.5	-5.58
13537	-29.4	-5.75
12023	-28.4	-5.32
6758	-30.2	-5.62
6555	-28.5	-5.54
13256	-29.3	-5.61

It is likely that the meteoric water line obtained for the Chain of Ponds rainfall data is not appropriate for the Piccadilly Valley area, particularly because of the heavier rains and greater elevations found in the Piccadilly Valley. It is also possible that some of the groundwater samples may contain fossil waters that have their origin from rains of a different climatic regime (and therefore would have had a different meteoric water line). As tritium cannot be used to date groundwater older than about 50 years, additional dating techniques would need to be employed in an attempt to determine more closely the age of the groundwater samples. However, as tritium was found in all but one of the samples, it is likely that most of the groundwater samples contain young waters or a mixture of old and young waters and as a result the dating techniques employed (such as carbon-14) would most likely give unreliable results.

Silicate hydrolysis may also influence the ^{18}O and D content of the water. This reaction can increase the rock in ^{18}O content whilst decreasing the water in ^{18}O; it may also increase the D content of the water. Thus, waters involved in silicate hydrolysis may plot to the left of the meteoric waterline (Coplen, 1993). It is possible that low temperature rock-water interactions are responsible for the relative depletion in $\delta^{18}O$ and δD in the Piccadilly Valley groundwater samples; however, it is beyond the scope of this report to determine whether this has occurred.

Fig 4.11 is enlarged in Fig 4.12 and includes a key for tritium concentrations, which reveals a degree of internal order in the isotopic signatures consistent with different origins for older and younger groundwaters. The samples containing measurable quantities of modern recharge water (tritium concentrations > 1.4 TU) are isotopically slightly heavier and plot above the older waters. It is probable that some of these samples contain water which has been recharged relatively rapidly, possibly reflecting the recent lighter summer and early autumn rains (April-May 1994 sampling), and show the effect of re-evaporation in the atmosphere. The effects of evaporation of water moving through the soil profile are not evident as the more positive δD and $\delta^{18}O$ signatures are independent of chloride concentrations (Figs 4.13 and 4.14).

Those samples for which the tritium concentrations are < 1.4 TU are generally isotopically more negative. The exceptions are bores 12825 and 12627 which appear as distinctly different waters and bores 6567, 6834 and 12429, which may be a mixture of relatively old and young waters. Bore 12627 plots to the right of the local meteoric water line, which suggests that this sample contains water that has been evaporated (confirmed by chlorine-36).

4.3 CHLORINE-36

4.3.1 Background

Chlorine-36 is a naturally occurring radioactive isotope with a half life of 301,000 +/- 4,000 years. It is produced primarily by cosmic-ray bombardment of the atmosphere and the Earth's surface. The chlorine-36 produced in this manner is mixed with atmospheric chlorine salts of terrestrial origin which contain essentially no ^{36}Cl. This produces a variation in the $^{36}Cl/Cl$ ratio in atmospheric precipitation that ranges from a few parts in 10^{15} in coastal areas to several hundred parts in 10^{15} in the interior of the continent (Davie et al., 1989). Nuclear weapons detonations, nuclear reactors and the use of neutron probes in environmental studies have added to the inventory of chlorine-36 (Bird et al., 1991).

It is the modification of the ^{36}Cl signal that allows information on the movement of salt and water within an aquifer to be deduced. Factors that may affect the ^{36}Cl signal include: radioactive decay; subsurface production; dissolution of ancient salt evaporites; evapotranspiration and ion filtration; the mixing of two water bodies; and the addition of modern salt originating from atmospheric precipitation (Davie et al., 1989). Figure 4.15 (after Bird et al., 1991) summarises the effect these processes can have on Cl and the $^{36}Cl/Cl$ ratios.

4.3.2 Chlorine-36 in Piccadilly Valley Groundwaters

The calculated $^{36}Cl/Cl$ ratios of modern atmospheric rainfall in the study area is estimated to be around 20 to 40 x 10^{-15} (Cresswell, R., pers. comm.) and reflect the proximity to the South Australian coast as a source of marine chloride. The $^{36}Cl/Cl$ ratios for Piccadilly Valley groundwater samples ranged from 9.0 to 110, while Cl concentrations varied from 41 to 246 mg/L (Table 4.4). The distribution of $^{36}Cl/Cl$ throughout the study area is shown in Figure 4.16.

Four samples (bores 13253, 14178, 6583 and 13543) had $^{36}Cl/Cl$ ratios that were significantly higher than that of recharge water and are thought to contain bomb pulse ^{36}Cl (which lags behind the tritium bomb pulse); this interpretation is substantiated by the elevated levels of tritium in these samples (Table 4.2).

Groundwater samples in the northwest of the study area have the lowest $^{36}Cl/Cl$ ratios, which suggest that little recharge is occurring in this area. The Aldgate Sandstone is thought to be confined by a thin layer of Woolshed Flat Shale in the northwest of the Piccadilly Valley, which may be impeding groundwater recharge. The distinctly lower $^{36}Cl/Cl$ ratios in this portion of the study area also suggests the possibility that the hydrogeological catchment boundary may continue to the northwest and may be distinct from the surface water catchment boundary; however, further sampling of

bores to the north of the study area would be required to determine the validity of this hypothesis. Two samples (bores 8924 and 6742) are anomalous as they have a relatively high tritium contents (2.3 and 1.9 TU respectively), but low $^{36}Cl/Cl$ ratios. This indicates that the mixing of waters with different isotopic signatures is occurring in these areas, perhaps as older groundwater flows from the northwest and encounters more recent groundwater recharge from the eastern and western margins of the study area.

$^{36}Cl/Cl$ plotted against Cl (Fig 4.17) illustrates some of the process occurring in the study area. The bores containing bomb pulse ^{36}Cl recharge water (bores 13253, 14178, 13543 and 6583) plot in a distinct group and contain a greater ^{36}Cl content than other bores with similar chloride concentrations; they also contain the highest tritium concentrations.

The chloride ratios found in bores 7224, 11601 and 12627 may represent modern recharge overprinted varying degrees of evaporation (also seen in the δD and $\delta^{18}O$ isotopes). The high tritium in 11601 (1.7 TU) and 7224 (3.8 TU), however, complicates the picture, suggesting that mixing may have occurred with bomb pulse waters. A lower level of ^{36}Cl may, therefore, represent the true input to the system at a ratio of ~25 x 10^{-15}. Interestingly, a subset of waters with this ratio, bores 6627, 6776 and 13596, plot as a reasonably distinct group on the $^{36}Cl/Cl$ vs Cl diagram, which is suggestive of either mixing with bomb pulse waters and/or chemical weathering/dissolution. Both of these processes are confirmed by the hydrochemical data for these samples (in Section 5.3.1).

To summarise, the distribution of ^{36}Cl within the Piccadilly Valley catchment groundwaters suggests a recent source of water, which enters at the margins of the catchment to the south and east, but is modified by mixing with waters introduced during the nuclear bomb test period. To the north and west, these recent waters either 1) mix with an older, more evaporated body of water, or, more likely, 2) mix with waters containing appreciable redissolved chloride from ancient deposits (containing dead chloride) located to the north of the catchment.

Table 4.4 April-May 1994 Piccadilly Valley Chlorine-36 Groundwater Data

Bore Number	Cl (mg/L)	^{36}Cl ($x10^6$) atoms/L	$^{36}Cl/Cl$ 10^{-15}
11935	58.0	9.6	9.7
6567	50.0	23.8	28.0
8924	54.8	13.7	14.7
12429	58.1	23.1	23.4
7224	42.0	30.0	42.1
6776	119.0	47.2	23.3
6746	101.0	18.5	11.0
6742	82.9	18.4	13.0
11934	111.0	19.7	10.0
6627	130.0	55.7	25.0
13253	82.8	115.3	82.0
13596	130.0	46.4	21.0
6782	68.4	23.4	20.0
14178	48.9	83.5	101.0
12825	50.6	21.3	25.0
6811	99.9	20.1	12.0
11601	105.0	66.6	37.0
12627	246.0	171.6	41.0
6583	42.2	78.8	110.0
6758	100.0	18.2	11.0
6750	96.9	14.8	9.0
13440	118.0	22.7	11.3
13543	51.2	83.8	96.3
6809	41.3	14.4	20.5
13537	100.0	15.8	9.3
6555	73.9	22.7	18.1

Fig 4.3 Tritium Concentration vs Bore Depth

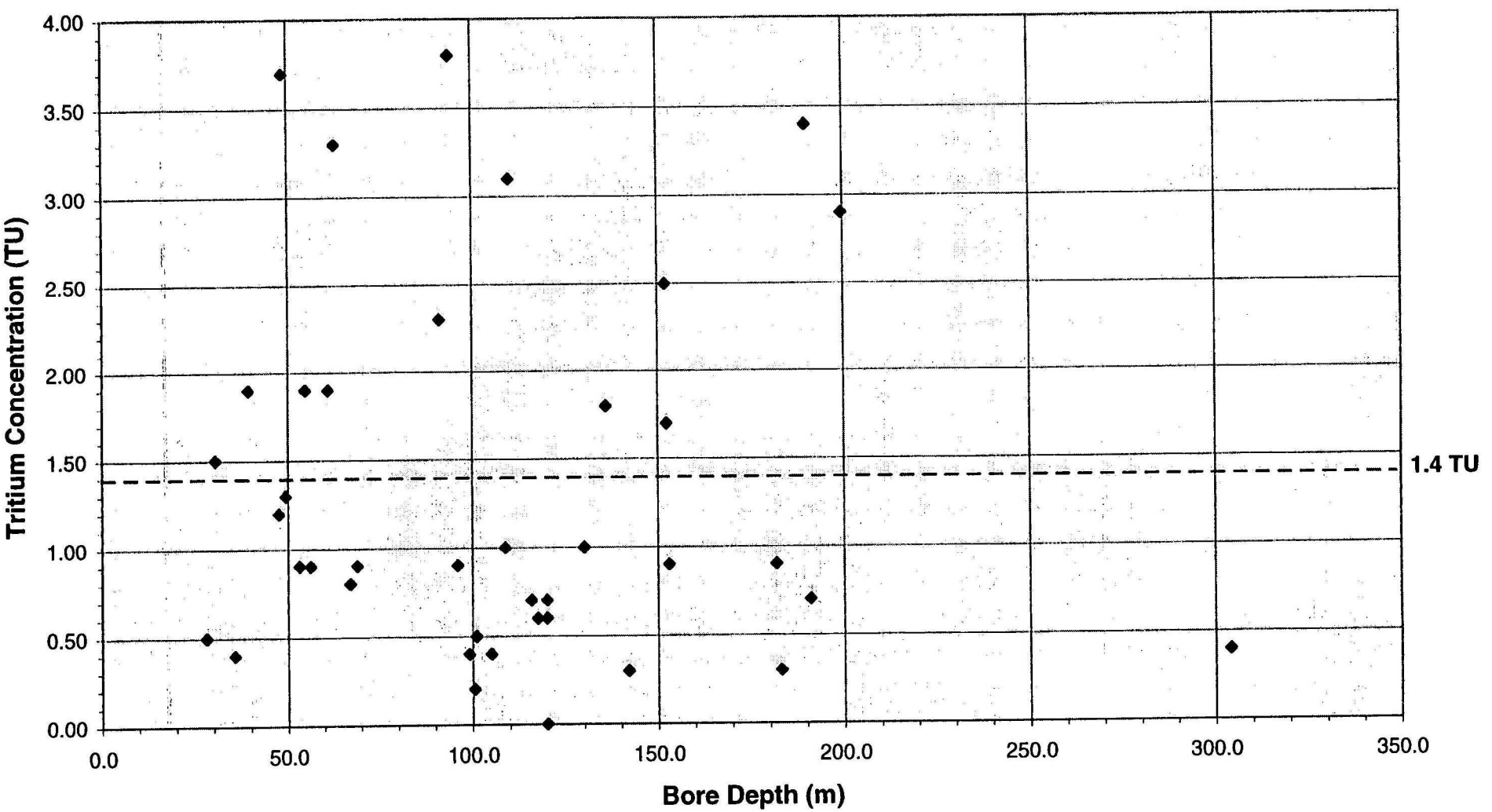


Fig 4.4 Tritium Concentration vs Depth to Aquifer

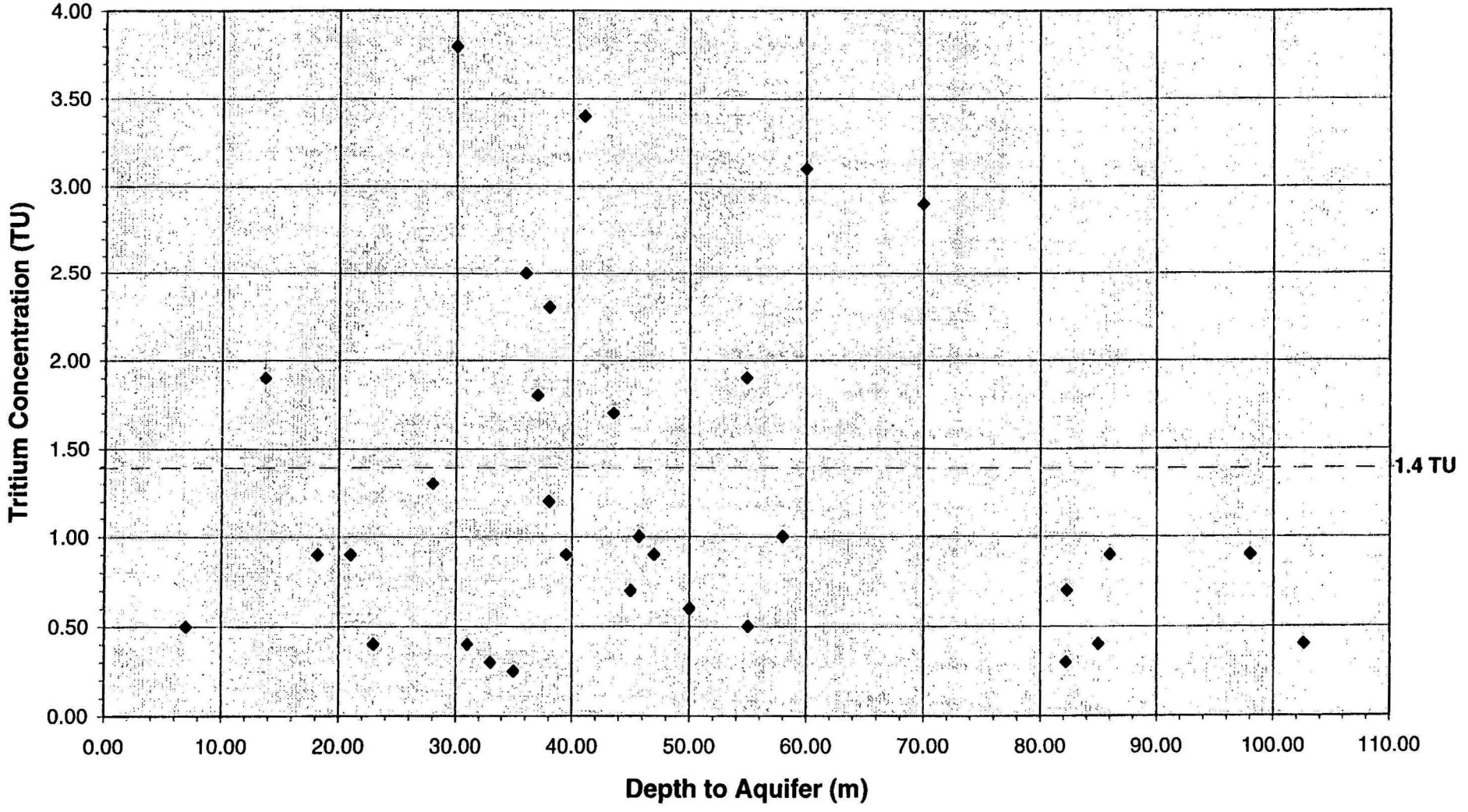


Fig 4.5 Tritium Concentration vs Dissolved Oxygen Concentaton

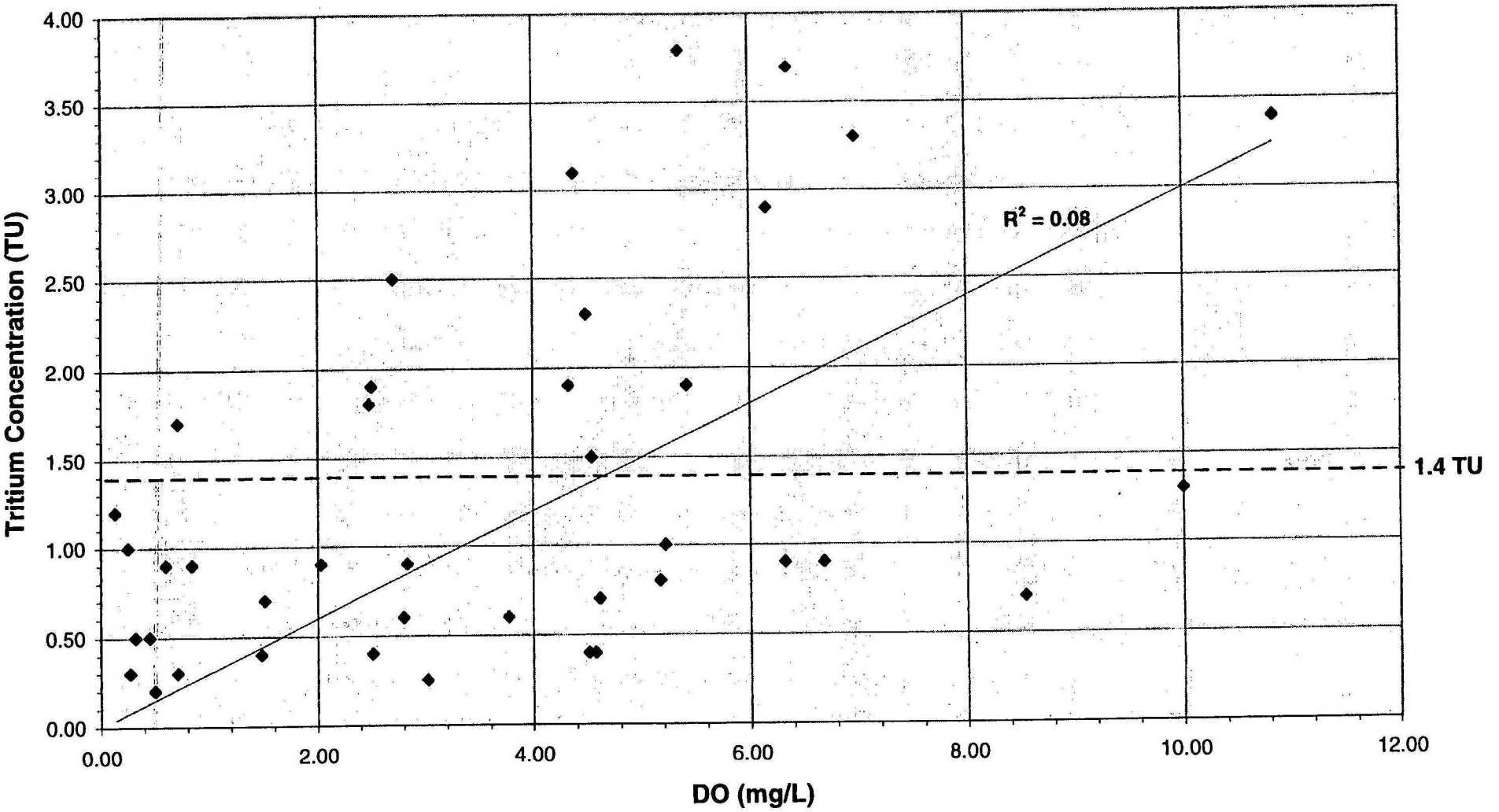


Fig 4.6 Tritium Concentration vs Depth to Water Table

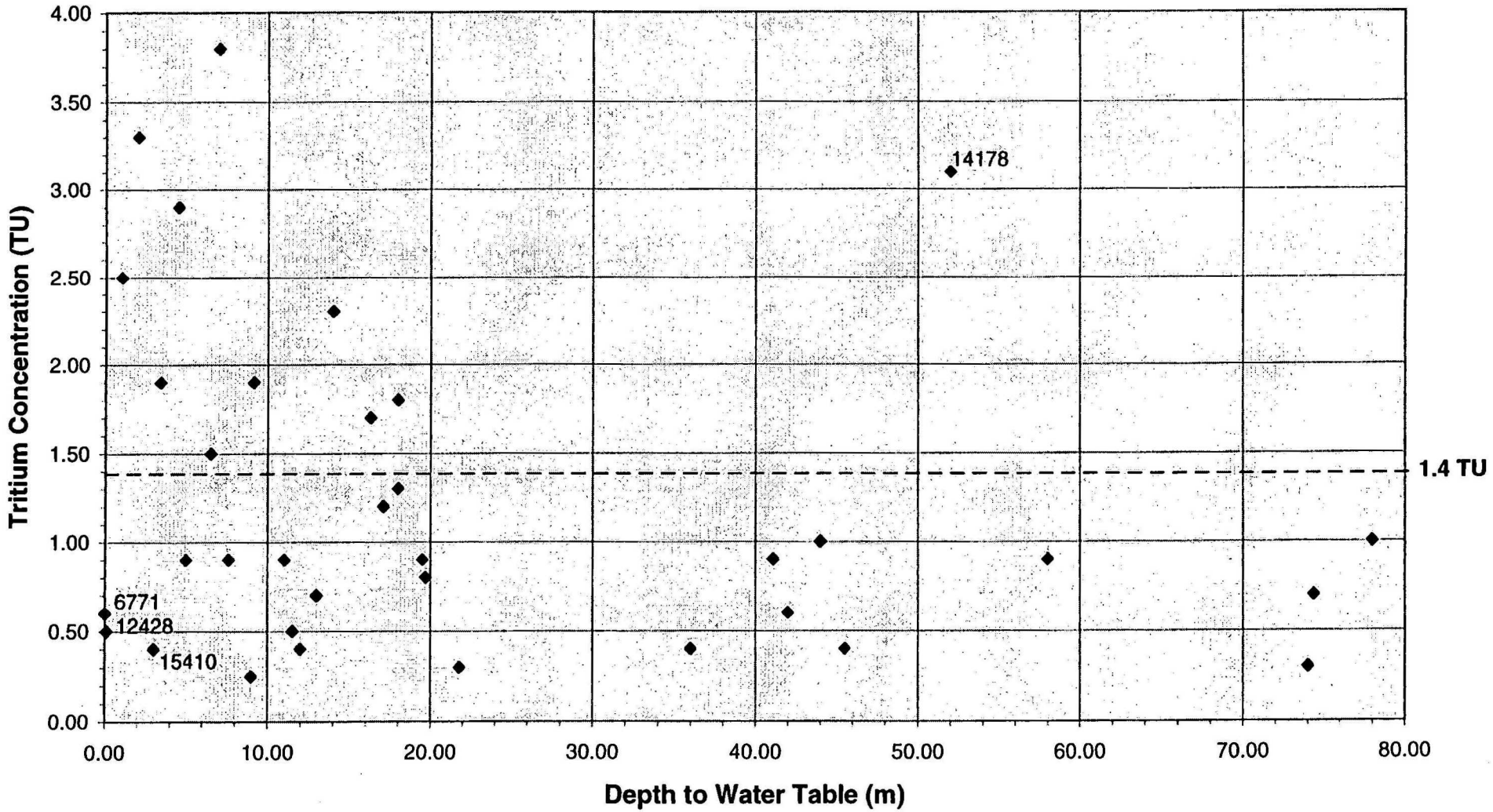
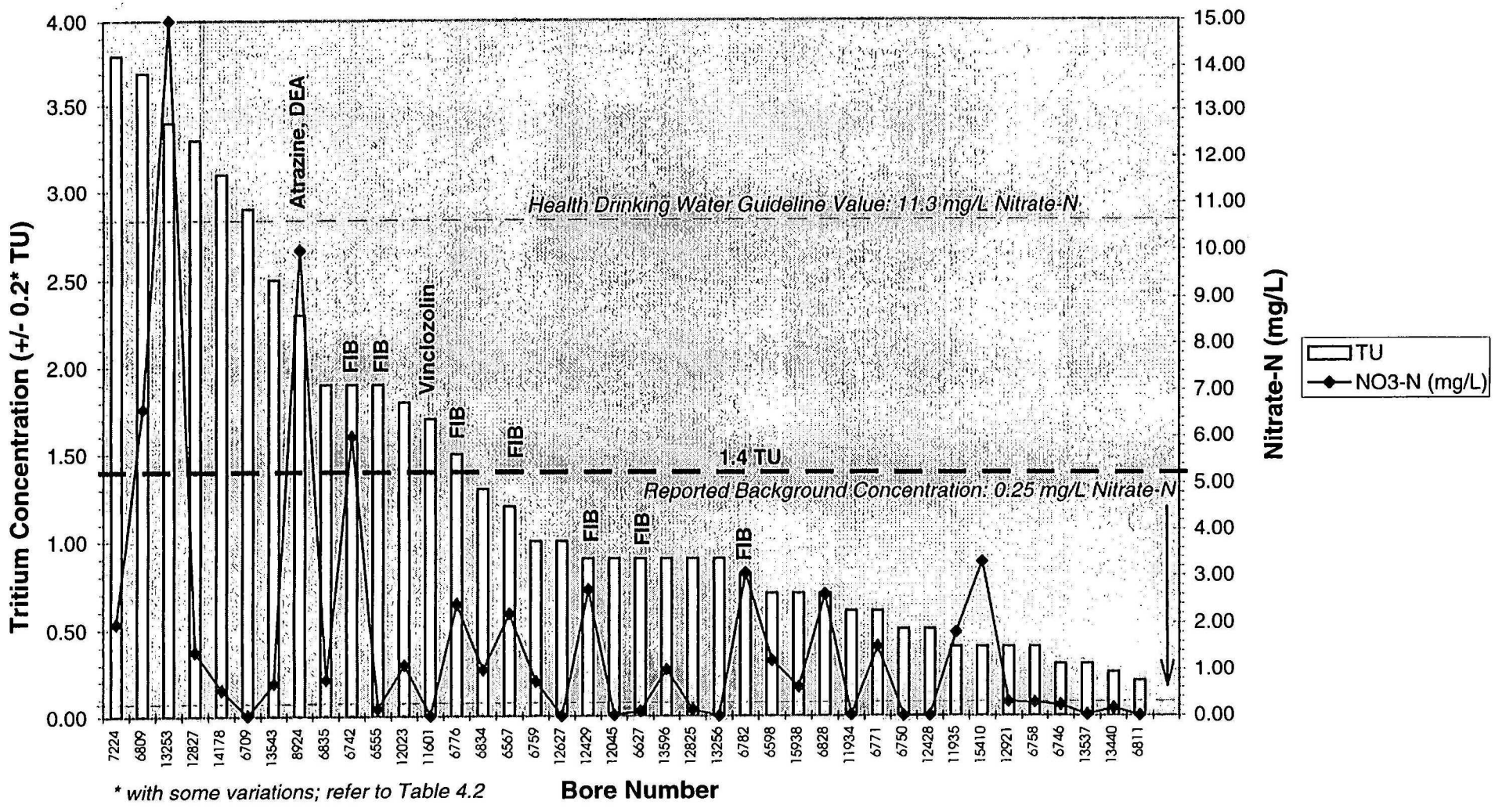


Fig 4.7 Piccadilly Valley Groundwaters: Tritium Concentration and Contaminants



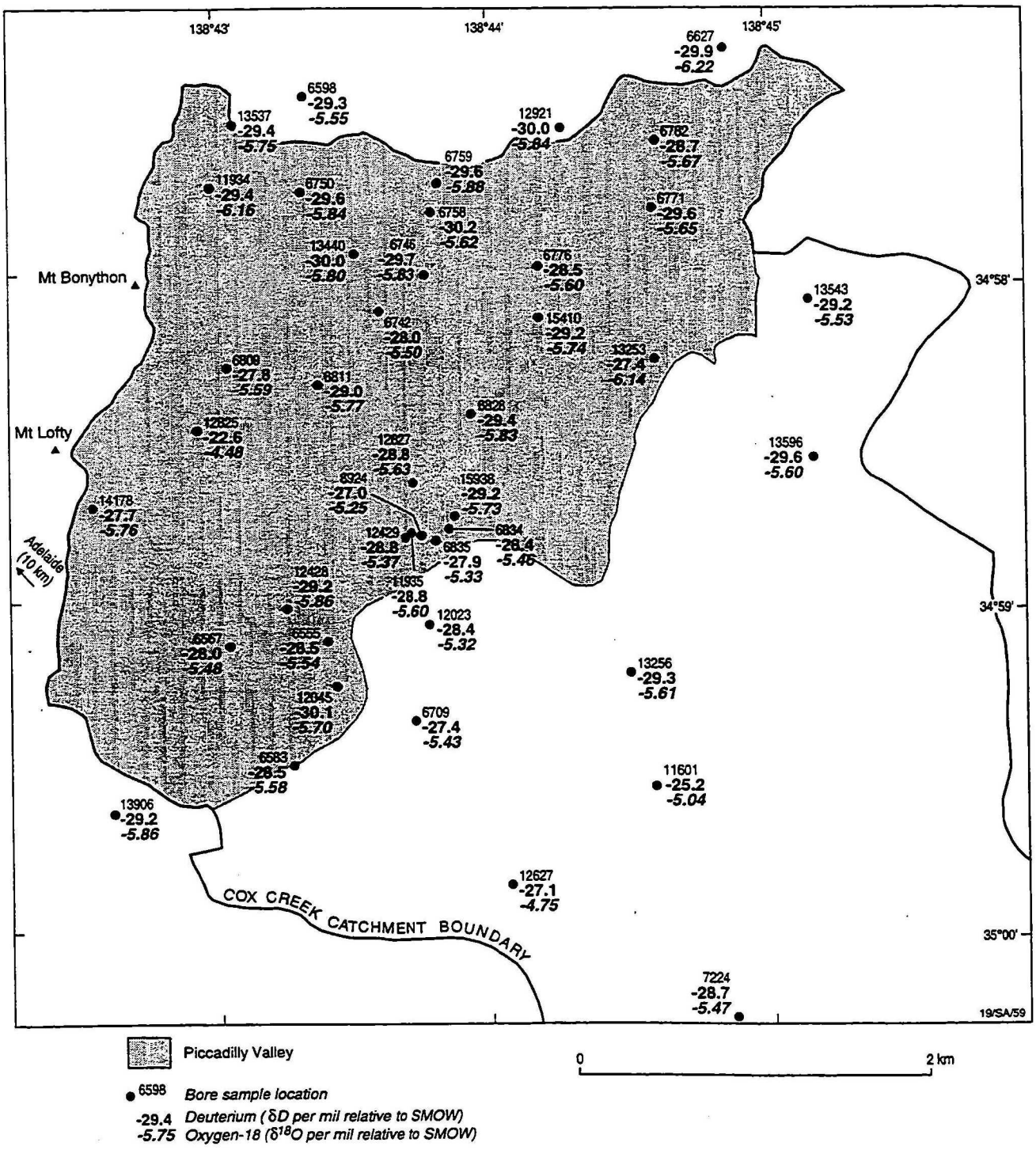


Figure 4.8 Deuterium (δD) and oxygen-18 ($\delta^{18}O$) isotopes in Piccadilly Valley Groundwaters

Fig 4.9 April-May 1994 Deuterium vs Oxygen-18 Isotopes in Piccadilly Valley Groundwaters

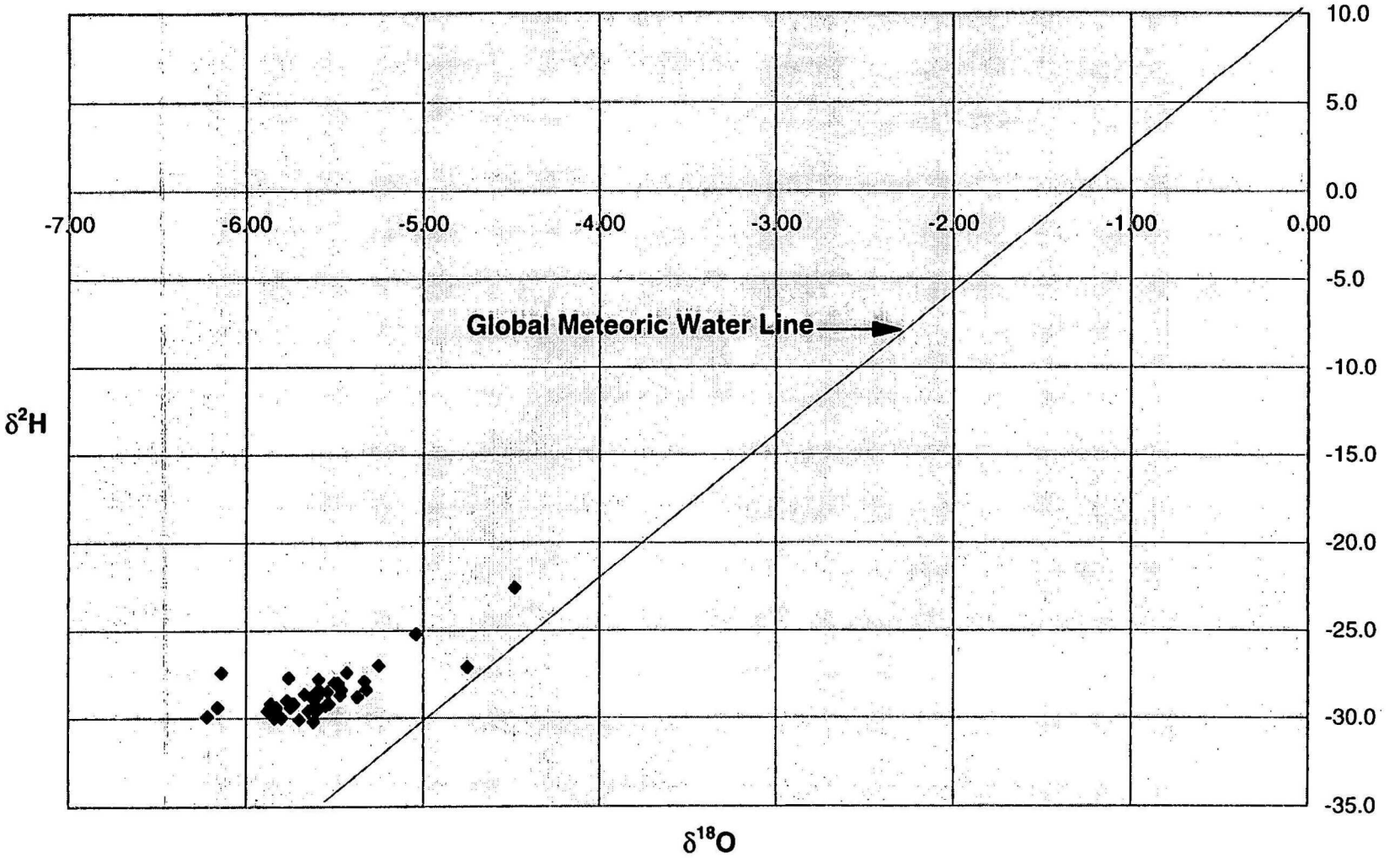


Fig 4.10 Deuterium and Oxygen-18 Isotopic Compositions of Rainwater and Piccadilly Valley Groundwaters

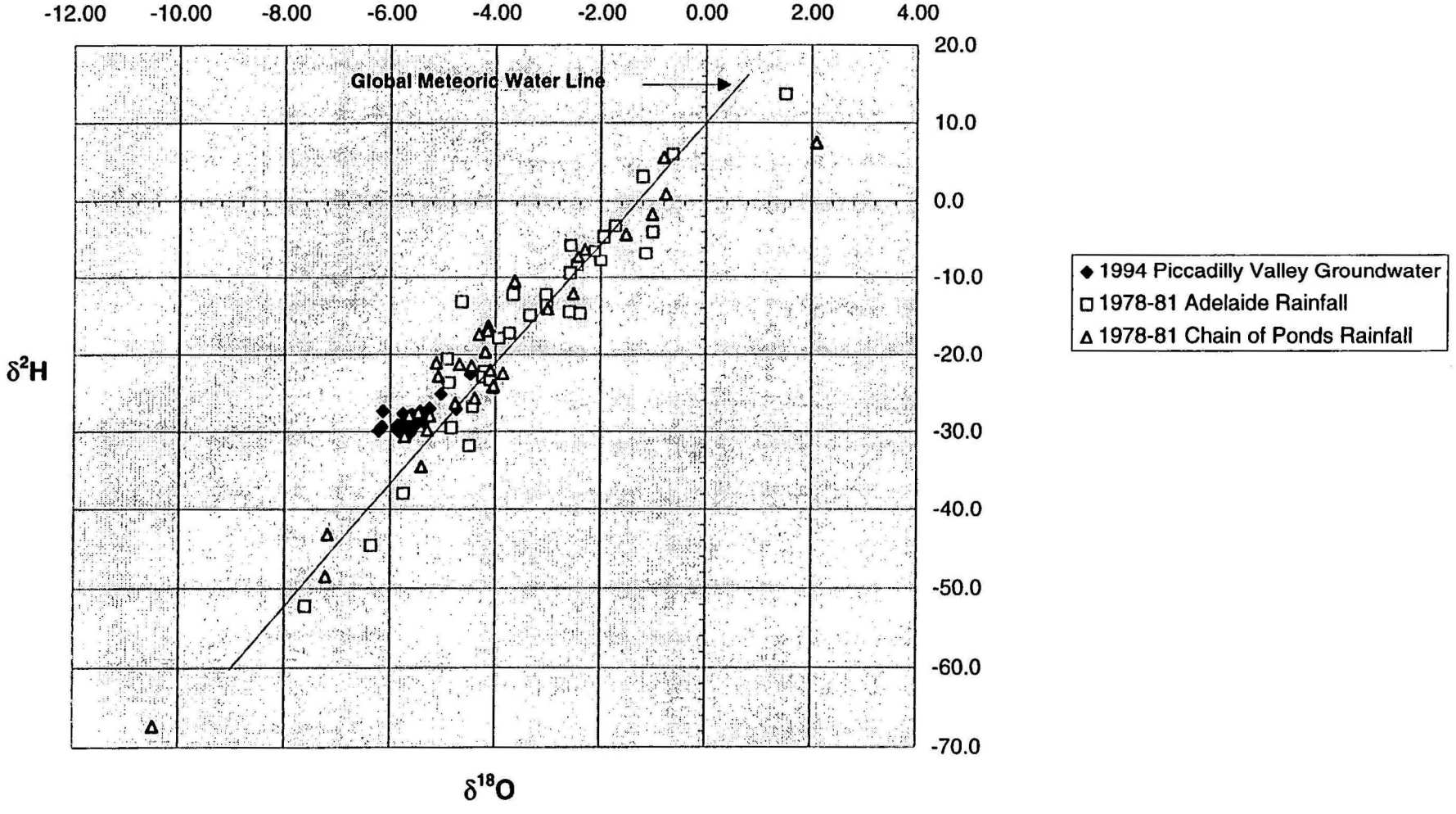


Fig 4.11 Deuterium and Oxygen-18 Isotopic Compositions of Chain of Ponds Rainfall and Piccadilly Valley Groundwaters

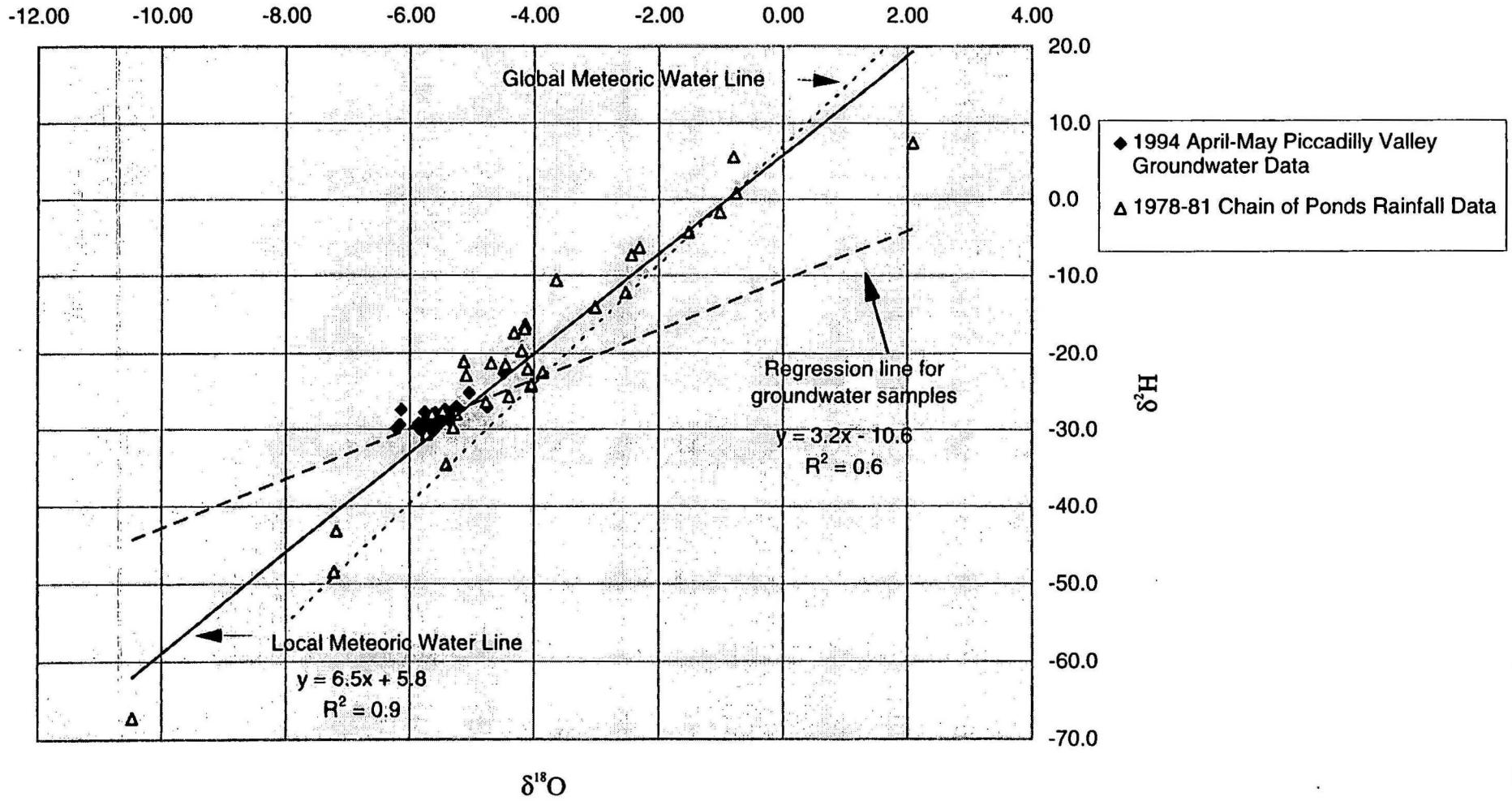


Fig 4.12 Piccadilly Valley: Groundwater Deuterium and Oxygen-18 Isotopes

(grouped by tritium concentration)

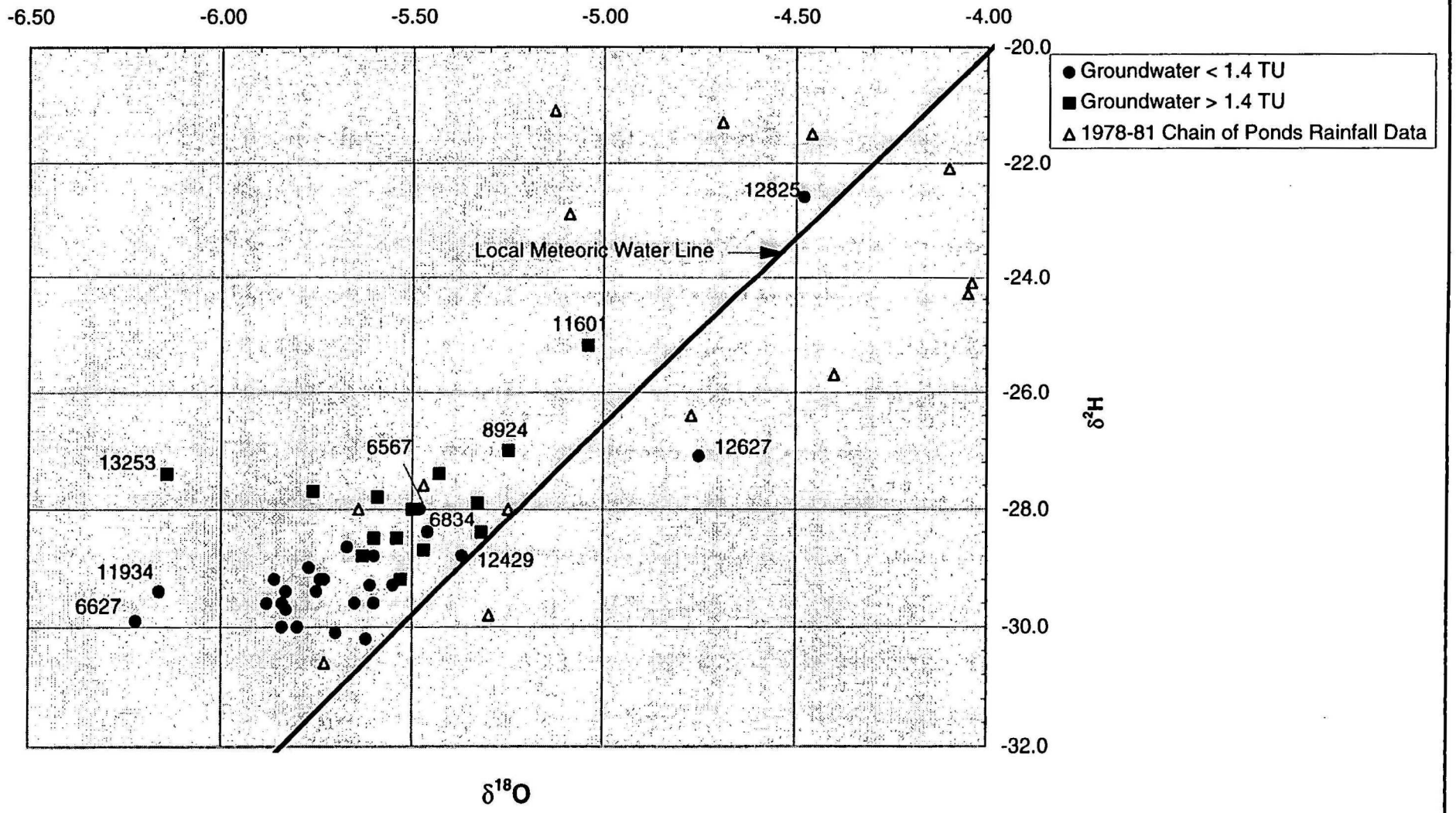


Fig 4.13 Piccdilly Valley Groundwaters: Deuterium vs Chloride Concentration

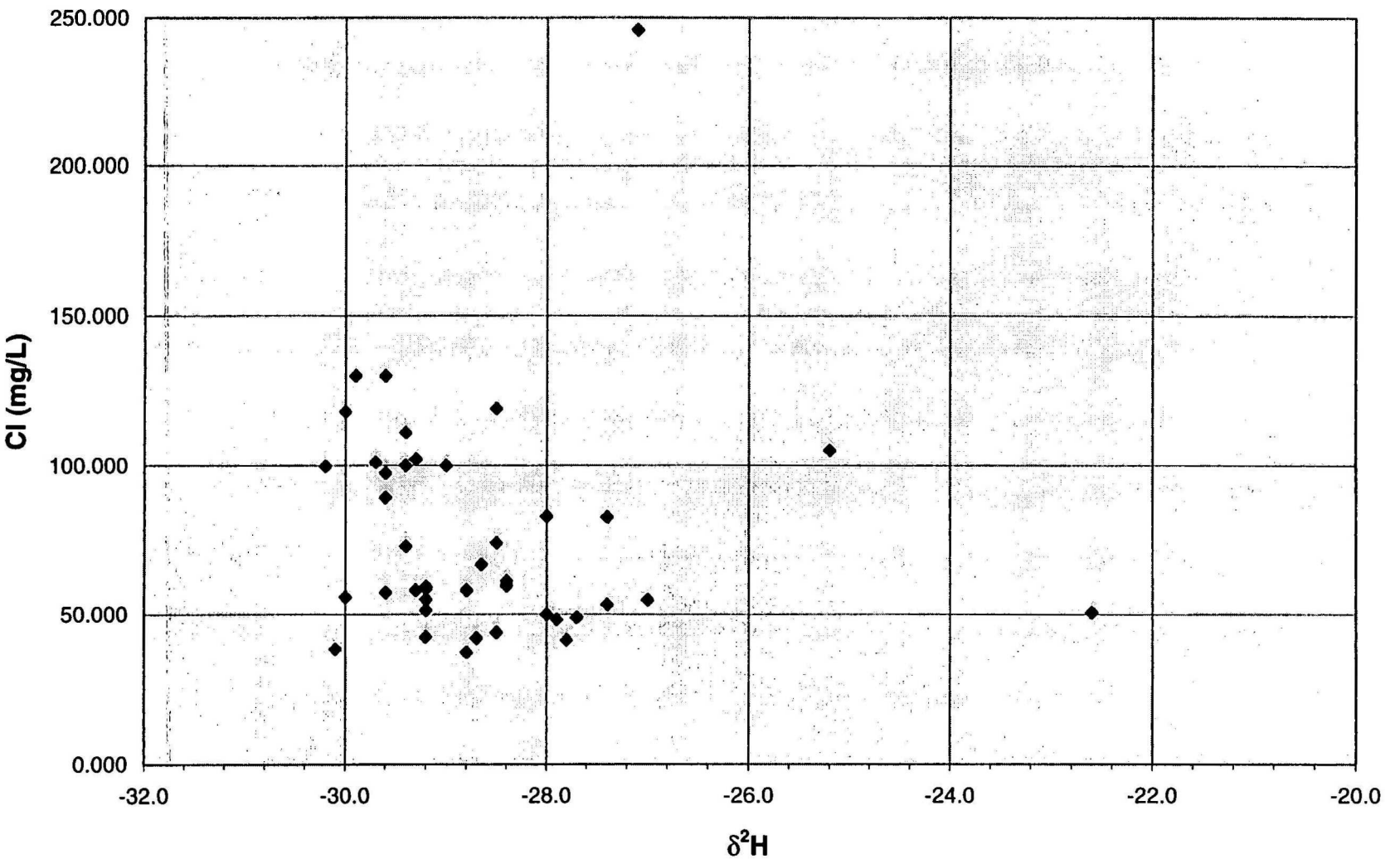
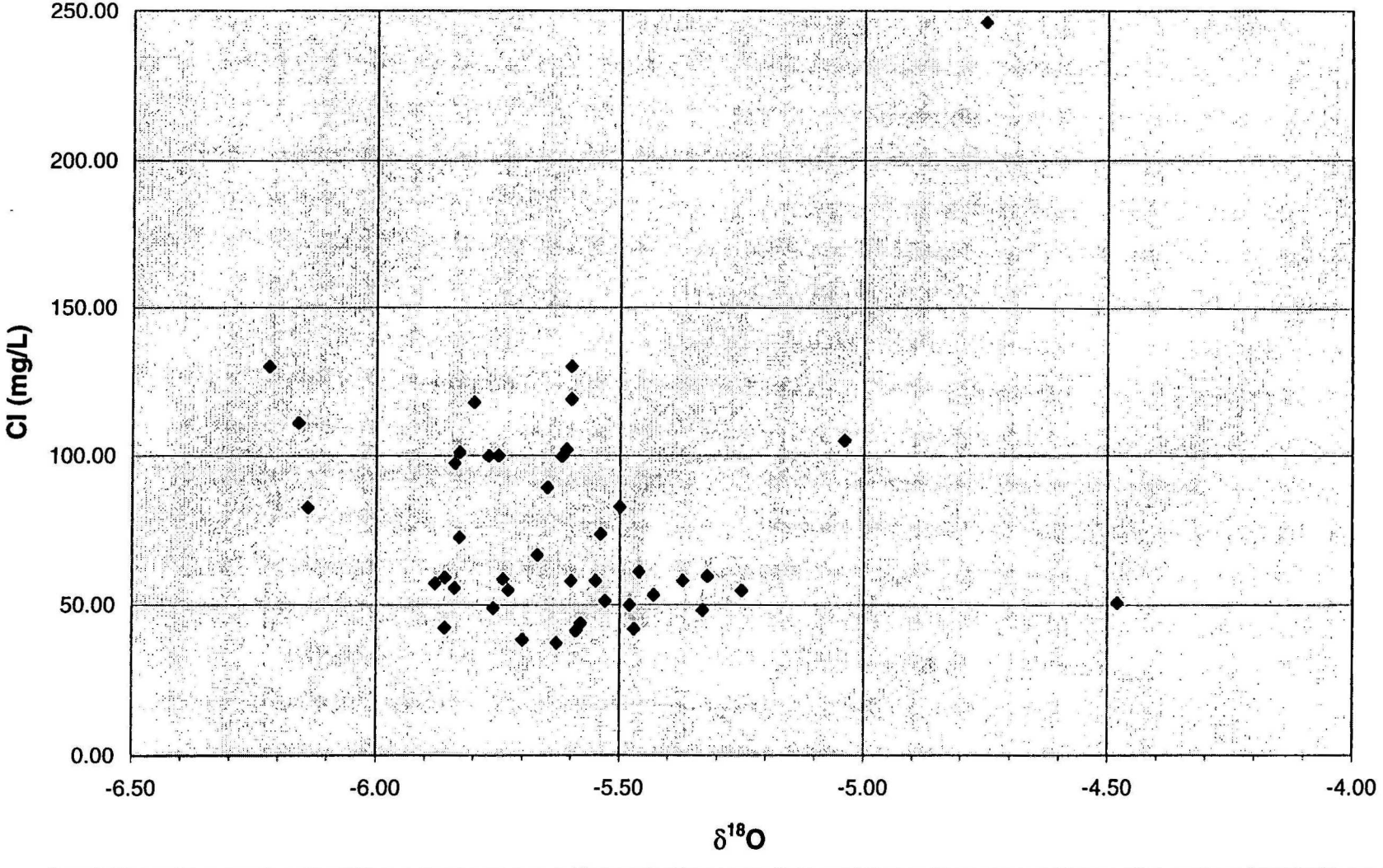


Fig 4.14 Piccadilly Valley Groundwaters: Oxygen-18 vs Chloride Concentration



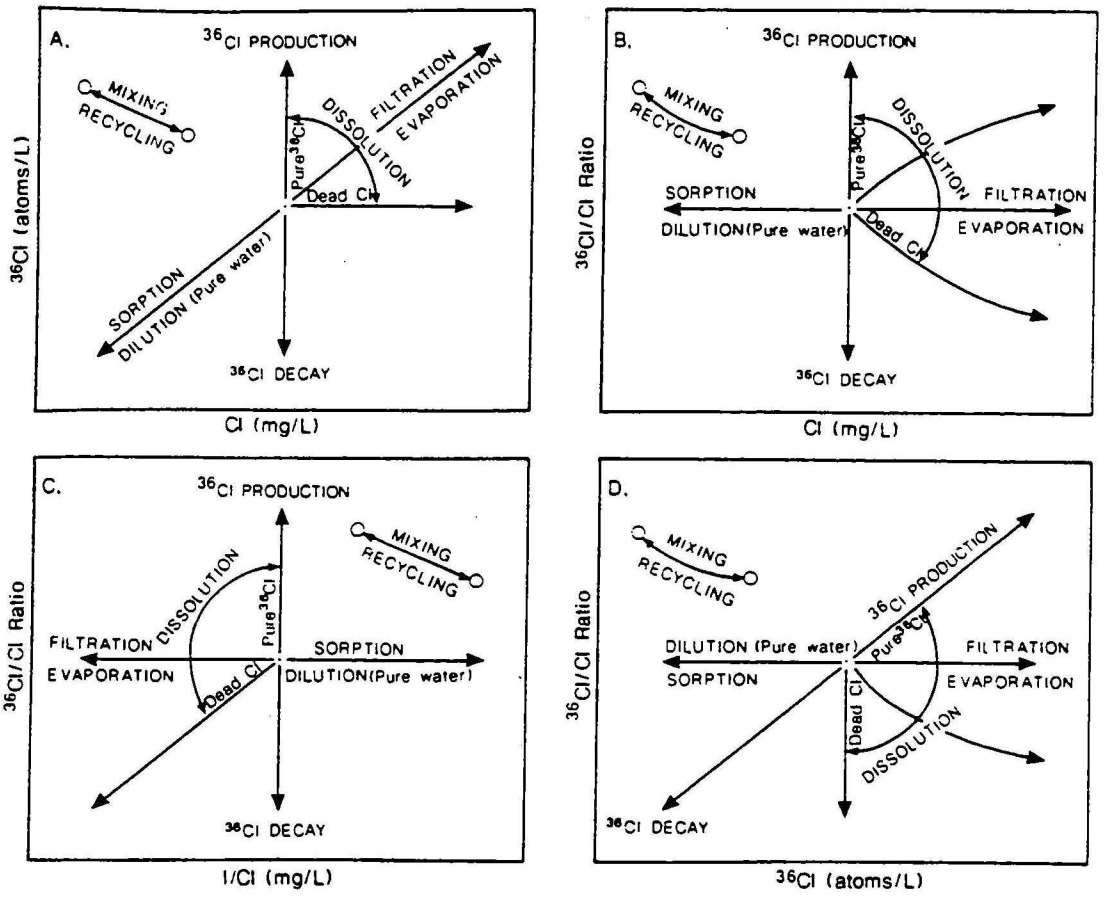


Figure 4.15 Effects of various processes on the chlorine-36 isotope and the chlorine-36 to chloride ratios (after Bird et al., 1991)

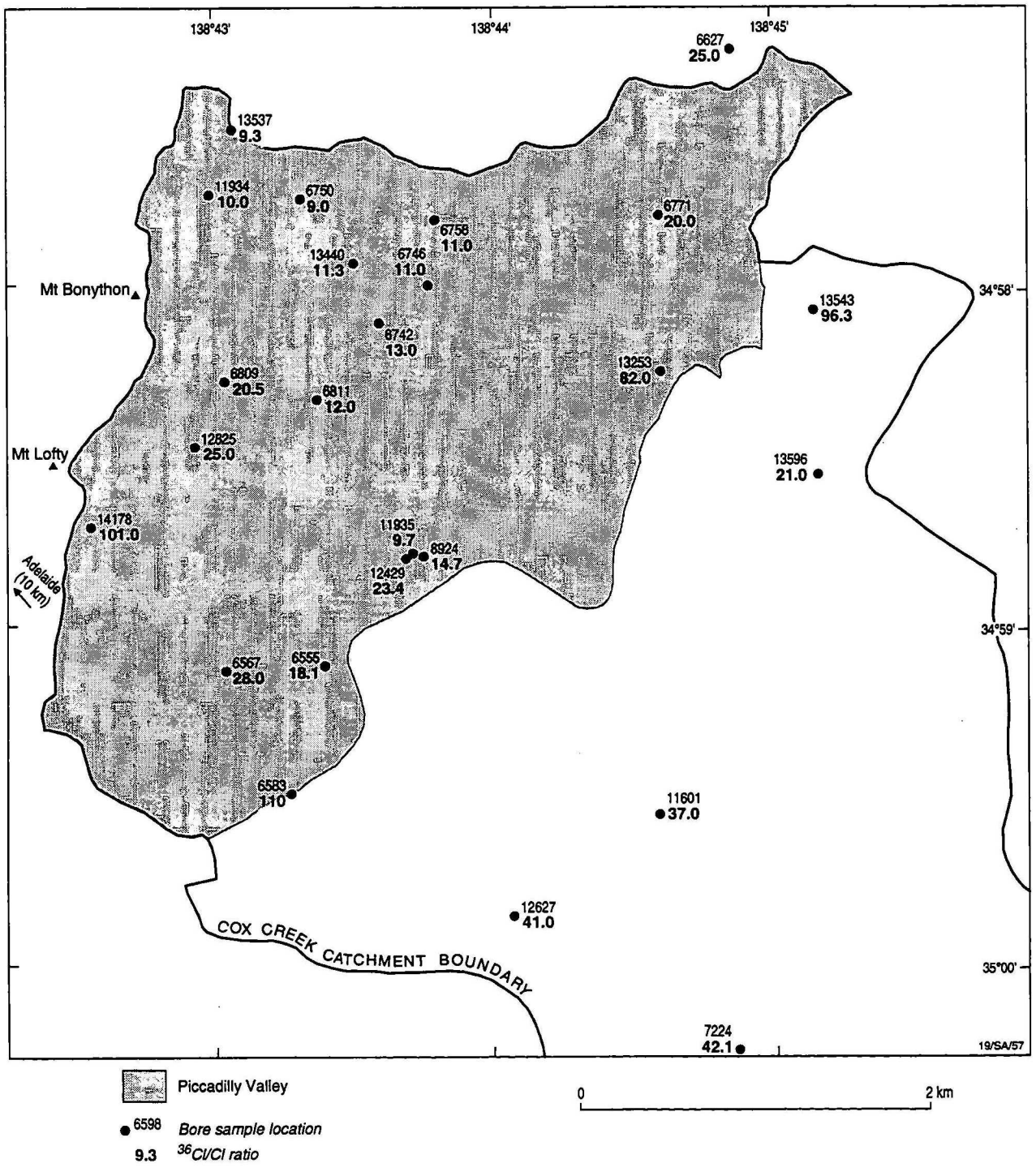
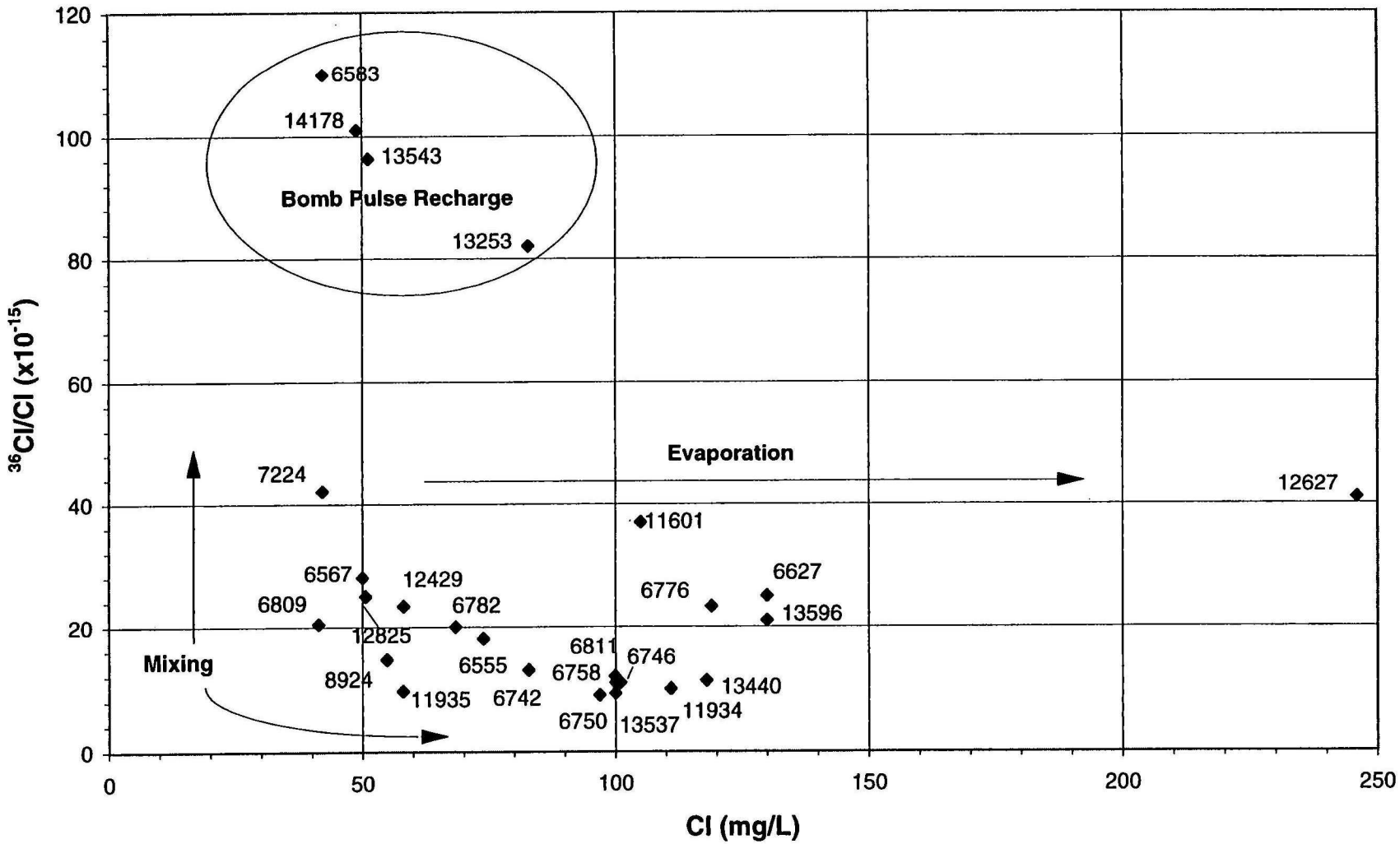


Figure 4.16 Distribution of chlorine-36 to chloride ratios in Piccadilly Valley Groundwaters

Fig 4.17 Piccadily Valley Groundwaters:
^{36}Cl to Chloride Ratio vs Chloride Concentration



5.0 FIELD MEASUREMENTS, MAJOR AND MINOR INORGANIC CHEMISTRY

5.1 FIELD MEASUREMENTS

The field measurements obtained during sampling (Table 5.1) include electrical conductivity (EC; Fig 5.1), pH (Fig 5.2), redox potential (Eh; Fig 5.3), dissolved oxygen (DO; Fig 5.4) and temperature (Fig 5.5). Table 5.1 includes the minimum, maximum and median values.

The relationship between DO and Eh (Fig 5.6) suggests, as one might expect, generally increasing Eh values with increasing DO. Of note are the outliers (bores 6709, 6627,6834 and 15938) in which the DO concentrations are higher than other bores with similar Eh values and may indicate air entrainment during pumping. The DO concentrations obtained in this study should therefore be used with some degree of caution. Turbine and submersible pumps have the potential to mix air with the water while the samples are being pumped to the surface, and as a result, they may not be representative of the actual groundwater conditions.

5.2 MAJOR AND MINOR INORGANIC CHEMISTRY

The major and minor inorganic chemistry data is presented in Table 5.2. Analyses were carried out by AGSO for TDS (determined by evaporation), lab pH, lab EC, major ion chemistry, silica, sulphur, iron, manganese and by the ACTEW laboratory for fluoride and iodide. Table 5.2 includes the minimum, maximum and median values for each parameter. For those samples in which the concentration was less than the limit of detection, a value of half the detection limit has been substituted for statistical purposes and graphing.

5.2.1 Comparison of Field and Laboratory Measurements

The comparison of field and lab measurements can provide a check on the laboratory data. Agreement between the two data sets raises the confidence in the data and gives an indication of whether secondary processes have occurred between sampling and laboratory measurement (Mazor, 1991). The Field EC versus lab EC (Fig 5.7) shows a strong linear correlation ($R^2 = 0.9$) which confirms the high quality of the EC data, except for the outlier (bore 6834) for which the field EC is believed to be erroneous. Lab EC versus lab TDS (Fig 5.8) shows a strong linear correlation ($R^2 = 0.9$). The field pH versus lab pH (Fig 5.9) also shows a strong linear correlation, with a slight increase in lab pH (data plots below the 1:1 ratio line). This increase in lab pH over

Table 5.1: April-May 1994 Piccadilly Valley Groundwaters - Field Measurements

Bore Number	Date Sampled	Total Depth* (m)	Field EC (µS/cm)	Field pH	Field Eh (mV)	Field DO (mg/L)	Field Temp (^{0}C)
6834	20.04.94	49.4	183	6.60	292	10.00	16.5
6835	21.04.94	54.8	335	5.69	386	2.50	15.9
11935	21.04.94	35.6	684	7.04	323	1.48	16.0
6598	22.04.94	115.8	493	6.35	437	4.61	16.5
6567	23.04.94	47.5	544	6.48	321	0.13	16.8
8924	24.04.94	91.2	422	5.98	448	4.49	16.1
12429	24.04.94	96.0	692	7.04	431	2.03	15.4
15938	25.04.94	191.0	579	6.88	355	8.54	16.4
12827	25.04.94	63.0	233	5.54	492	6.98	14.1
7224	26.04.94	94.0	233	5.36	429	5.36	15.4
12045	26.04.94	56.2	295	6.00	306	2.83	15.2
6776	27.04.94	30.5	685	6.31	412	4.54	14.5
15410	27.04.94	99.0	475	6.54	397	4.57	17.0
6750	28.04.94	101.0	788	6.93	230	0.32	17.1
6746	29.04.94	142.0	525	5.98	347	0.27	14.8
6742	29.04.94	39.3	427	5.62	402	4.33	14.3
13440	01.05.94	120.0	537	5.67	353	3.02	14.1
6759	01.05.94	130.0	310	5.73	395	5.22	14.0
11934	02.05.94	120.0	632	6.25	259	2.80	14.4
6627	02.05.94	181.8	968	7.05	282	6.68	15.4
13253	03.05.94	190.0	511	5.39	455	10.84	14.7
13596	03.05.94	68.9	655	6.11	385	6.32	14.9
12428	04.05.94	28.0	635	7.03	209	0.45	15.4
13906	04.05.94	131.6	307	6.01	269	0.11	13.0
6828	05.05.94	120.0	727	6.95	431	1.51	17.0
6771	05.05.94	117.6	631	6.66	345	3.77	16.3
13543	06.05.94	152.0	264	5.34	405	2.70	16.2
12921	06.05.94	304.0	700	6.05	412	4.51	17.3
6782	08.05.94	67.1	526	6.80	412	5.17	15.9
14178	09.05.94	110.0	219	5.08	440	4.38	12.6
12825	09.05.94	153.0	376	6.85	313	0.60	13.0
6811	10.05.94	100.5	724	6.77	223	0.50	18.2
6809	10.05.94	48.7	241	5.39	452	6.36	14.9
11601	11.05.94	152.4	632	5.95	292	0.71	16.4
6709	11.05.94	199.6	469	6.72	204	6.16	17.8
12627	12.05.94	108.8	976	5.80	289	0.25	16.7
6583	12.05.94	29.0	203	4.27	474	2.40	16.4
13537	13.05.94	183.0	788	6.82	245	0.71	19.0
12023	13.05.94	136.0	463	6.42	382	2.48	17.4
6758	14.05.94	105.0	561	5.99	376	2.51	16.7
6555	15.05.94	61.0	428	5.93	365	5.42	16.3
13256	15.05.94	53.2	621	6.30	283	0.84	17.0
Minimum		28.0	183	4.27	204	0.11	12.6
Maximum		304.0	976	7.05	492	10.84	19.0
Median		103.0	526	6.18	371	2.93	16.1

*** Obtained from Department of Mines and Energy, SA Logs**

Table 5.2: April-May 1994 Piccadilly Valley Groundwaters - Major Inorganic Chemistry

Bore Number	Lab TDS (Evap)	Lab pH	Lab EC (µS/cm)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Si (mg/L)	S (mg/L)	HCO_3 (mg/L)	Cl (mg/L)	SO_4 (mg/L)	Fe (mg/L)	Mn (mg/L)	F (mg/L)	I (mg/L)
6834	386	7.38	549	33.90	33.20	49.10	3.69	15.89	8.49	170.00	61.10	20.50	0.04	0.0025	0.37	0.03
6835	244	6.36	354	5.40	15.80	36.10	3.23	15.80	13.20	33.75	48.20	34.40	1.31	0.025	0.50	0.03
11935	446	7.56	713	45.20	40.90	44.80	4.53	15.60	9.48	240.65	58.00	24.60	0.07	0.026	0.40	0.03
6598	314	7.08	511	26.30	24.10	41.30	3.27	14.60	2.94	140.00	58.00	7.83	0.02	0.0025	0.32	0.03
6567	316	7.49	553	29.40	31.10	38.35	3.55	12.80	4.22	175.00	49.85	10.90	0.05	0.059	0.39	0.03
8924	292	6.77	495	15.30	25.40	44.30	2.34	11.70	3.58	95.00	54.80	9.30	0.03	0.008	0.41	0.03
12429	424	7.64	748	49.00	43.30	46.00	4.58	15.70	12.50	251.25	58.10	32.70	0.02	0.0025	0.39	0.03
15938	358	7.51	629	39.40	33.30	41.60	3.64	14.50	8.16	201.90	54.90	20.70	0.13	0.059	0.32	0.03
12827	218	6.08	246	6.60	7.00	28.80	1.94	10.10	2.21	33.15	37.30	6.01	0.03	0.0025	0.07	0.03
7224	212	5.72	221	1.66	2.70	39.90	1.35	14.80	3.14	13.75	42.00	8.12	1.06	0.067	0.10	0.03
12045	232	6.27	259	6.18	11.70	28.20	2.44	14.30	2.03	58.75	38.40	5.62	8.44	0.357	0.23	0.03
6776	492	7.13	649	22.90	24.30	78.90	5.54	21.60	8.91	120.65	119.00	25.40	0.02	0.0025	0.33	0.03
15410	360	7.03	495	25.10	23.70	44.60	3.49	14.70	5.28	131.25	58.60	13.40	0.02	0.006	0.29	0.03
6750	533	7.63	845	57.70	43.05	71.05	4.88	18.40	6.09	300.25	97.45	15.60	0.52	0.2665	0.38	0.03
6746	316	6.75	513	10.50	15.90	71.70	5.86	23.70	4.34	88.75	101.00	12.40	0.27	0.016	0.47	0.03
6742	252	6.09	392	4.92	9.39	58.40	3.75	16.20	3.17	28.75	82.90	9.18	0.41	0.033	0.29	0.03
13440	298	6.22	509	1.99	8.45	92.20	6.00	21.50	4.75	46.25	118.00	12.80	3.98	0.186	0.53	0.03
6759	202	6.10	279	1.78	3.86	48.20	3.88	16.60	2.56	28.75	57.20	7.32	6.92	0.094	0.30	0.03
11934	478	6.80	597	3.31	19.10	106.00	5.21	23.90	5.66	115.00	111.00	15.20	5.90	0.034	0.79	0.03
6627	658	7.77	1050	65.00	52.90	89.30	5.10	12.60	28.20	290.00	130.00	79.70	0.58	0.093	0.31	0.03
13253	312	6.04	504	7.60	26.40	27.90	2.60	11.70	14.40	15.00	82.80	43.30	0.14	0.053	0.16	0.03
13596	416	6.77	667	18.00	16.40	98.60	3.22	23.40	6.30	108.75	130.00	17.80	0.01	0.036	0.69	0.03
12428	402	7.75	643	43.60	38.80	40.70	4.49	15.30	4.83	246.25	59.20	13.40	0.65	0.061	0.38	0.03
13906	168	6.31	267	5.17	10.40	31.20	3.34	8.60	2.63	52.50	42.40	7.54	14.46	0.165	0.27	0.03
6828	390	7.76	690	41.90	40.40	48.80	4.35	16.10	5.97	235.00	72.80	16.70	0.03	0.0025	0.36	0.03
6771	496	7.22	628	29.80	30.30	58.80	4.40	18.40	7.01	161.25	89.30	19.70	0.01	0.0025	0.39	0.03
13543	302	6.17	248	2.01	4.03	41.50	1.08	11.40	2.83	20.00	51.20	8.20	0.65	0.073	0.18	0.03
12921	634	6.75	716	79.70	19.40	45.30	2.37	11.80	72.80	67.50	55.70	194.00	0.35	0.040	0.20	0.03
6782	440	7.23	529	25.45	28.60	42.55	3.08	17.75	7.14	136.88	66.55	20.70	0.12	0.008	0.37	0.03
14178	204	5.46	206	1.35	4.15	29.10	2.13	5.42	1.65	8.75	48.90	5.07	3.89	0.054	0.03	0.03
12825	286	7.25	347	8.46	18.10	33.80	4.54	12.20	2.26	85.00	50.60	6.41	0.31	0.037	0.35	0.03
6811	564	7.62	817	45.00	46.60	67.20	5.39	19.10	6.90	280.00	99.90	19.50	0.85	0.197	0.47	0.03
6809	232	5.73	241	1.83	3.67	38.20	1.83	11.50	1.50	5.00	41.30	4.57	0.94	0.031	0.24	0.03
11601	438	6.60	607	20.60	15.50	83.10	4.49	20.70	14.80	96.25	105.00	42.40	6.94	1.034	0.35	0.03
6709	386	7.28	496	46.20	15.50	41.10	2.77	17.60	3.03	168.75	53.20	8.44	10.39	0.557	0.22	0.03
12627	718	6.50	1000	20.90	25.70	153.00	3.38	30.10	8.75	87.50	246.00	24.50	4.86	0.472	0.94	0.03
6583	86	4.74	167	0.62	4.08	24.20	0.76	5.64	2.30	0.003	43.90	7.03	0.74	0.003	0.03	0.03
13537	544	7.64	779	42.00	45.60	69.70	6.22	16.60	5.34	276.90	100.00	15.60	0.50	0.005	0.55	0.03
12023	336	6.97	417	26.90	12.20	49.00	2.19	21.30	3.17	113.75	59.50	9.09	0.14	0.230	0.37	0.03
6758	378	6.32	507	8.11	12.65	82.50	6.13	21.65	4.36	87.50	99.70	11.85	1.28	0.3235	0.47	0.16
6555	300	6.30	384	2.54	7.86	66.50	6.24	21.90	3.63	61.25	73.90	10.50	5.91	0.086	0.83	0.03
13256	410	6.75	603	15.10	15.00	96.90	4.86	19.50	10.30	123.75	102.00	28.80	5.13	0.579	0.53	0.03
Minimum	86	4.74	167	0.62	2.70	24.20	0.76	5.42	1.50	0.003	37.30	4.57	0.01	0.0025	0.03	0.03
Maximum	718	7.77	1050	79.70	52.90	153.00	6.24	30.10	72.80	300.25	246.00	194.00	14.46	1.034	0.94	0.16
Median	359	6.77	512	19.30	18.60	45.65	3.67	15.85	5.06	102.50	59.35	13.40	0.51	0.050	0.37	0.03

field pH suggests that small losses of CO_2 via secondary reactions in the period between sampling and laboratory measurements have occurred.

5.2.2 Major and Minor Inorganic Constituents

The major and minor inorganic constituents of Piccadilly Valley Groundwaters (Table 5.2) are reviewed in this section. Bar graphs were plotted for each parameter. The 1996 NH&MRC/ARMCANZ Australian Drinking Water Guidelines are referred to when indicated in order to provide a value against which the data may be compared, as well as to determine the groundwaters suitability for drinking. Most of the discussion on sources of constituents is condensed from Bouwer (1978) and Hem (1985).

Lab Total Dissolved Solids (TDS): The TDS (Fig 5.10) values ranged from 86 to 718 mg/L with a median value of 359 mg/L. Six of 42 bores (14.3%) exceeded the aesthetic drinking water guideline value of 500 mg/L for good quality drinking water, although up to 1000 mg/L may generally be considered to be acceptable for human consumption. By way of comparison, the TDS content of seawater is about 34 000 mg/L. The TDS values are plotted on a map of the study area in Fig 5.11. Of the six bores exceeding the aesthetic guideline value, all except bore 12627 are located within the Aldgate Sandstone in the northern portion of the study area. Bore 12627 is located in the Barossa Complex in the south of the study area. The deuterium and oxygen-18 isotopes (Section 4.2), as well as chlorine-36 (Section 4.3), indicate that the water from bore 12627 has undergone evaporation. This bore is located adjacent to a pond which is filled by bore water and would prone to evaporation. Presumably water in this bore is being recycled between the pond and the aquifer, resulting in an elevated TDS value. The elevated TDS values in the remaining bores (principally located in the northern portion of the study area) have hydrochemical facies-types associated with older waters which have travelled a longer distance along a flow-path (Section 5.3.1).

Lab pH: The pH values (Fig 5.12) ranged from 4.74 to 7.77 with a median value of 6.77. Fifteen of 42 bores (35.7%) were below the lower limit of the aesthetic guideline value of 6.5. This suggests that the water from these bores may be corrosive and is not an indication that the water will adversely affect human health.

Lab Electrical Conductivity (EC): The EC values (Fig 5.13) measured at 25°C ranged from 167 to 1050 µS/cm with a median value of 512 µS/cm. EC measures the ability of the water to conduct an electric current and provides an indication of the ionic concentration.

Calcium: Calcium concentrations ranged from 0.62 to 79.70 mg/L (Fig 5.14) with a median value of 19.30 mg/L. Sources of calcium are igneous-rock minerals such as

silicates, pyroxenes, amphiboles, feldspars and silicate minerals produced during metamorphism. In sedimentary rock, calcium occurs as carbonate (calcite and aragonite), calcium magnesium carbonate (dolomite), calcite (limestone), calcium sulphate (gypsum and anhydrite) and calcium fluoride.

Magnesium: Magnesium concentrations ranged from 2.70 to 52.90 mg/L (Fig 5.15) with a median value of 18.60 mg/L. Magnesium in groundwater from igneous rocks primarily derives from ferromagnesian minerals like olivine, pyroxenes, amphiboles and dark-coloured micas. In metamorphic rocks, magnesium occurs in minerals such as chlorite, montmorillonite and serpentine. In sedimentary rocks, magnesium occurs as magnesite and other carbonates. Most groundwaters usually contain relatively small amounts of magnesium, except when they have been in contact with dolomite. Figure 5.16 suggests that Piccadilly Valley groundwaters have, with some exceptions, been in contact with dolomite due to the nearly equal proportions of calcium and magnesium ions (although a slightly greater proportion of magnesium ions is generally evident).

Sodium: Sodium concentrations ranged from 24.20 to 153 mg/L (Fig 5.17) with a median value of 45.7 mg/L. Sodium is primarily derived from feldspars in igneous rock and its weathering products (clay minerals). Shale and clay layers often yield water with a relatively high sodium content. Other sources of sodium include rainwater, pollution (e.g., sewage effluent and agrochemicals), irrigation leachate, connate water and water of marine origin. As the study area is close to the ocean, the local rainwater most likely would carry large quantities of oceanic aerosols that are rich in sodium.

Potassium: Potassium concentrations ranged from 0.76 to 6.24 mg/L (Fig 5.18) with a median value of 3.67 mg/L. Potassium is less common than sodium in igneous rock, but more abundant in sedimentary rock as potassium feldspars. These minerals are very insoluble and as a result potassium levels in groundwater are normally much lower than sodium concentrations.

Silicon/Silica: The element silicon (Si) is the second most abundant element (after oxygen) of the earth's upper crust. Dissolved silicon does not generally behave like a charged ion and as a result it is usually referred to as the oxide silica (SiO_2). Most silica in water is derived from the chemical breakdown of silicate minerals during the weathering process. Silicon (Si) concentrations ranged from 5.42 to 30.1 mg/L (Fig 5.19) with a median value of 15.85 mg/L.

Sulphur and Sulphate: Sulphate is an oxidised form of sulphur. Sulphur concentrations ranged from 1.5 to 72.8 mg/L with a median value of 5.06 mg/L (Fig 5.20). Sulphate concentrations ranged from 4.57 to 194 mg/L (Fig 5.21) with a median value of 13.40 mg/L. Sulfate is formed by oxidation of pyrite and other sulphides widely distributed in igneous and sedimentary rocks. Sulphate

concentrations in drinking water should not exceed 250 mg/L, as above this concentration the water may have a bitter taste.

Bicarbonate: Bicarbonate concentrations ranged from <0.005 to 300.3 mg/L (Fig 5.22) with a median value of 102.5 mg/L. Within the pH range of these waters, bicarbonate is the main component of alkalinity. Its sources include CO_2 from the atmosphere, CO_2 produced by the biota within the soil, the activity of sulphate reducers and other bacteria in deeper formations, and various carbonate rocks and minerals. Bicarbonate concentrations may also increase through the dissolution of silicate rocks.

Chloride: Chloride concentrations ranged from 37.3 to 246 mg/L (Fig 5.23) with a median value of 59.4 mg/L. No samples exceeded the aesthetic drinking water guideline value of 250 mg/L. Sources of chloride in groundwater are evaporite deposits, salty connate water and marine water. Igneous rock materials contribute little chloride. The primary source of chloride is thought to be derived from cyclic redistribution of oceanic chloride by atmospheric processes such as wind and rain. As the Piccadilly Valley study area is close to the ocean, the local precipitation most likely would carry large quantities of oceanic aerosols that are rich in chloride. Groundwaters containing significant amounts of chloride also tend to have high amounts of sodium (as is evident in Fig 5.24) suggesting the possibility of contact with water of marine origin.

Iron: Iron concentrations ranged from 0.01 to 14.46 mg/L (Fig 5.25) with a median value of 0.51 mg/L. Iron concentrations greater than the aesthetic drinking water guideline value of 0.03 mg/L were detected in 60% of the bores (25/42). Iron in public water supplies is highly undesirable, mainly due to aesthetic considerations; as it affects the taste of drinking water and stains laundry and plumbing fixtures. Iron compounds that settle in the distribution system gradually reduce the flow of water. A slimy coating on piping may also result due to the presence of iron bacteria, which derive their energy from the oxidation of ferrous into ferric iron (ANZECC, 1992).

The elevated iron concentrations found in Piccadilly Valley Groundwaters are naturally occurring and have as their source the igneous and metamorphic rocks found within the study area. The iron concentrations are plotted on a map of the study area in Fig 5.26. The bores containing iron concentrations greater than the guideline value were erratically distributed throughout the catchment and found within each rock type. The availability of iron for aqueous solution is affected by environmental conditions, especially changes in the degree of oxidation or reduction. Within the range of pH and Eh values obtained from field measurements, the predominant forms of iron are likely to be ferrous iron (Fe^{+2}) and ferric hydroxide precipitates ($Fe(OH)_3$). High concentrations of dissolved ferrous iron can occur in solution at the sites where either the reduction of ferric oxyhydroxides or oxidation of ferrous sulphides is occurring (Hem, 1989).

Manganese: Manganese concentrations ranged from <0.005 to 1.03 mg/L (Fig 5.27) with a median value of 0.05 mg/L. Manganese concentrations greater than the aesthetic drinking water guideline value of 0.1 mg/L were detected in a quarter (11/42) of the samples. Three bore samples (11601, 6709 and 13256), all of which were located in the Barossa Complex (Fig 5.28), had manganese concentrations exceeding the health drinking water guideline value of 0.5 mg/L. Manganese-containing minerals (biotite and horneblende) are common in igneous rocks and as a result higher concentrations of manganese in groundwaters from the Barossa Complex would be expected. Elevated concentrations of manganese may also be linked with the application of manganese-containing fungicides such as mancozeb.

At concentrations greater than 0.1 mg/L manganese may impart an undesirable taste and cause the staining of plumbing fixtures and laundry with black-coloured oxides. Some naturally occurring nuisance micro organisms can concentrate manganese and give rise to taste, odour and turbidity problems in distribution systems. The health-based guideline value of 0.5 mg/L for manganese in drinking water has been derived assuming that 10 mg/day is the amount of manganese that can be safely consumed from all sources. In one case involving human consumption of well water with a manganese concentration of about 14 mg/L, symptoms included lethargy, muscle tremors and mental disturbances; however, as concentrations of other metals were also high, the reported effects may not have been due solely to manganese (1996 NH&MRC/ARMCANZ).

Manganese tends to occur naturally at higher concentrations in oxygen-depleted water. A plot of manganese concentration versus DO (Fig 5.29) suggests that the higher manganese concentrations generally occur at lower DO concentrations. Under conditions to be expected in natural-water systems, any dissolved manganese will be in the 2^+ oxidation state. Many metamorphic and igneous minerals likely to be found in the study area contain divalent manganese as a minor constituent. The chemistry of manganese is somewhat like that of iron in that both metals participate in redox processes in weathering environments. Manganese concentrations above the guideline values were found throughout the study area and coincided with elevated iron concentrations in all but one case (bore 12023).

Fluoride: Fluoride concentrations ranged from 0.03 to 0.94 mg/L (Fig 5.30) with a median value of 0.37 mg/L. Sources of fluoride in groundwater are minerals such as calcium fluoride (fluorite), apatite, certain amphiboles, cryolite (in igneous rocks) and fluorspar (in sedimentary rocks). Some fluoride in drinking water is beneficial because it reduces tooth decay. At higher levels, however, fluorosis can occur. For this reason the health drinking water guideline value has been set at 1.5 mg/L.

Iodide: Iodide is widely distributed in the environment, but not in great abundance. The only bore in which iodide was detected (limit of detection <0.05 mg /L) was bore 6758 with a concentration of 0.16 mg/L, which only just exceeds the health drinking water guideline value of 0.1 mg/L. Bore 6758 is located in Aldgate Sandstone. The element iodine is present naturally in seawater and nitrate minerals, mostly in the form of iodide salts. It may be present in water due to leaching from salt and mineral

deposits. Iodine is an essential trace element for humans and is used in the synthesis of thyroid hormones. Prisoners drinking water containing up to 1 mg/L iodine for five years showed no signs of iodism or hypothyroidism, but some changes in uptake of iodine by the thyroid gland were observed (1996 NH&MRC/ARMCANZ).

5.3 HYDROCHEMICAL CLASSIFICATION

The major cations and anions were converted to milliequivalents per litre and their relative percentages calculated (Table 5.3). The relative percentage compositions of the major ion concentrations were plotted onto a trilinear Durov diagram (Fig 5.31) as described by Zaporozec (1972). The Durov diagram is useful for representing the cation and anion compositions of many samples on a single graph in which major groupings or trends in the data can be visually discerned. The data points in the main square field in Fig 5.31 generally plot in a straight line. The linear trend is from the NaCl vertex (in the upper right corner of the main square field) towards the mixed cation-anion (Mg-Ca-Na-HCO_3-Cl) type of water (in the central portion of the main square field). Different symbols are used to represent the formation type in which each bore was drilled. The clustering of waters within particular formations is not apparent. This is probably due to the intersection of several formations by some bores and/or due to the intermixing of waters from different formations via fractures. The outliers (bores 12921 and 13253) are characterised by elevated sulphate concentrations.

The compositions of identifiable groups of water types were categorised into hydrochemical facies (Table 5.3). The hydrochemical facies were expressed by those elements for which the concentrations comprised greater than 20% of the total cation and anion concentrations, respectively in milliequivalents per litre. The ions are listed in ascending order, with the cations followed by the anions. The facies are plotted on a map of the study area in Fig 5.32.

5.3.1 Chemical Evolution in Crystalline Rocks

Crystalline rocks, such as the igneous or metamorphic types of rocks found in the Piccadilly Valley, contain appreciable amounts of quartz and aluminosilicate minerals such as feldspars and micas. As these minerals were originally formed at temperatures and pressures far above those occurring at or near the earth's surface, they are thermodynamically unstable and tend to dissolve when in contact with water. The dissolution processes cause the water to acquire dissolved constituents and the rock to become altered mineralogically along joint planes.

The dissolution of feldspars, micas and other silicate minerals is strongly influenced by the chemically aggressive nature of water caused by dissolved carbon dioxide (which forms carbonic acid). When carbonate charged waters that are low in dissolved solids encounter silicate minerals, the cations and silica are leached leaving an aluminosilicate residue (usually a clay mineral such as kaolinite, illite or

Table 5.3: Calculation of Relative Percentages of Major Ions and Hydrochemical Facies for Piccadilly Valley Groundwaters

Bore Number	Geology	Ca (mg/L)	Ca (meq/L)	Ca (%meq)	Mg (mg/L)	Mg (meq/L)	Mg (%meq)	Na (mg/L)	Na (meq/L)	Na (%meq)	K (mg/L)	K (meq/L)	K (%meq)	Na +K (%meq)	Total Cations (meq/L)	HCO3 (mg/L)	HCO3 (meq/L)	HCO3 (%meq)	Cl (mg/L)	Cl (meq/L)	Cl (%meq)	SO4 (mg/L)	SO4 (meq/L)	SO4 (%meq)	Total Anions (meq/L)	TDI (meq)	Hydrochemical Facies
6834	Pbr	33.90	1.69	25.42	33.20	2.73	41.06	49.10	2.14	32.10	3.69	0.09	1.42	33.52	6.65	170.00	2.79	56.44	61.10	1.72	34.91	20.50	0.43	8.65	4.94	11.59	Mg-Na-Ca-HCO3-Cl
6835	Pbh	5.40	0.27	8.36	15.80	1.30	40.35	36.10	1.57	48.73	3.23	0.08	2.56	51.29	3.22	33.75	0.55	21.04	48.20	1.36	51.72	34.40	0.72	27.24	2.63	5.85	Na-Mg-Cl-SO4-HCO3
11935	Pbr	45.20	2.26	29.35	40.90	3.37	43.79	44.80	1.95	25.36	4.53	0.12	1.51	26.86	7.69	240.65	3.94	64.74	58.00	1.64	26.86	24.60	0.51	8.41	6.09	13.78	Mg-Ca-Na-HCO3-Cl
6598	Pbr	26.30	1.31	25.36	24.10	1.98	38.32	41.30	1.80	34.71	3.27	0.08	1.62	36.33	5.18	140.00	2.29	56.05	58.00	1.64	39.97	7.83	0.16	3.98	4.09	9.27	Mg-Na-Ca-HCO3-Cl
6567	Pbh	29.40	1.47	25.36	31.10	2.56	44.24	38.35	1.67	28.84	3.55	0.09	1.57	30.41	5.79	175.00	2.87	63.72	49.85	1.41	31.24	10.90	0.23	5.04	4.50	10.29	Mg-Na-Ca-HCO3-Cl
8924	Pbh	15.30	0.76	15.77	25.40	2.09	43.18	44.30	1.93	39.81	2.34	0.06	1.24	41.05	4.84	95.00	1.56	47.23	54.80	1.55	46.89	9.30	0.19	5.87	3.30	8.14	Mg-Na-HCO3-Cl
12429	Pbh	49.00	2.45	30.09	43.30	3.56	43.85	46.00	2.00	24.62	4.58	0.12	1.44	26.07	8.13	251.25	4.12	63.97	58.10	1.64	25.46	32.70	0.68	10.58	6.44	14.56	Mg-Ca-Na-HCO3-Cl
15938	Pbr	39.40	1.97	29.75	33.30	2.74	41.46	41.60	1.81	27.38	3.64	0.09	1.41	28.79	6.61	201.90	3.31	62.57	54.90	1.55	29.28	20.70	0.43	8.15	5.29	11.90	Mg-Ca-Na-HCO3-Cl
12827	Pbr	6.60	0.33	14.92	7.00	0.58	26.09	28.80	1.25	56.74	1.94	0.05	2.25	58.99	2.21	33.15	0.54	31.58	37.30	1.05	61.15	6.01	0.13	7.27	1.72	3.93	Na-Mg-Cl-HCO3
7224	Pr	1.66	0.08	3.99	2.70	0.22	10.71	39.90	1.74	83.64	1.35	0.03	1.66	85.30	2.08	13.75	0.23	14.27	42.00	1.18	75.02	8.12	0.17	10.71	1.58	3.65	Na-Cl
12045	Pbh	6.18	0.31	12.04	11.70	0.96	37.60	28.20	1.23	47.91	2.44	0.06	2.44	50.35	2.56	58.75	0.96	44.51	38.40	1.08	50.08	5.62	0.12	5.41	2.16	4.72	Na-Mg-Cl-HCO3
6776	Pbr	22.90	1.14	17.01	24.30	2.00	29.77	78.90	3.43	51.10	5.54	0.14	2.11	53.21	6.72	120.65	1.98	33.73	119.00	3.36	57.25	25.40	0.53	9.02	5.86	12.58	Na-Mg-Cl-HCO3
15410	Pbr	25.10	1.25	23.94	23.70	1.95	37.27	44.60	1.94	37.08	3.49	0.09	1.71	38.79	5.23	131.25	2.15	52.68	58.60	1.65	40.48	13.40	0.28	6.83	4.08	9.32	Mg-Na-Ca-HCO3-Cl
6750	Pbr	57.70	2.88	29.88	43.05	3.54	36.76	71.05	3.09	32.07	4.88	0.12	1.30	33.37	9.64	300.25	4.92	61.55	97.45	2.75	34.38	15.60	0.32	4.06	7.99	17.63	Mg-Na-Ca-HCO3-Cl
6746	Pbr	10.50	0.52	10.27	15.90	1.31	25.65	71.70	3.12	61.14	5.86	0.15	2.94	64.08	5.10	88.75	1.45	31.89	101.00	2.85	62.46	12.40	0.26	5.66	4.56	9.66	Na-Mg-Cl-HCO3
6742	Pbr	4.92	0.25	6.72	9.39	0.77	21.14	58.40	2.54	69.51	3.75	0.10	2.62	72.14	3.65	28.75	0.47	15.70	82.90	2.34	77.93	9.18	0.19	6.37	3.00	6.66	Na-Mg-Cl
13440	Pbr	1.99	0.10	2.00	8.45	0.70	14.02	92.20	4.01	80.88	6.00	0.15	3.10	83.98	4.96	46.25	0.76	17.41	118.00	3.33	76.47	12.80	0.27	6.12	4.35	9.31	Na-Cl
6759	Pbr	1.78	0.09	3.41	3.86	0.32	12.21	48.20	2.10	80.57	3.88	0.10	3.81	84.38	2.60	28.75	0.47	21.06	57.20	1.61	72.13	7.32	0.15	6.81	2.24	4.84	Na-Cl-HCO3
11934	Pbh	3.31	0.17	2.55	19.10	1.57	24.25	106.00	4.61	71.14	5.21	0.13	2.06	73.20	6.48	115.00	1.88	35.35	111.00	3.13	58.72	15.20	0.32	5.93	5.33	11.81	Na-Mg-Cl-HCO3
6627	Pbr	65.00	3.24	27.93	52.90	4.35	37.49	89.30	3.88	33.45	5.10	0.13	1.12	34.58	11.61	290.00	4.75	47.15	130.00	3.67	36.38	79.70	1.66	16.46	10.08	21.69	Mg-Na-Ca-HCO3-Cl
13253	Pbr	7.60	0.38	9.90	26.40	2.17	56.69	27.90	1.21	31.67	2.60	0.07	1.74	33.41	3.83	15.00	0.25	7.06	82.80	2.34	67.06	43.30	0.90	25.88	3.48	7.31	Mg-Na-Cl-SO4
13596	Pbr	18.00	0.90	13.57	16.40	1.35	20.39	98.60	4.29	64.80	3.22	0.08	1.24	66.04	6.62	108.75	1.78	30.62	130.00	3.67	63.01	17.80	0.37	6.37	5.82	12.44	Na-Mg-Cl-HCO3
12428	Pbr	43.60	2.18	29.99	38.80	3.19	44.02	40.70	1.77	24.41	4.49	0.11	1.58	25.99	7.25	246.25	4.04	67.44	59.20	1.67	27.90	13.40	0.28	4.66	5.99	13.24	Mg-Ca-Na-HCO3-Cl
13906	Pbu	5.17	0.26	10.09	10.40	0.86	33.48	31.20	1.36	53.09	3.34	0.09	3.34	56.43	2.56	52.50	0.86	38.87	42.40	1.20	54.04	7.54	0.16	7.09	2.21	4.77	Na-Mg-Cl-HCO3
6828	Pbr	41.90	2.09	27.33	40.40	3.32	43.46	48.80	2.12	27.75	4.35	0.11	1.45	29.21	7.65	235.00	3.85	61.60	72.80	2.05	32.84	16.70	0.35	5.56	6.25	13.90	Mg-Na-Ca-HCO3-Cl
6771	Pbr	29.80	1.49	22.36	30.30	2.49	37.49	58.80	2.56	38.46	4.40	0.11	1.69	40.15	6.65	161.25	2.64	47.43	89.30	2.52	45.21	19.70	0.41	7.36	5.57	12.22	Na-Mg-Ca-HCO3-Cl
13543	Pr	2.01	0.10	4.43	4.03	0.33	14.64	41.50	1.81	79.71	1.08	0.03	1.22	80.93	2.26	20.00	0.33	16.87	51.20	1.44	74.34	8.20	0.17	8.79	1.94	4.21	Na-Cl
12921	Pbr	79.70	3.98	52.30	19.40	1.60	20.99	45.30	1.97	25.91	2.37	0.06	0.80	26.71	7.60	67.50	1.11	16.47	55.70	1.57	23.39	194.00	4.04	60.13	6.72	14.32	Ca-Na-Mg-SO4-Cl
6782	Pbr	25.45	1.27	22.87	28.60	2.35	42.38	42.55	1.85	33.33	3.08	0.08	1.42	34.75	5.55	136.88	2.24	49.29	66.55	1.88	41.25	20.70	0.43	9.47	4.55	10.10	Mg-Na-Ca-HCO3-Cl
14178	Pbu	1.35	0.07	3.90	4.15	0.34	19.75	29.10	1.27	73.20	2.13	0.05	3.15	76.36	1.73	8.75	0.14	8.81	48.90	1.38	84.71	5.07	0.11	6.48	1.63	3.36	Na-Cl
12825	Pbh	8.46	0.42	12.07	18.10	1.49	42.58	33.80	1.47	42.03	4.54	0.12	3.32	45.35	3.50	85.00	1.39	47.16	50.60	1.43	48.32	6.41	0.13	4.52	2.95	6.45	Na-Mg-Cl-HCO3
6811	Pbr	45.00	2.25	24.56	46.60	3.83	41.95	67.20	2.92	31.98	5.39	0.14	1.51	33.49	9.14	280.00	4.59	58.74	99.90	2.82	36.07	19.50	0.41	5.20	7.81	16.95	Mg-Na-Ca-HCO3-Cl
6809	Pbh	1.83	0.09	4.34	3.67	0.30	14.37	38.20	1.66	79.06	1.83	0.05	2.23	81.29	2.10	5.00	0.08	6.11	41.30	1.17	86.81	4.57	0.10	7.09	1.34	3.44	Na-Cl
11601	Pr	20.60	1.03	17.04	15.50	1.28	21.14	83.10	3.61	59.92	4.49	0.11	1.90	61.82	6.03	96.25	1.58	29.09	105.00	2.96	54.63	42.40	0.88	16.28	5.42	11.46	Na-Mg-Cl-HCO3
6709	Pr	46.20	2.31	42.38	15.50	1.28	23.45	41.10	1.79	32.87	2.77	0.07	1.30	34.17	5.44	168.75	2.77	62.26	53.20	1.50	33.78	8.44	0.18	3.96	4.44	9.88	Ca-Na-Mg-HCO3-Cl
12827	Pr	20.90	1.04	10.53	25.70	2.11	21.36	153.00	6.66	67.23	3.38	0.09	0.87	68.10	9.90	87.50	1.43	16.14	246.00	6.94	78.12	24.50	0.51	5.74	8.88	18.78	Na-Mg-Cl
6583	Pbu	0.62	0.03	2.15	4.08	0.34	23.34	24.20	1.05	73.17	0.76	0.02	1.34	74.51	1.44	0.00	0.00	0.00	43.90	1.24	89.43	7.03	0.15	10.57	1.38	2.82	Na-Mg-Cl
13537	Pbr	42.00	2.10	23.19	45.60	3.75	41.51	69.70	3.03	33.54	6.22	0.16	1.76	35.30	9.04	276.90	4.54	59.06	100.00	2.82	36.71	15.60	0.32	4.23	7.68	16.72	Mg-Na-Ca-HCO3-Cl
12023	Pbh	26.90	1.34	29.61	12.20	1.00	22.14	49.00	2.13	47.01	2.19	0.06	1.24	48.25	4.53	113.75	1.86	49.95	59.50	1.68	44.97	9.09	0.19	5.07	3.73	8.27	Na-Ca-Mg-HCO3-Cl
6758	Pbr	8.11	0.40	7.79	12.65	1.04	20.05	82.50	3.59	69.13	6.13	0.16	3.02	72.16	5.19	87.50	1.43	31.92	99.70	2.81	62.59	11.85	0.25	5.49	4.49	9.68	Na-Cl-HCO3
6555	Pbh	2.54	0.13	3.31	7.86	0.65	16.91	66.50	2.89	75.61	6.24	0.16	4.17	79.78	3.83	61.25	1.00	30.35	73.90	2.08	63.04	10.50	0.22	6.61	3.31	7.13	Na-Cl-HCO3
13256	Pr	15.10	0.75	11.91	15.00	1.23	19.51	96.90	4.22	66.62	4.86	0.12	1.96	68.58	6.33	123.75	2.03	36.84	102.00	2.88	52.27	28.80	0.60	10.89	5.51	11.83	Na-Cl-HCO3

montmorillonite). The cations released to the water are normally Na, K, Mg and Ca. Another consequence of this process is a rise in pH and in HCO_3 concentration in the groundwater (Freeze and Cherry, 1979). As chloride and sulphate are not significant constituents in silicate rocks, there is generally no great increase in these anions as groundwater moves along flow paths in these rocks.

5.3.2 Hydrochemical Evolution of Piccadilly Valley Groundwaters

Table 5.4 includes the pH, TDS and tritium values for each sample, as well as the average values for each facies-type group of waters. Of note are the Na-Cl waters (group 5) which have both the lowest average pH and TDS values and the highest average tritium concentrations. The TDS of groundwater, as it moves along its flow path normally increases with mineral dissolution in the aquifer. Assuming that a low TDS arises from a shorter residence time, this would suggest that the Na-Cl (group 5) waters are recharge-type waters. As the Piccadilly Valley is located close to the ocean, Na-Cl dominated rainwaters would be expected. The average pH values of this group of waters (5.86) is also consistent with the pH of rainwater. The tritium concentrations of these waters also suggests that they are recharge waters. The exception is bore 13440, which had no detectable tritium; therefore, it is unlikely that the Na-Cl in this sample is derived from modern recharge water, but instead may originate from the dissolution of chloride-rich minerals along the flow path.

The mixed cation (Mg,Ca,Na)-HCO_3-Cl group of waters (group 1) have the highest average TDS (425 mg/L) and pH (7.41) values, followed by the Na-Mg-Cl-HCO_3 type of waters (group 2) which have an average TDS value of 338 and pH of 6.66. These groups are considered to be representative of relatively old or discharge-type waters (and had corresponding lower tritium concentrations). The bores presumed to be located in discharge areas in Section 4.1.2 (6771, 12428, 15410 and 6811) are all group 1 bores. As with the Na-Cl bores, there are in some cases bores which have anomalous tritium concentrations for their particular their facies group. Some examples are bores 8924, 6709 and 12023, which have elevated tritium concentrations, yet their hydrochemistry falls within group 1. This is presumably due to the mixing of recent recharge water with older waters. The facies types represented by groups 3 and 4 are presumably intermediate types of waters and represent mixing between the three groups of water (groups 5 with groups 1 and 2).

The sulphate-rich facies types (group 6) are distinctly different within the group itself and from the other groups. Bore 12921 has one of the most elevated TDS values (634 mg/L) and a low tritium concentration. One would presume that it is an older discharge-type of water. Bores 6835 and 13253 have relatively low salinities and high tritium concentrations; following the same logic, one would presume that these waters are more likely to be recharge-type waters. The hydrochemistry from the group 6 bores most likely reflects contact with localised sources of sulphate (eg., gypsum, anhydrite, oxidised pyrite) by infiltrating rainwater.

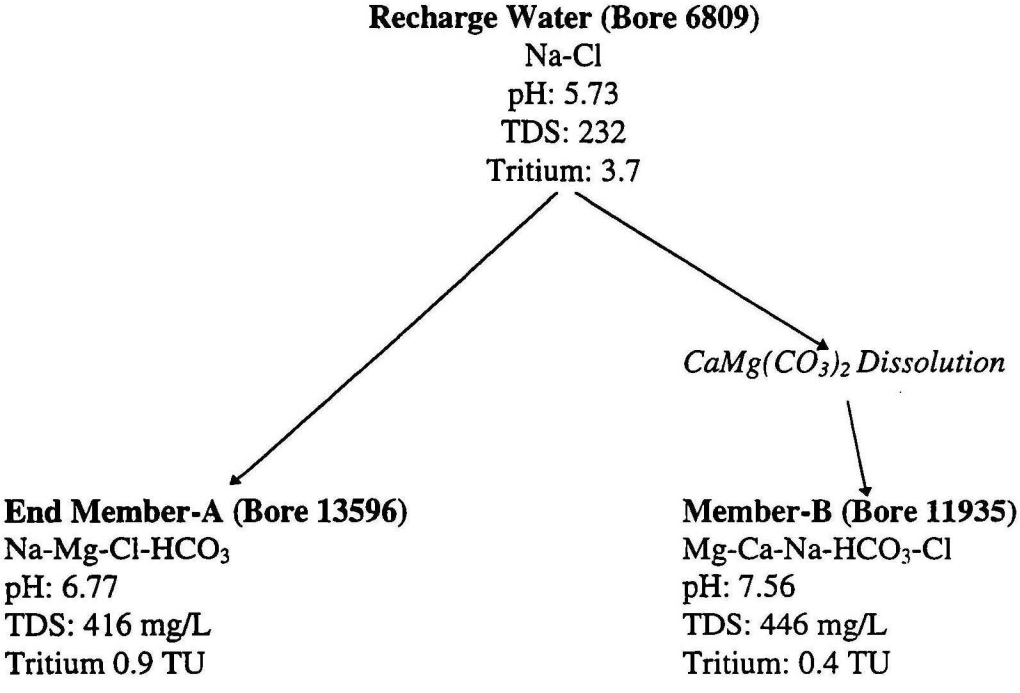
Table 5.4: Hydrochemical Facies Groups and Associated Parameters for Piccadilly Valley Groundwaters

Bore Number	Facies	Group	Lab pH	Average pH	TDS (mg/L)	Average TDS	Tritium (TU)	Average TU
11935	Mg-Ca-Na-HCO3-Cl	1	7.56	7.41	446	425	0.4	0.95
12429	Mg-Ca-Na-HCO3-Cl	1	7.64		424		0.9	
15938	Mg-Ca-Na-HCO3-Cl	1	7.51		358		0.7	
12428	Mg-Ca-Na-HCO3-Cl	1	7.75		402		0.5	
6834	Mg-Na-Ca-HCO3-Cl	1	7.38		386		1.3	
6598	Mg-Na-Ca-HCO3-Cl	1	7.08		314		0.7	
6567	Mg-Na-Ca-HCO3-Cl	1	7.49		316		1.2	
15410	Mg-Na-Ca-HCO3-Cl	1	7.03		360		0.4	
6750	Mg-Na-Ca-HCO3-Cl	1	7.63		533		0.5	
6627	Mg-Na-Ca-HCO3-Cl	1	7.77		658		0.9	
6828	Mg-Na-Ca-HCO3-Cl	1	7.76		390		0.7	
6782	Mg-Na-Ca-HCO3-Cl	1	7.23		440		0.8	
6811	Mg-Na-Ca-HCO3-Cl	1	7.62		564		0.2	
13537	Mg-Na-Ca-HCO3-Cl	1	7.64		544		0.3	
6771	Na-Mg-Ca-HCO3-Cl	1	7.22		496		0.6	
8924	Mg-Na-HCO3-Cl	1	6.77		292		2.3	
12023	Na-Ca-Mg-HCO3-Cl	1	6.97		336		1.8	
6709	Ca-Na-Mg-HCO3-Cl	1	7.28		386		2.9	
12827	Na-Mg-Cl-HCO3	2	6.08	6.66	218	338	3.3	1.26
12045	Na-Mg-Cl-HCO3	2	6.27		232		0.9	
6776	Na-Mg-Cl-HCO3	2	7.13		492		1.5	
6746	Na-Mg-Cl-HCO3	2	6.75		316		0.3	
11934	Na-Mg-Cl-HCO3	2	6.80		478		0.6	
13596	Na-Mg-Cl-HCO3	2	6.77		416		0.9	
13906	Na-Mg-Cl-HCO3	2	6.31		168			
12825	Na-Mg-Cl-HCO3	2	7.25		286		0.9	
11601	Na-Mg-Cl-HCO3	2	6.60		438		1.7	
6759	Na-Cl-HCO3	3	6.10	6.37	202	323	1	1.05
6758	Na-Cl-HCO3	3	6.32		378		0.4	
6555	Na-Cl-HCO3	3	6.30		300		1.9	
13256	Na-Cl-HCO3	3	6.75		410		0.9	
6742	Na-Mg-Cl	4	6.09	5.78	252	352	1.9	1.45
12627	Na-Mg-Cl	4	6.50		718		1	
6583	Na-Mg-Cl	4	4.74		86			
7224	Na-Cl	5	5.72	5.86	212	250	3.8	2.67
13440	Na-Cl	5	6.22		298		0.25	
13543	Na-Cl	5	6.17		302		2.5	
14178	Na-Cl	5	5.46		204		3.1	
6809	Na-Cl	5	5.73		232		3.7	
6835	Na-Mg-Cl-SO4-HCO3	6	6.36	6.38	244	397	1.9	1.90
12921	Ca-Na-Mg-SO4-Cl	6	6.75		634		0.4	0.40
13253	Mg-Na-Cl-SO4	6	6.04		312		3.4	3.40

Each of the major ions were plotted against the total dissolved ions (TDI) in figures 5.33 and 5.34. Each of these figures show a positive correlation that demonstrates increasing ion concentrations with increasing total dissolved ions. The Na, K, Mg, Ca and HCO_3 ions (Fig 5.33) in particular show the largest increases. In contrast, the plots of Cl and SO_4 (Fig 5.34) show relatively little increase in concentration with TDI. Figure 5.35 demonstrates an increase in pH with increasing TDS, as would be expected with the observed increases in bicarbonate concentrations.

Two linear trends are apparent in Figures 5.33 and 5.34 with a scattering of points between them, which is indicative of mixing. Two lines have been arbitrarily drawn to illustrate the general trends and labelled 'A' and 'B' - one trend is towards end-member A and the other is towards end-member B. End-member A is relatively depleted in Ca, Mg, HCO_3 and SO_4, but relatively enriched in Na and Cl. In contrast, end-member B is enriched in Ca, Mg, HCO_3 and SO_4, but depleted in Na and Cl. The fact that end-member B is considerably enriched in Ca, Mg and HCO_3 suggests that it has been influenced by the dissolution of dolomite and silicate minerals. The Woolshed Flat Shale has a dolomitic member and it is possible that those bores plotting along the linear trend towards point B have waters which have been in contact with the Woolshed Flat Shale.

Taking bores representative of end-members A and B of high TDI and comparing them to a bore representative of the point of origin with low TDI from which the two trends diverge, one can observe the following:



The recharge water is a Na-Cl type of water with low TDS from which the groundwater evolves to either end-member A or B. End-member A is represented by a Na-Mg-Cl-HCO_3 type of facies and end-member-B a Mg-Ca-Na-HCO_3-Cl type of facies, both of which have higher TDS and pH values and lower tritium concentrations (indicating a greater age) than the recharge type of water. Mixing is occurring between rainwater recharge these two end-members.

Fig 5.1 April-May 1994 Field Electrical Conductivity of Piccadilly Valley Groundwaters

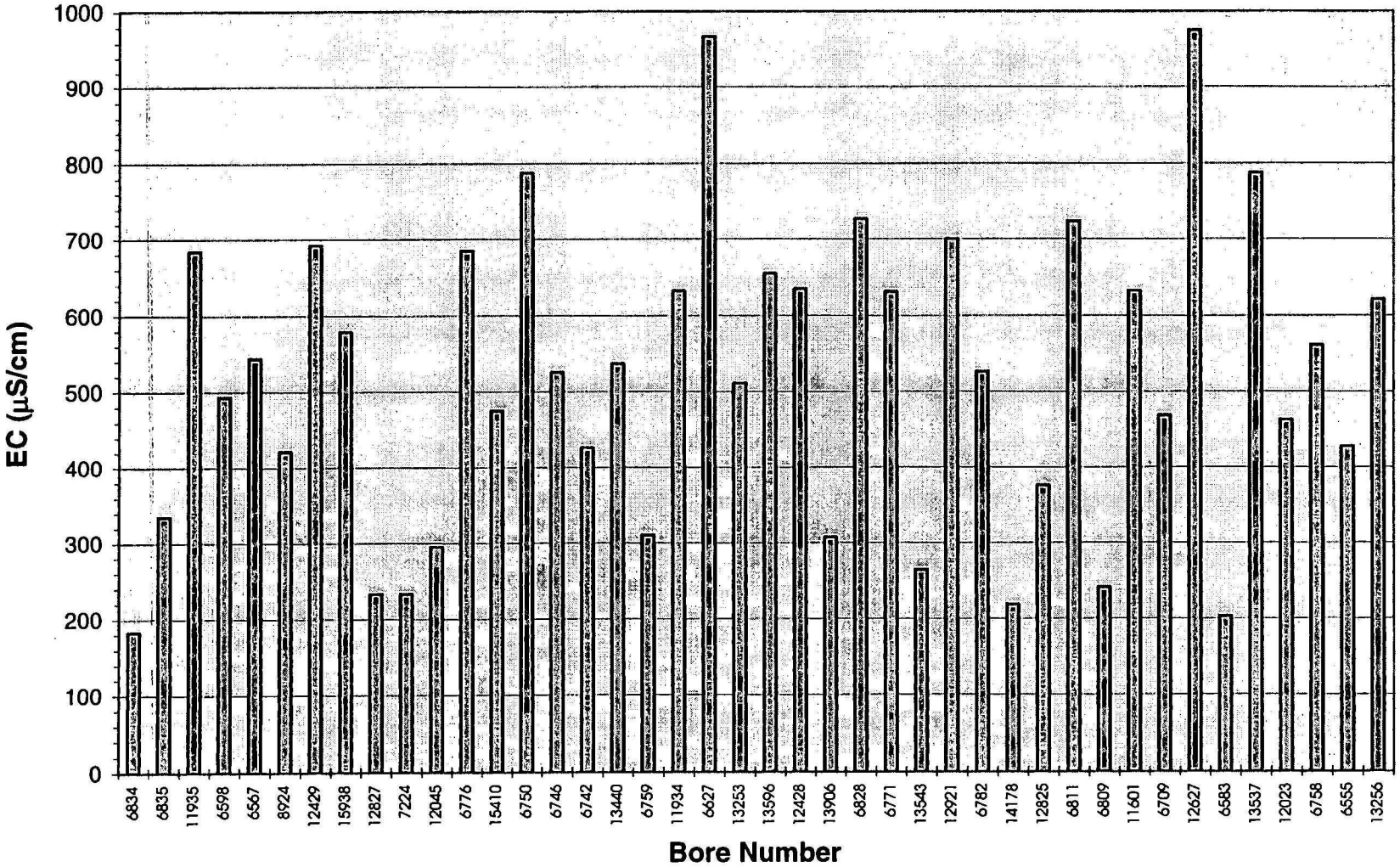


Fig 5.2 April-May 1994 Field pH of Piccadilly Valley Groundwaters

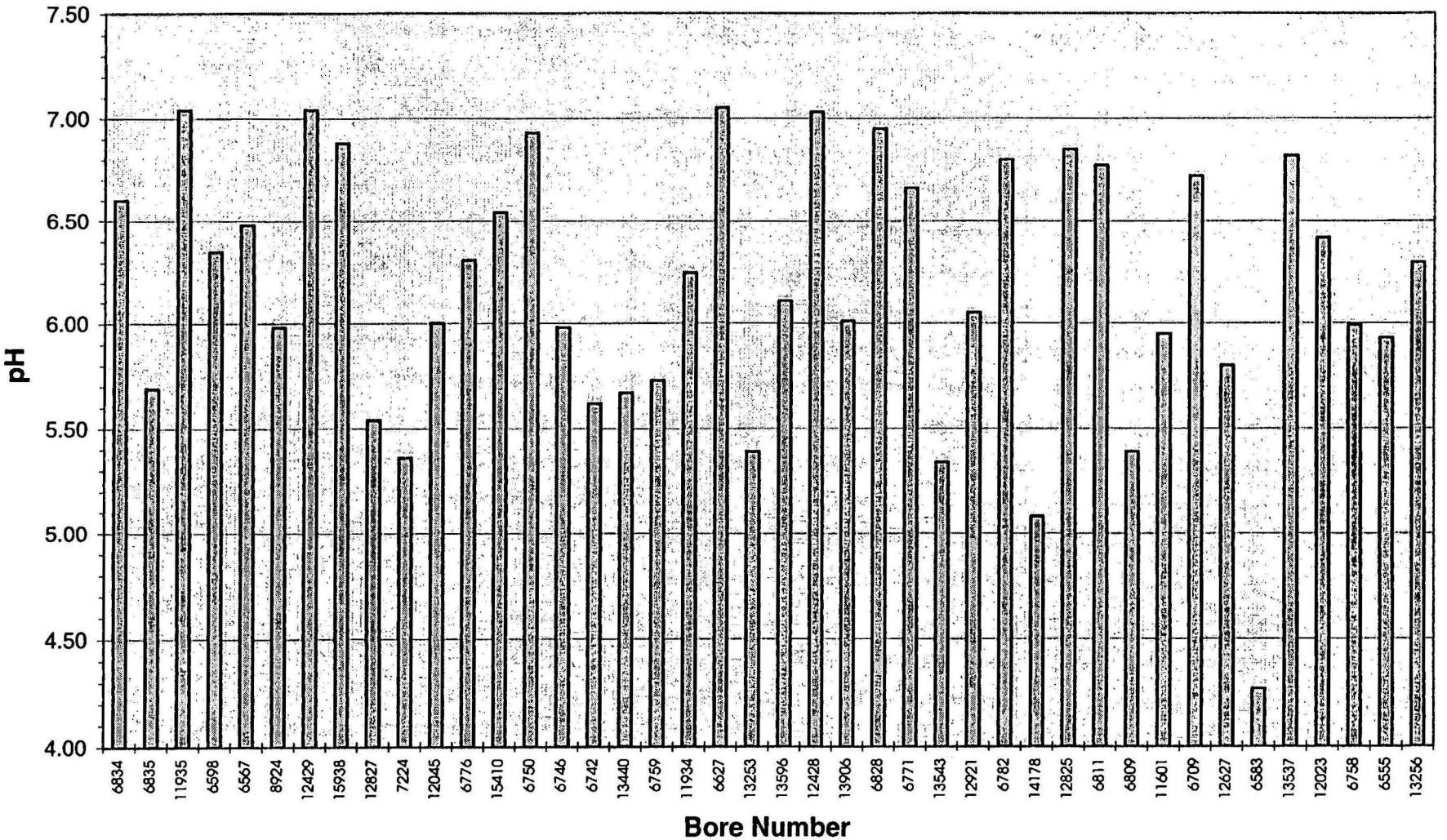


Fig 5.3 April-May 1994 Field Eh of Piccadilly Valley Groundwaters

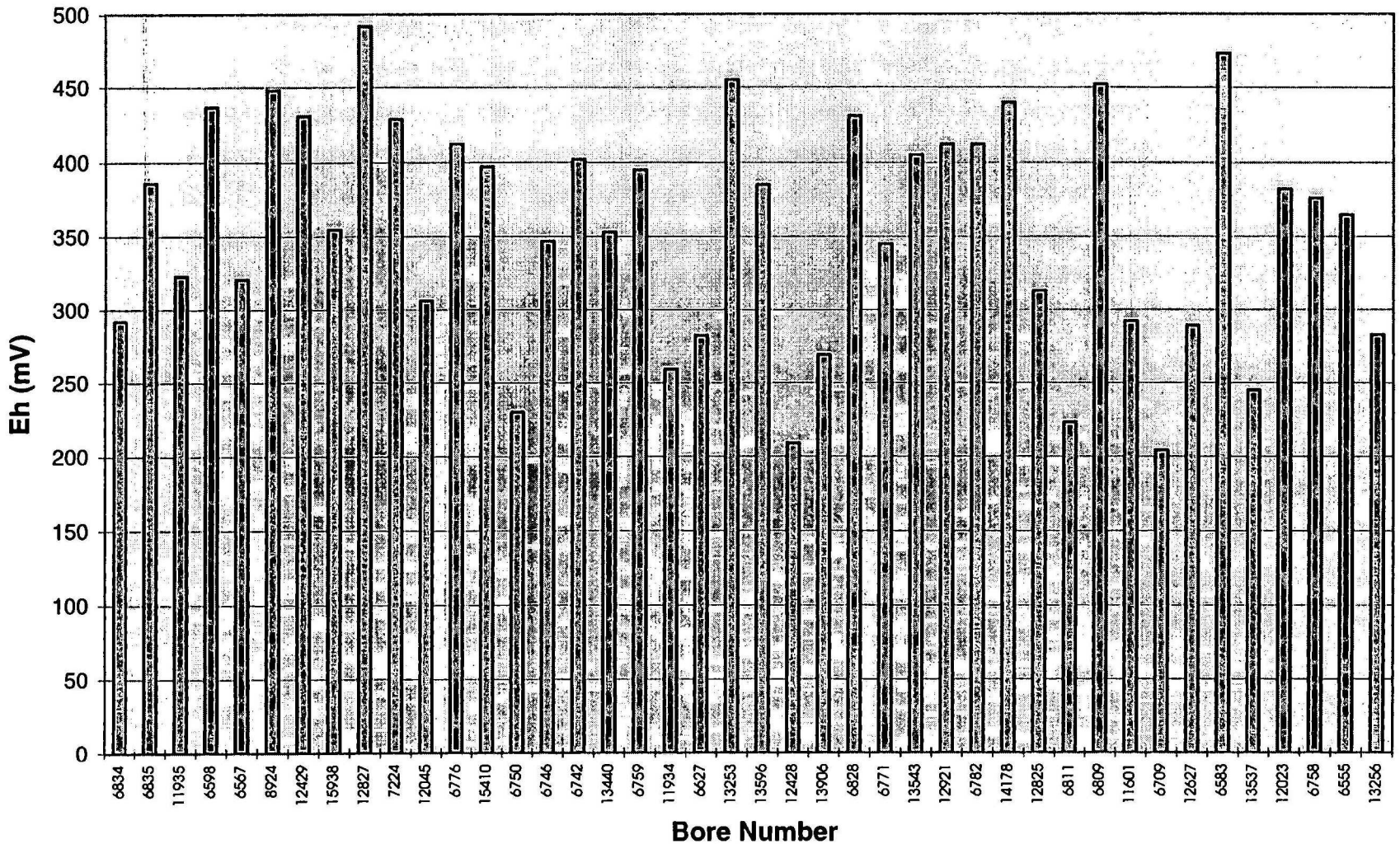


Fig 5.4 April-May 1994 Field Dissolved Oxygen of Piccadilly Valley Groundwaters

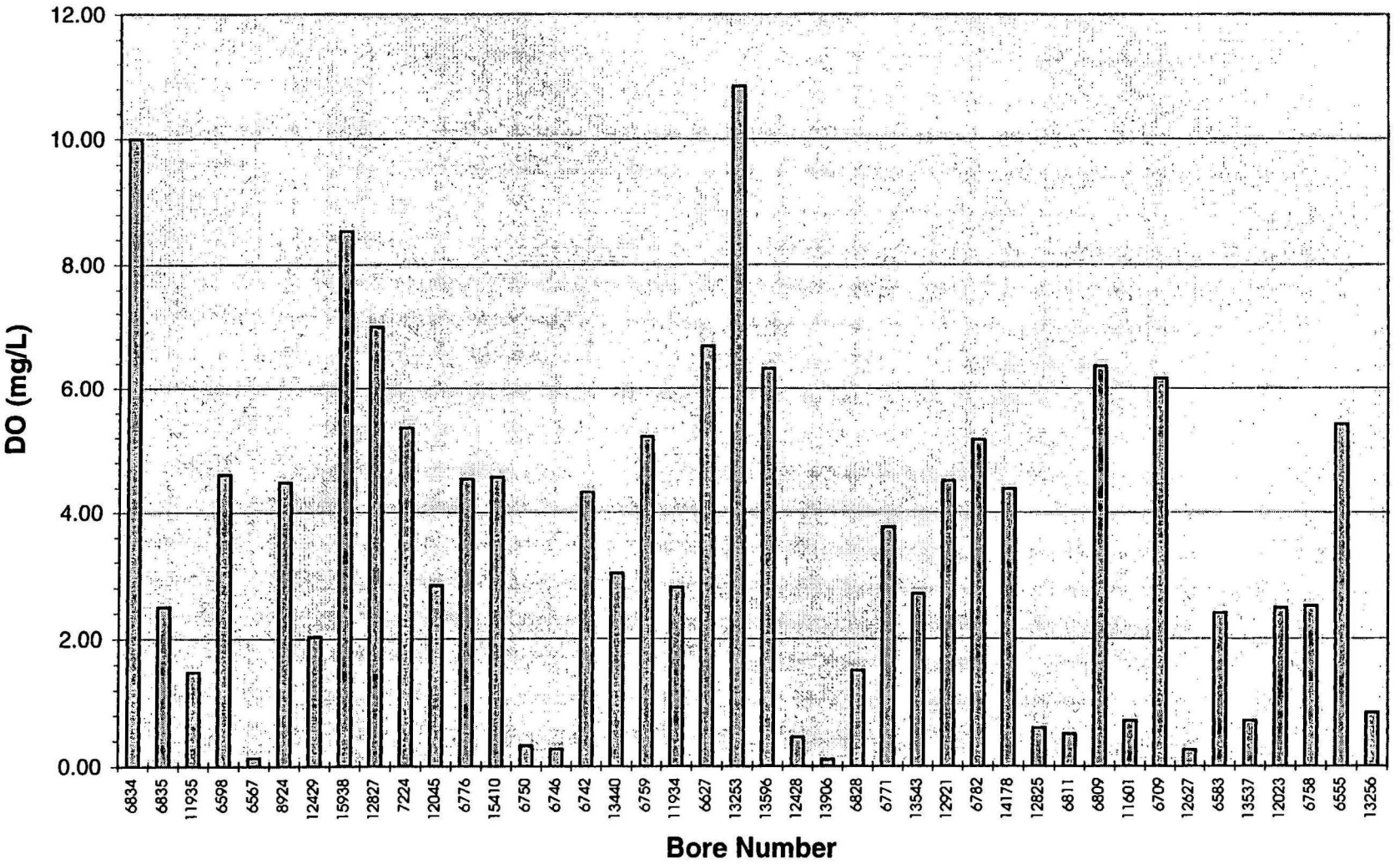


Fig 5.5 April-May 1994 Temperature of Piccadilly Valley Groundwaters

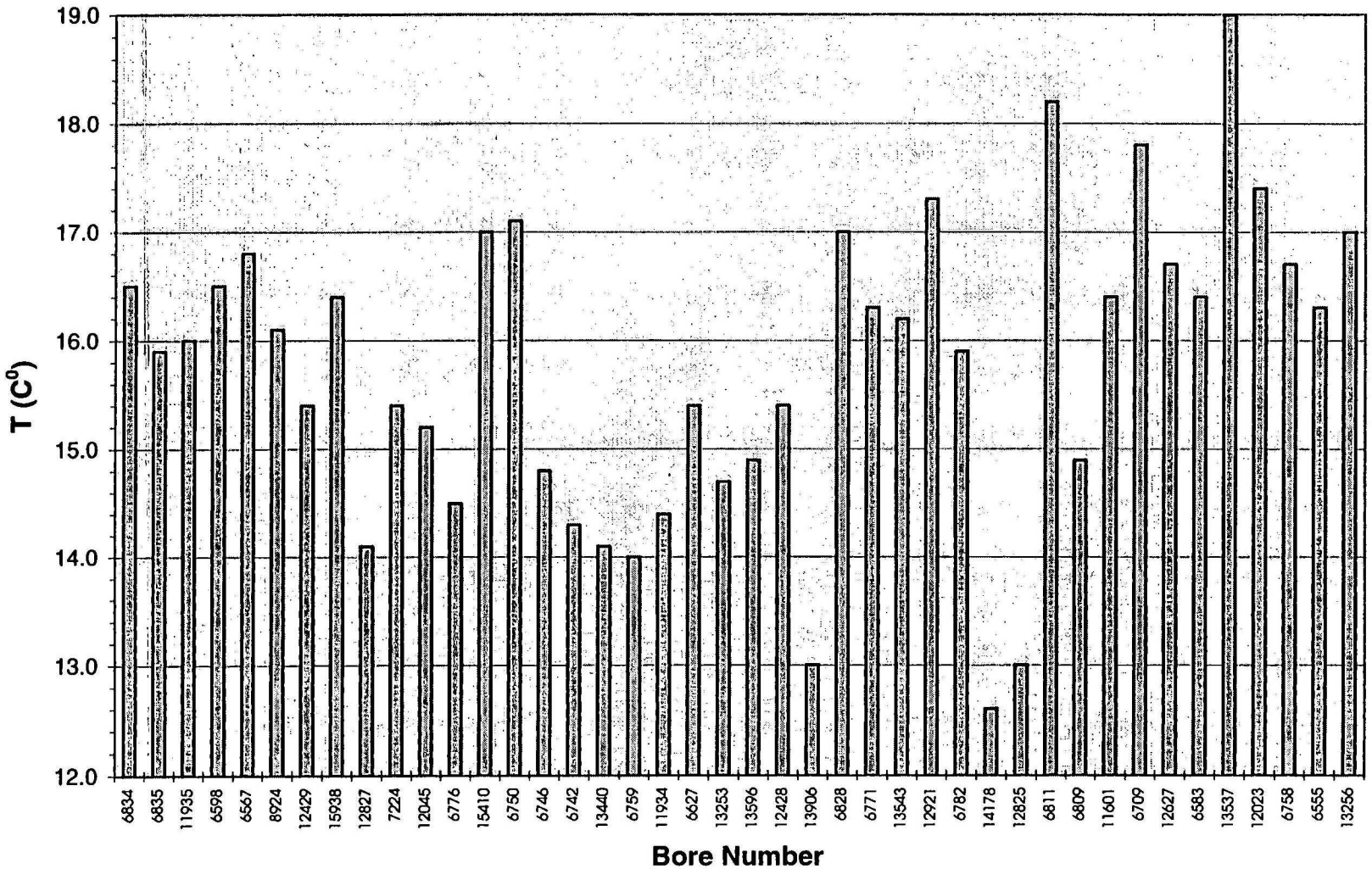


Fig 5.6 Dissolved Oxygen vs Eh

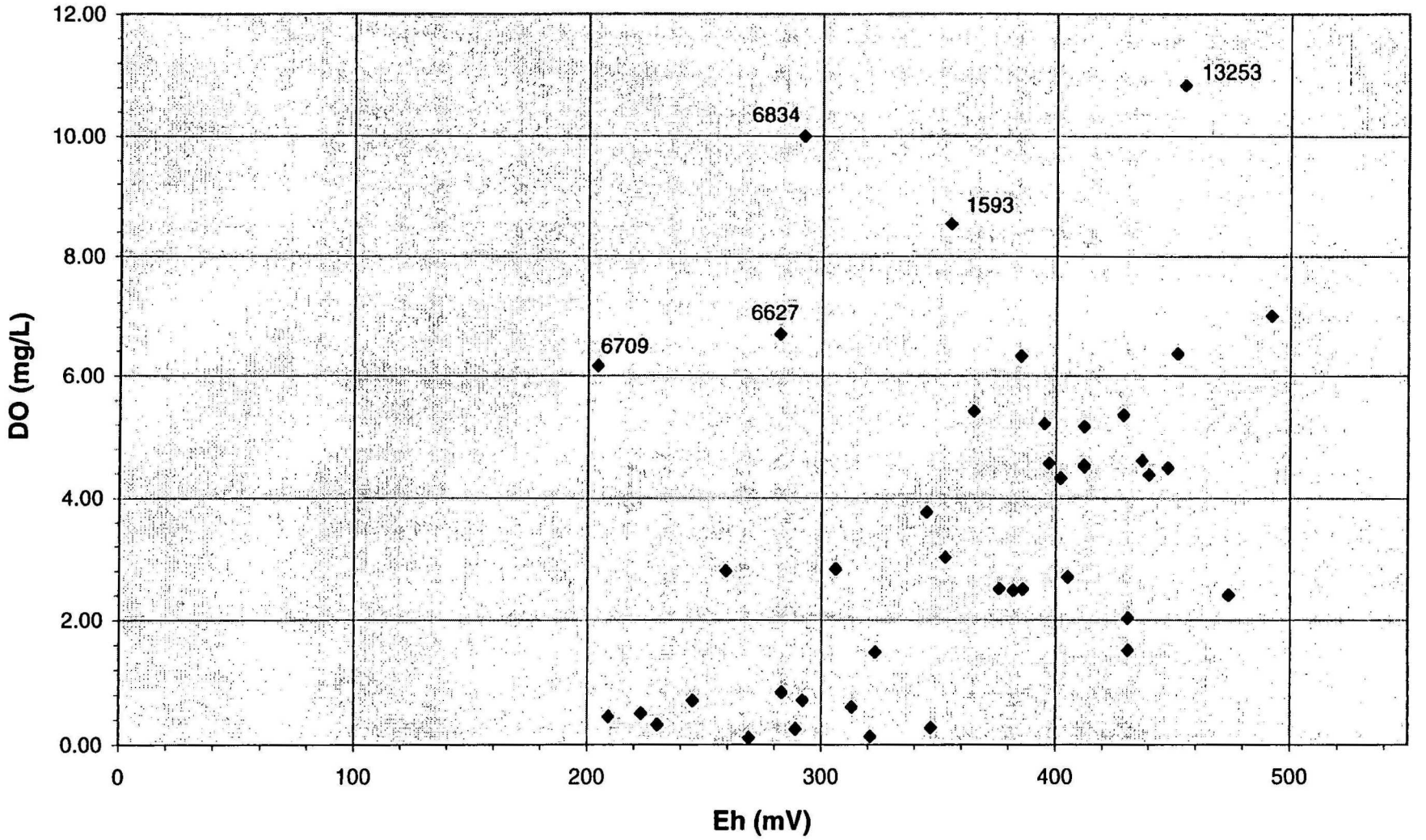


Fig 5.7 Field EC vs Lab EC

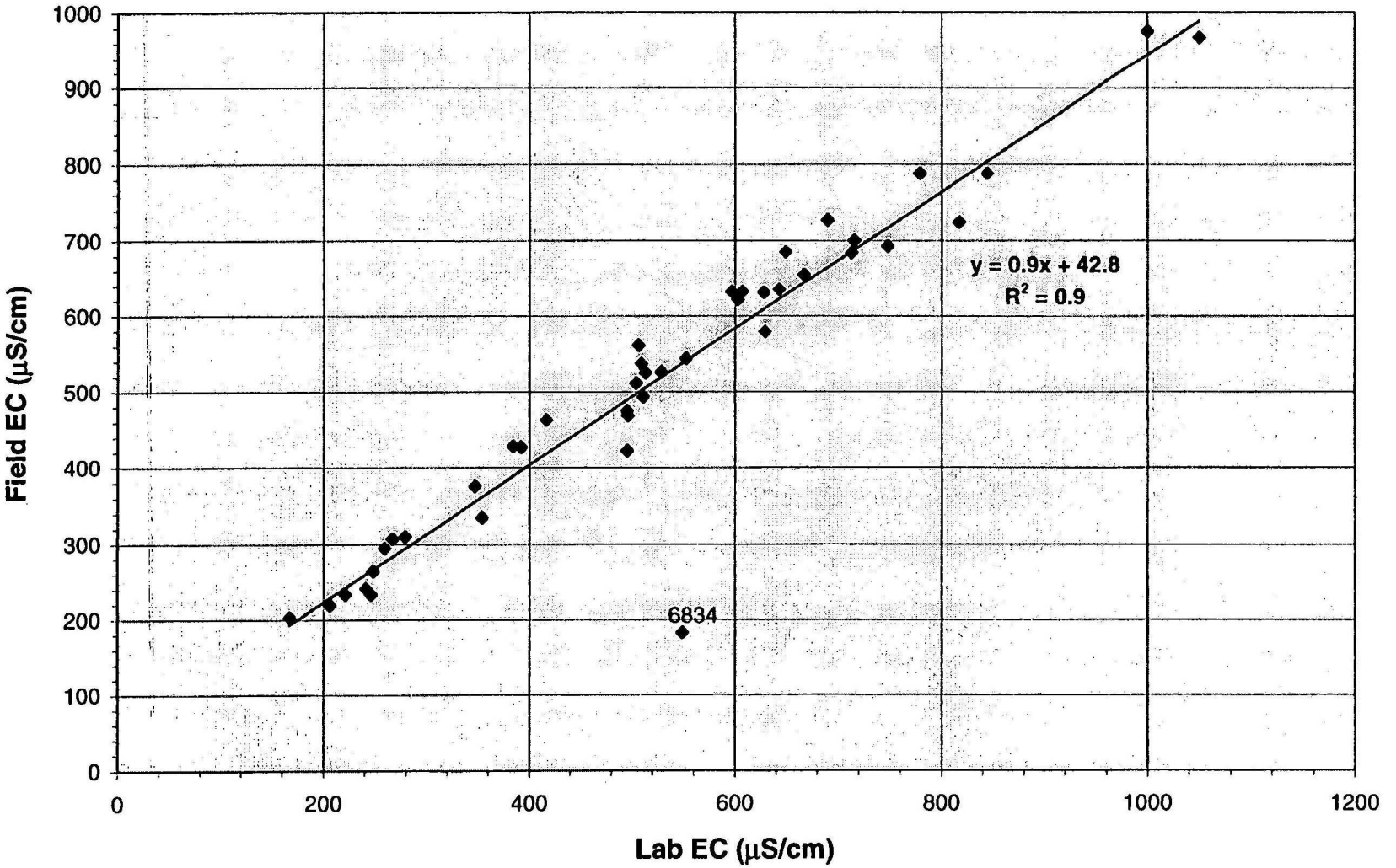


Fig 5.8 Lab EC vs Lab TDS

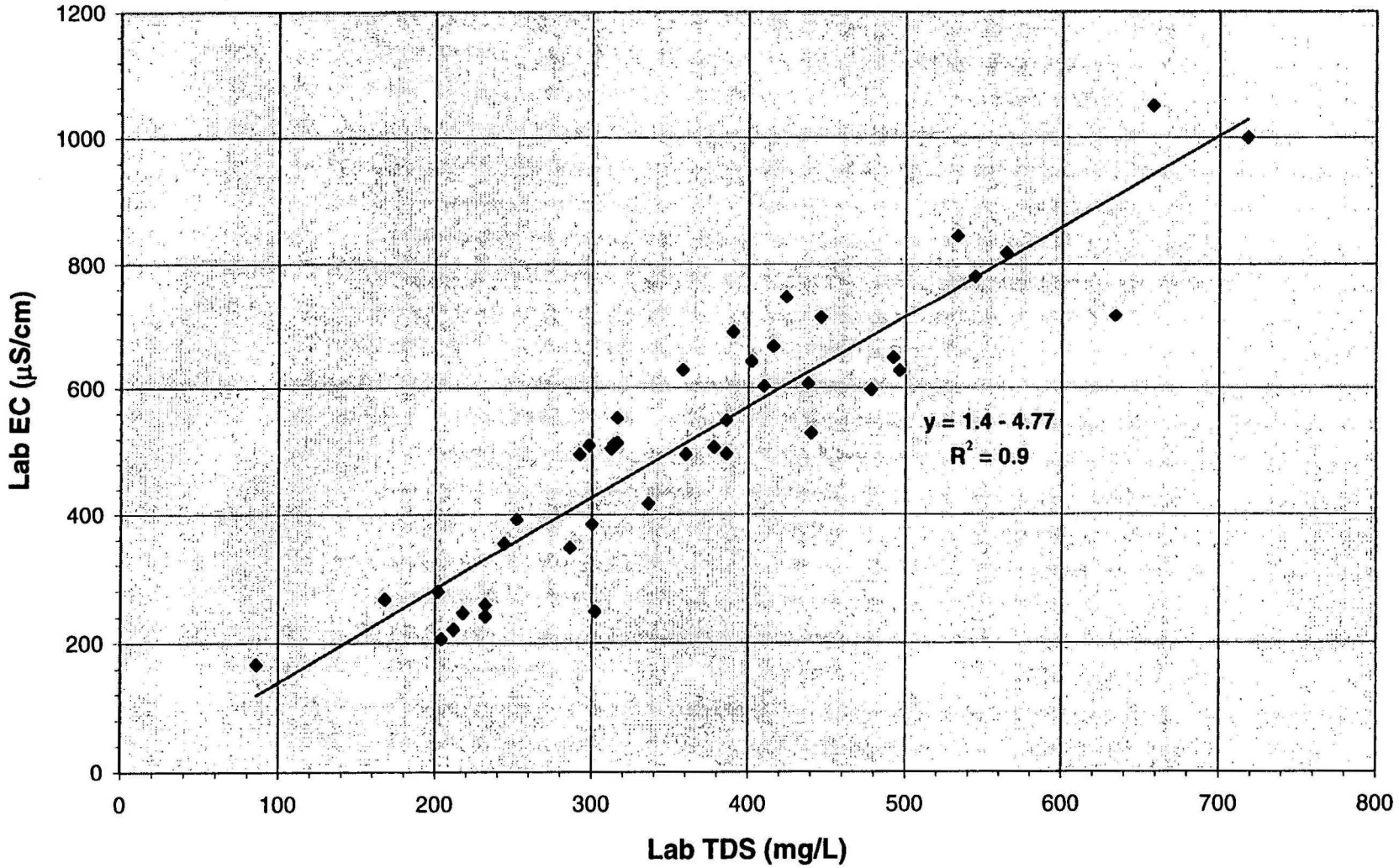


Fig 5.9 Field pH vs Lab pH

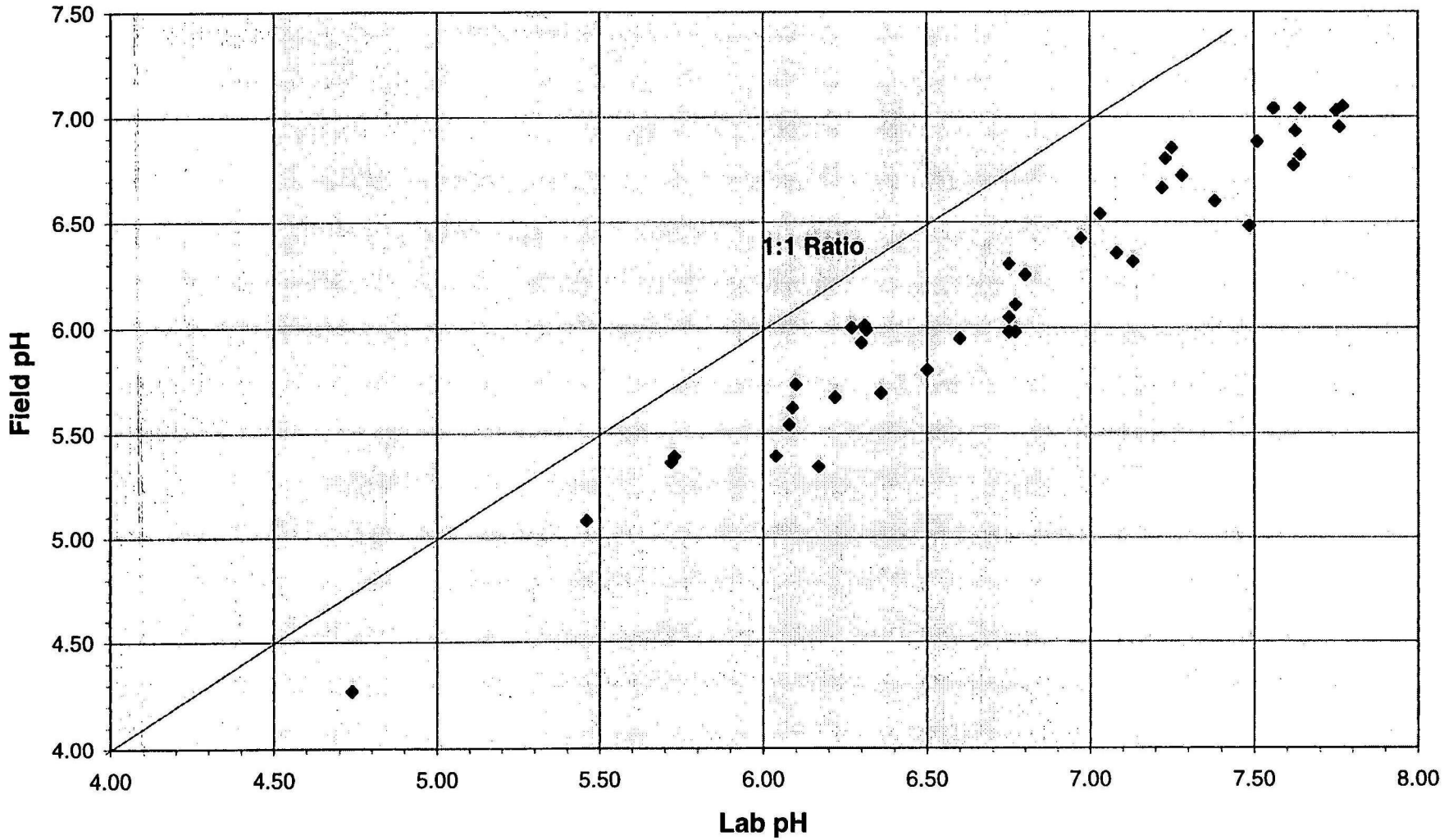
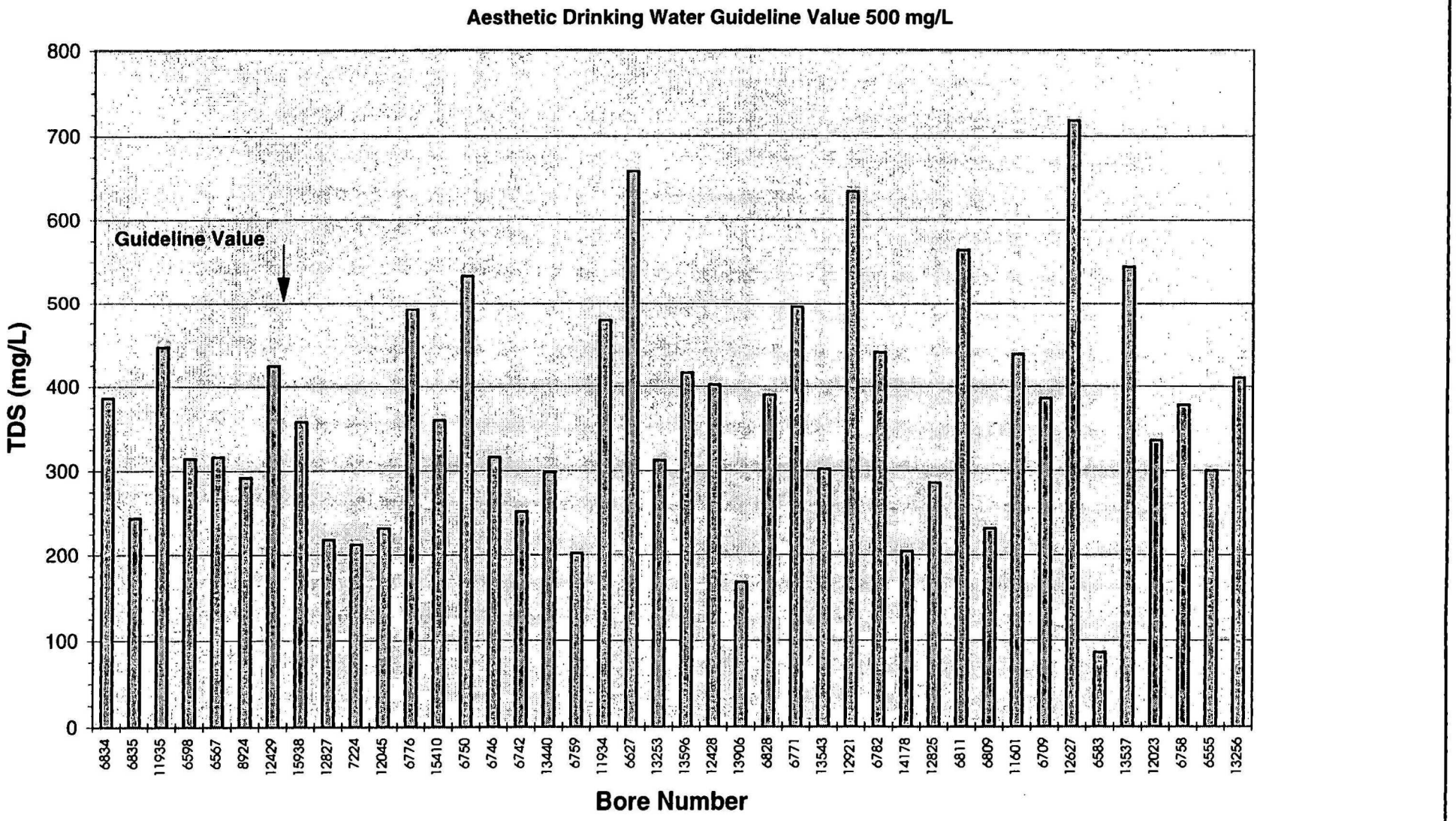


Fig 5.10 Piccadilly Valley: April-May 1994 Groundwater - TDS



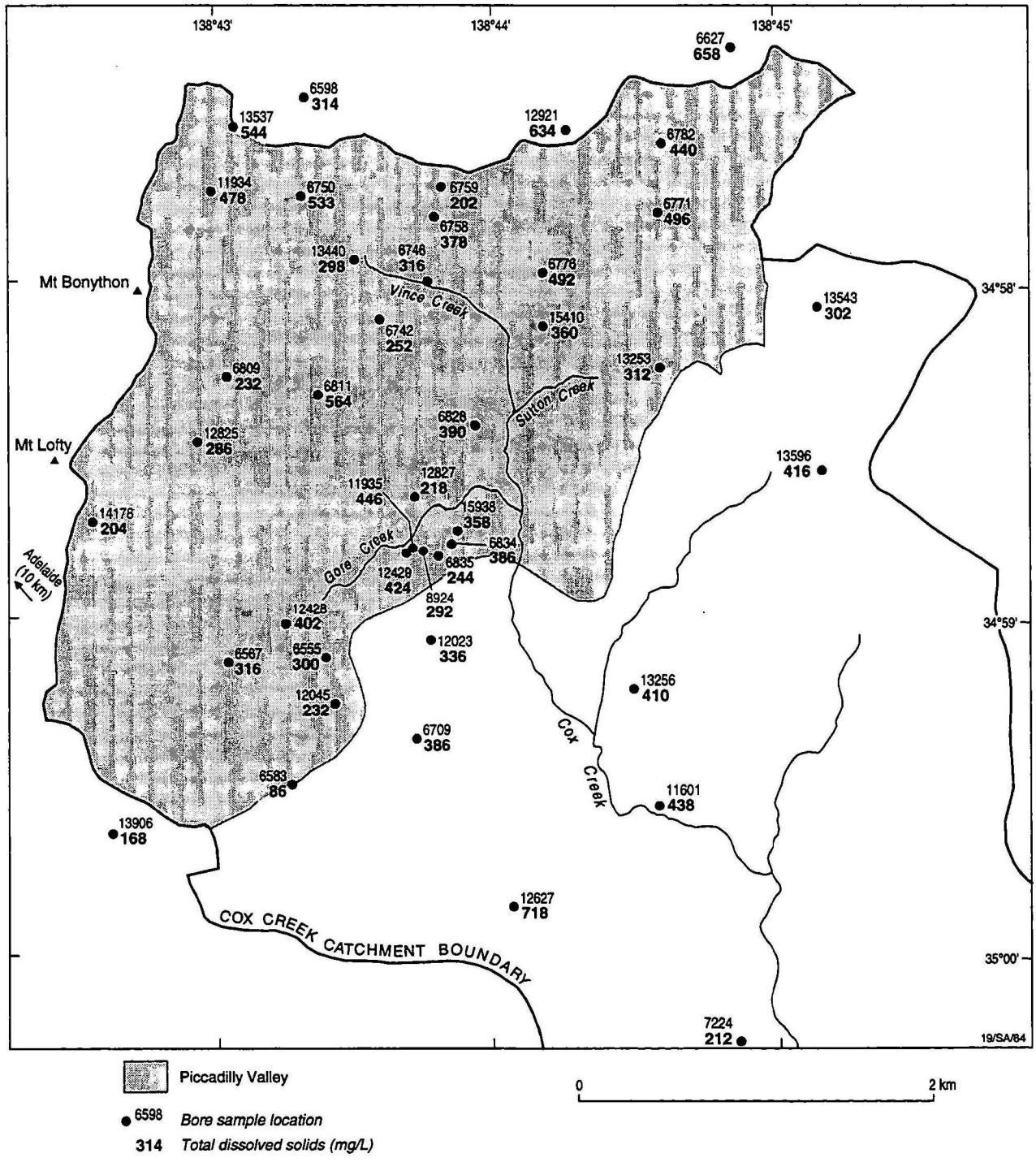


Figure 5.11 Distribution of TDS concentrations in Piccadilly Valley Groundwaters

Fig 5.12 Piccadilly Valley: April-May 1994 Groundwater - Lab pH Values

Aesthetic Drinking Water Guideline Value between 6.5-8.5

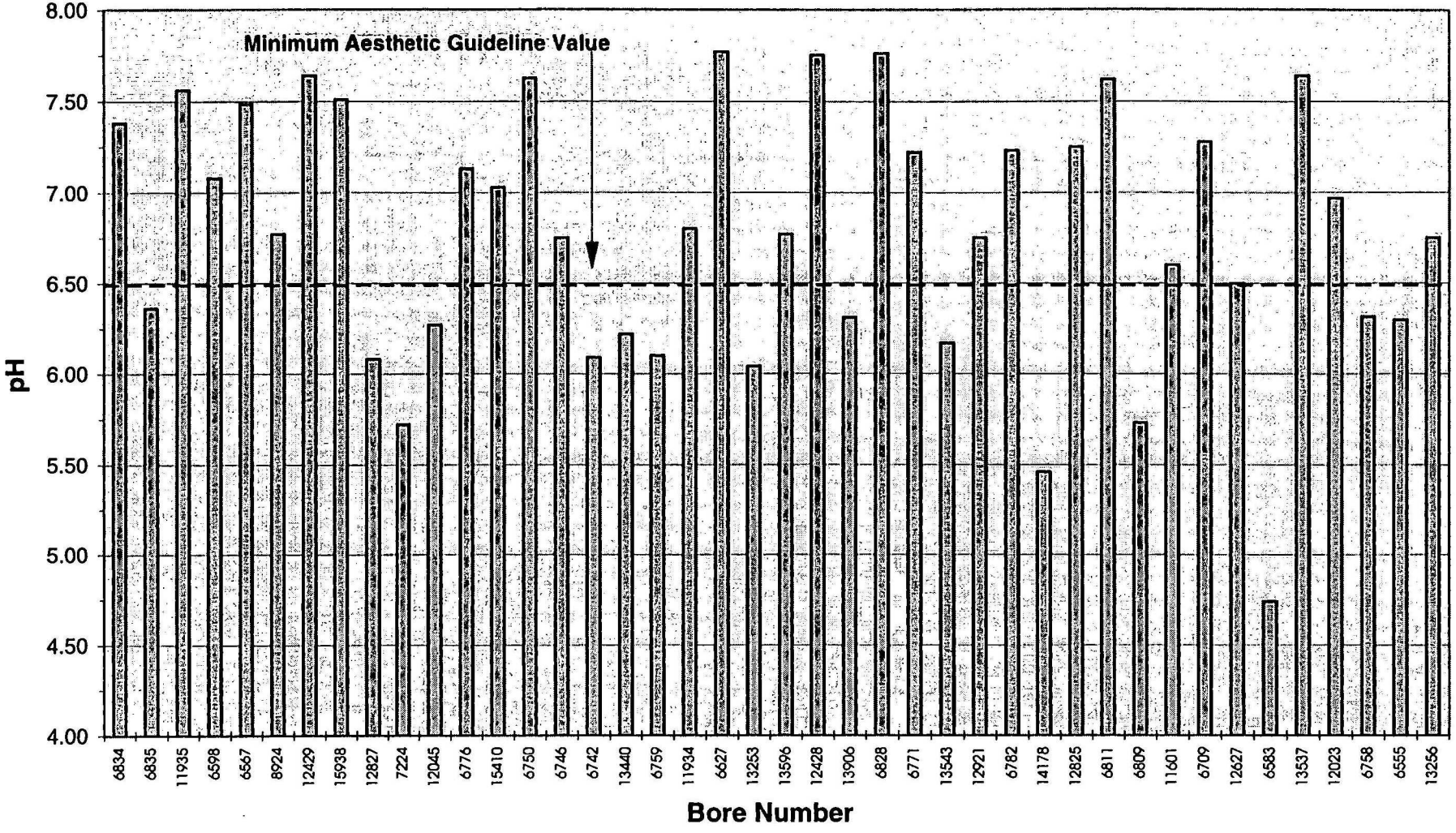


Fig 5.13 Piccadilly Valley: April-May 1994 Groundwater - Lab EC

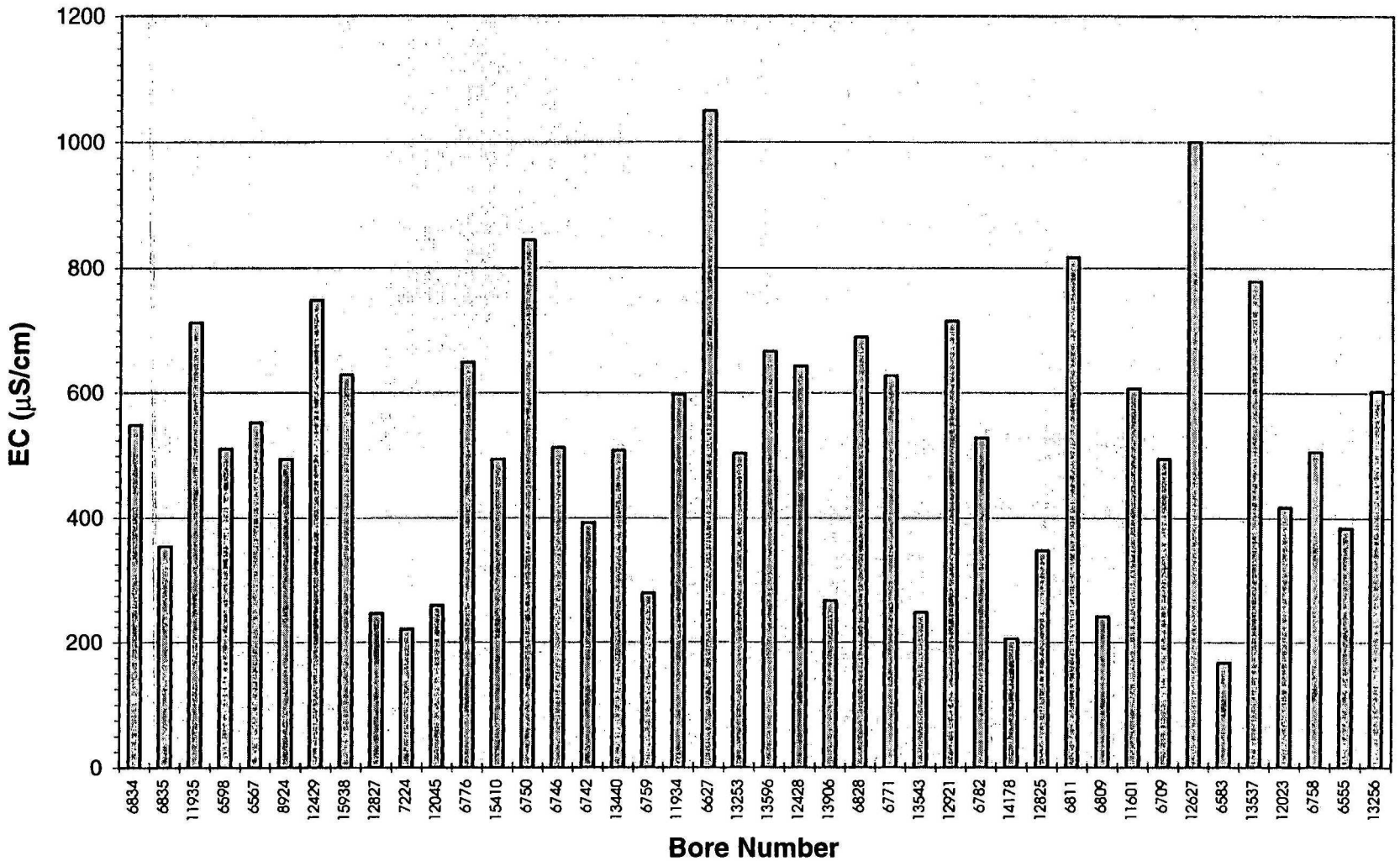


Fig 5.14 Piccadilly Valley: April-May 1994 Groundwater - Calcium Concentrations

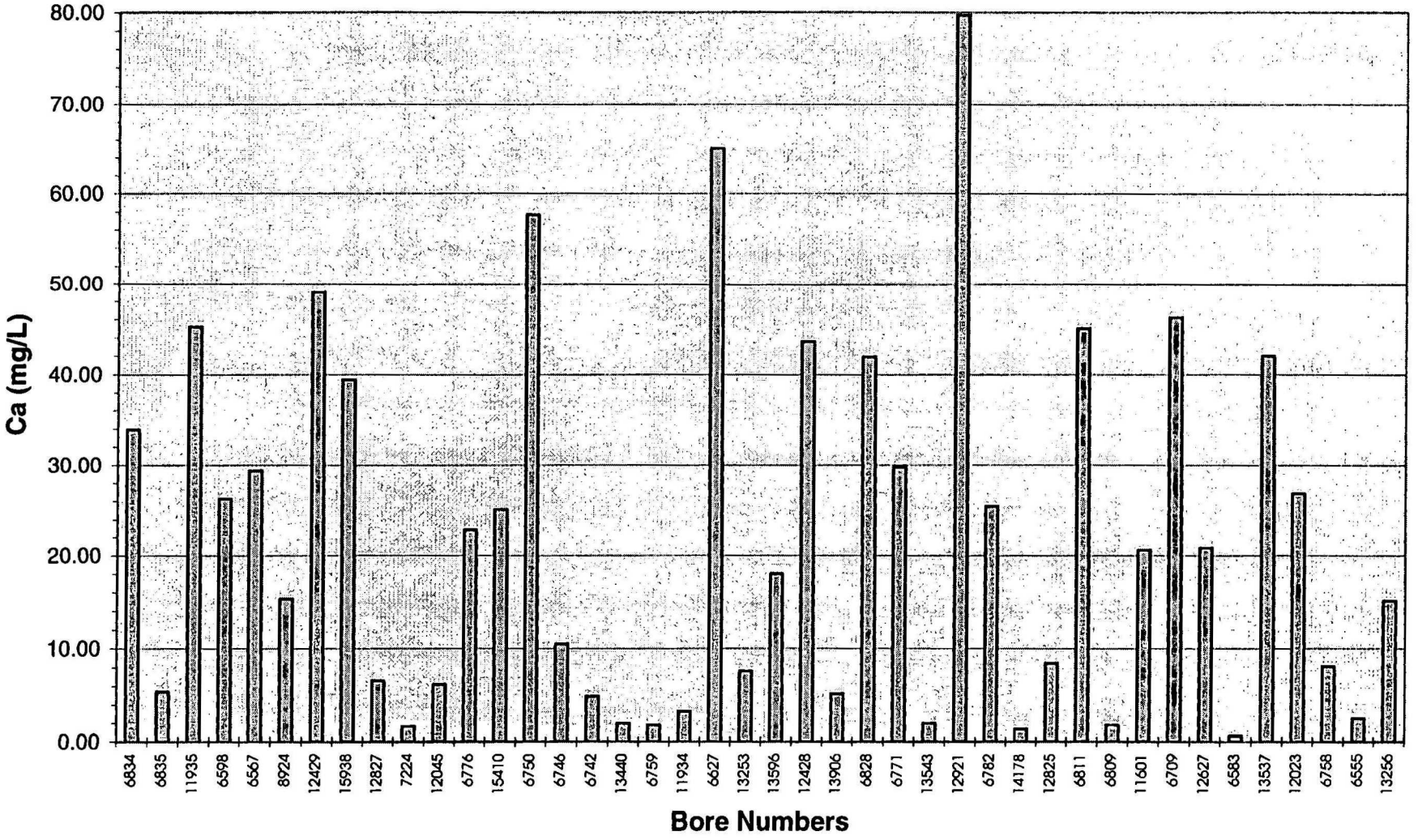


Fig 5.15 Piccadilly Valley: April-May 1994 Groundwater - Magnesium Concentrations

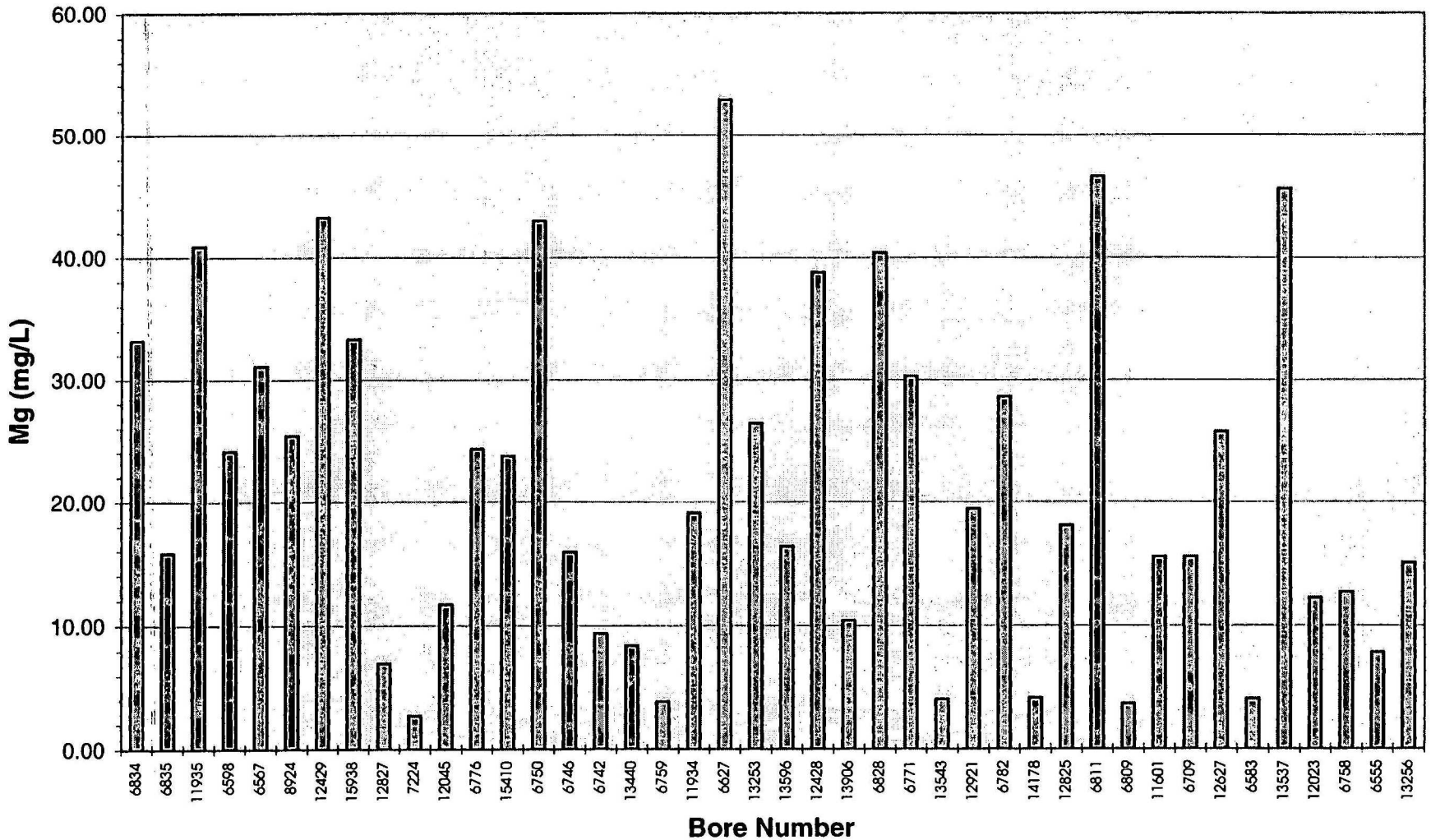


Fig 5.16 Piccadilly Valley: April-May 1994 Groundwater Magnesium vs Calcium Concentrations

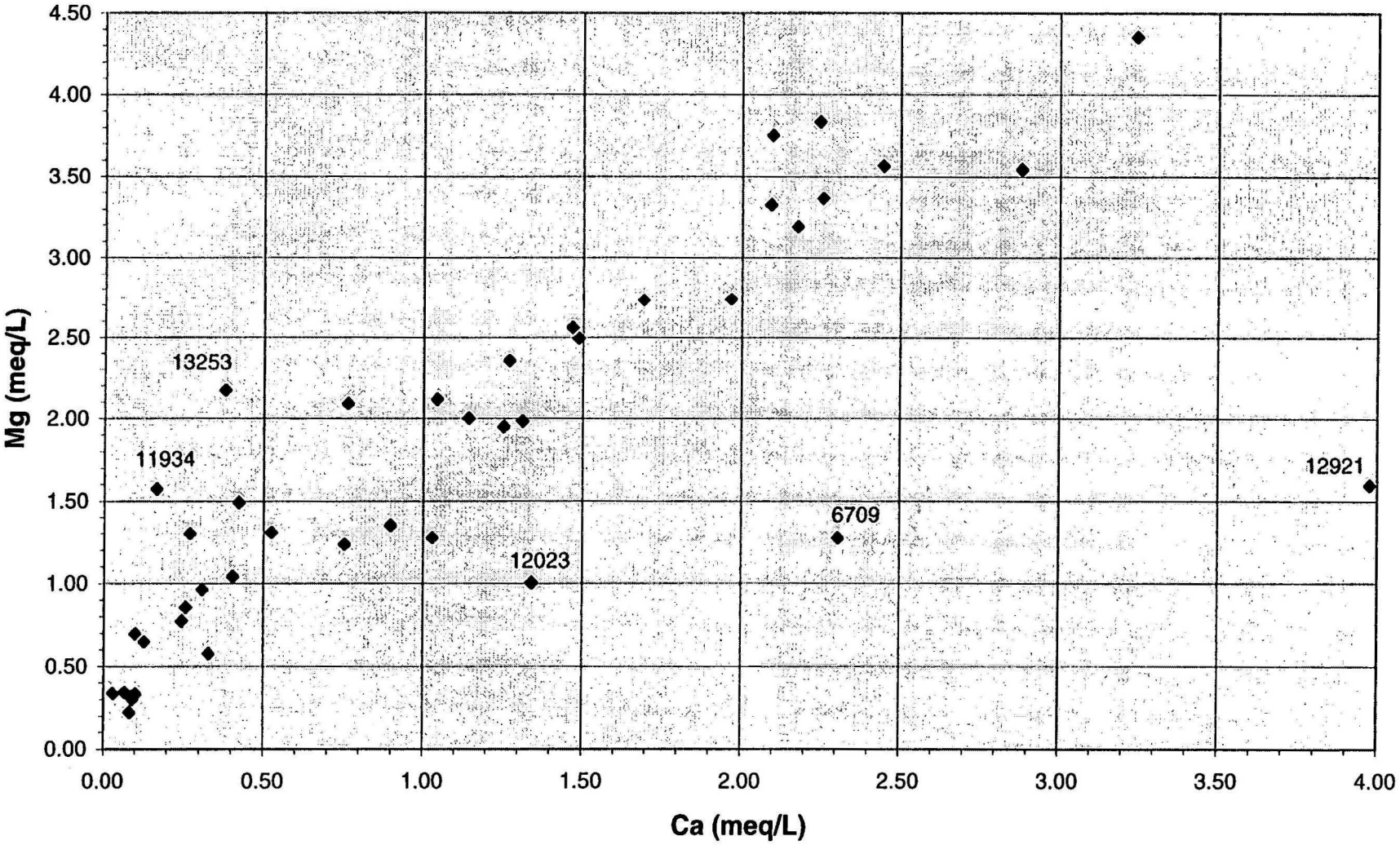


Fig 5.17 Piccadilly Valley: April-May 1994 Groundwater - Sodium Concentrations

Aesthetic Drinking Water Guideline 180 mg/L

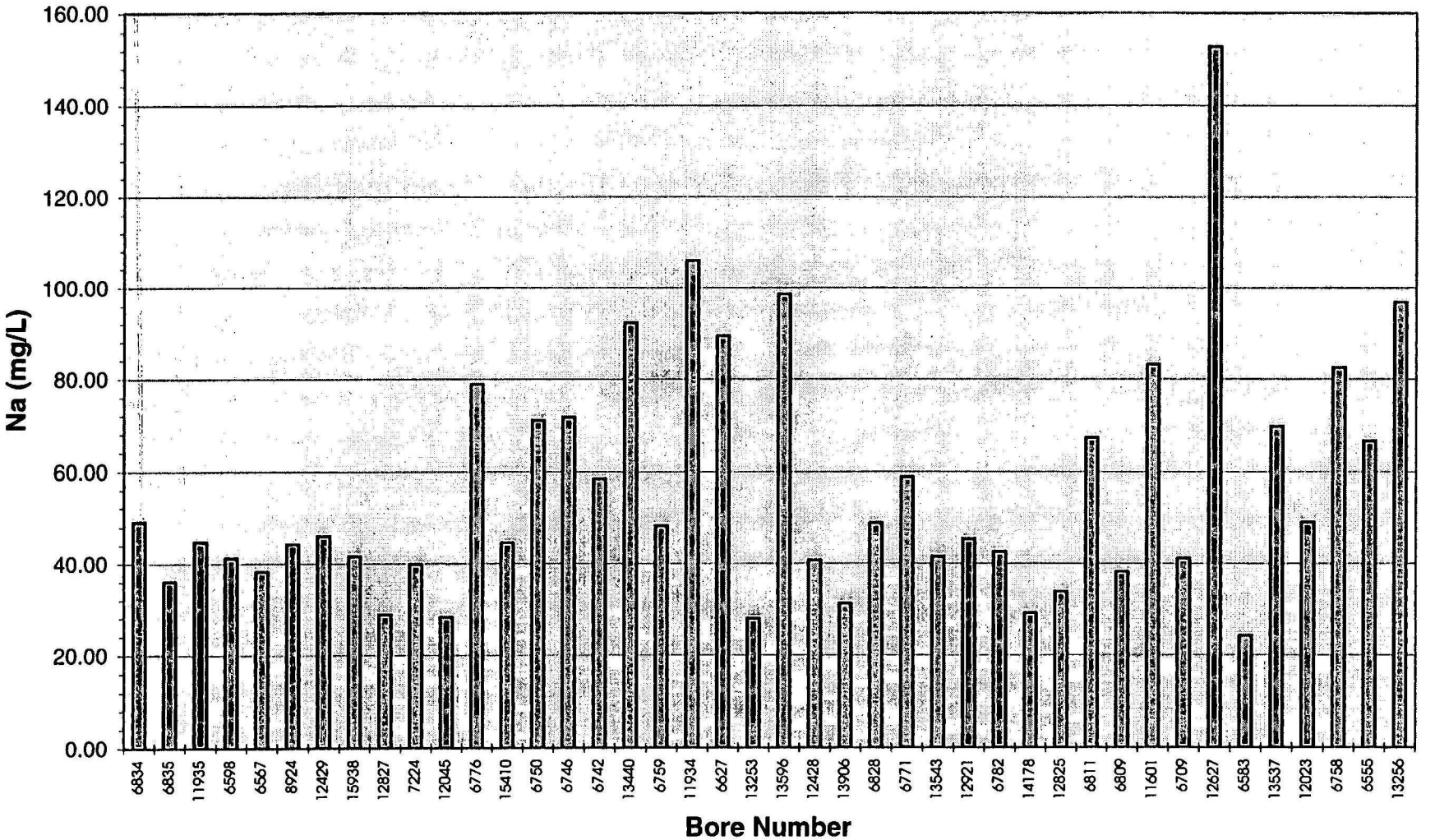


Fig 5.18 Piccadilly Valley: April-May 1994 Groundwater - Potassium Concentrations

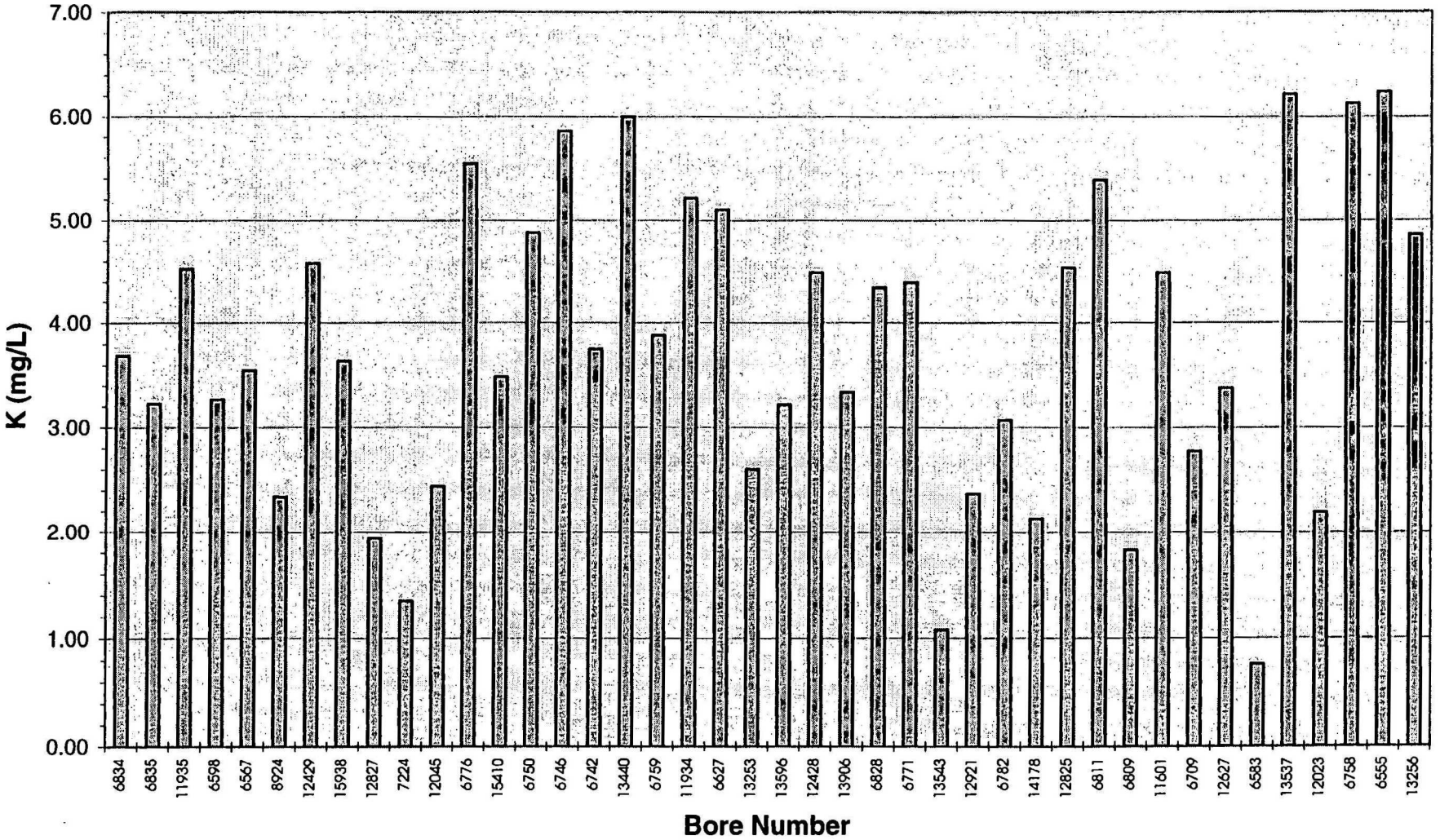


Fig 5.19 Piccadilly Valley: April-May 1994 Groundwater - Silica Concentrations

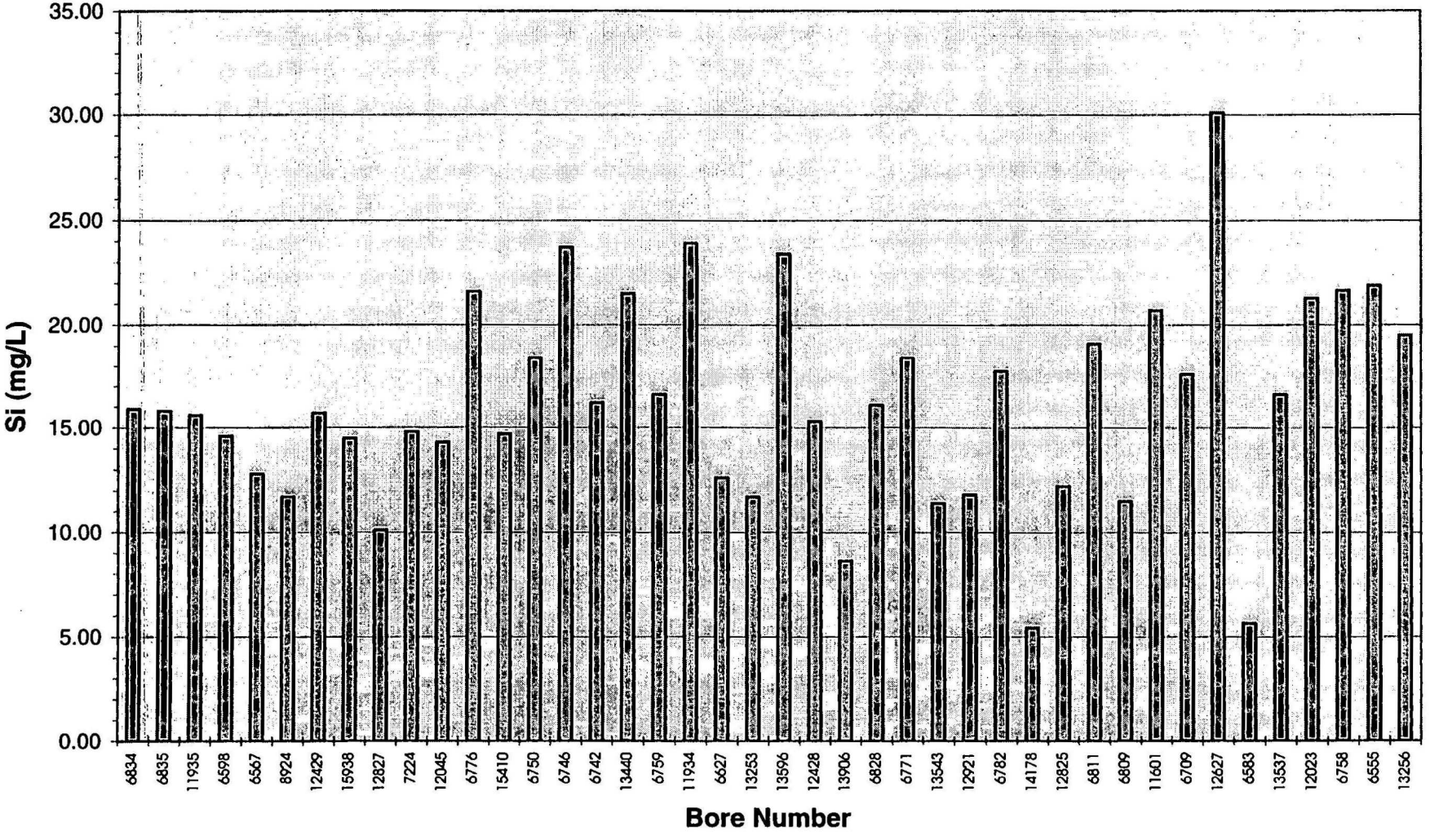


Fig 5.20 Piccadilly Valley: April-May 1994 Groundwater - Total Sulphur Concentrations

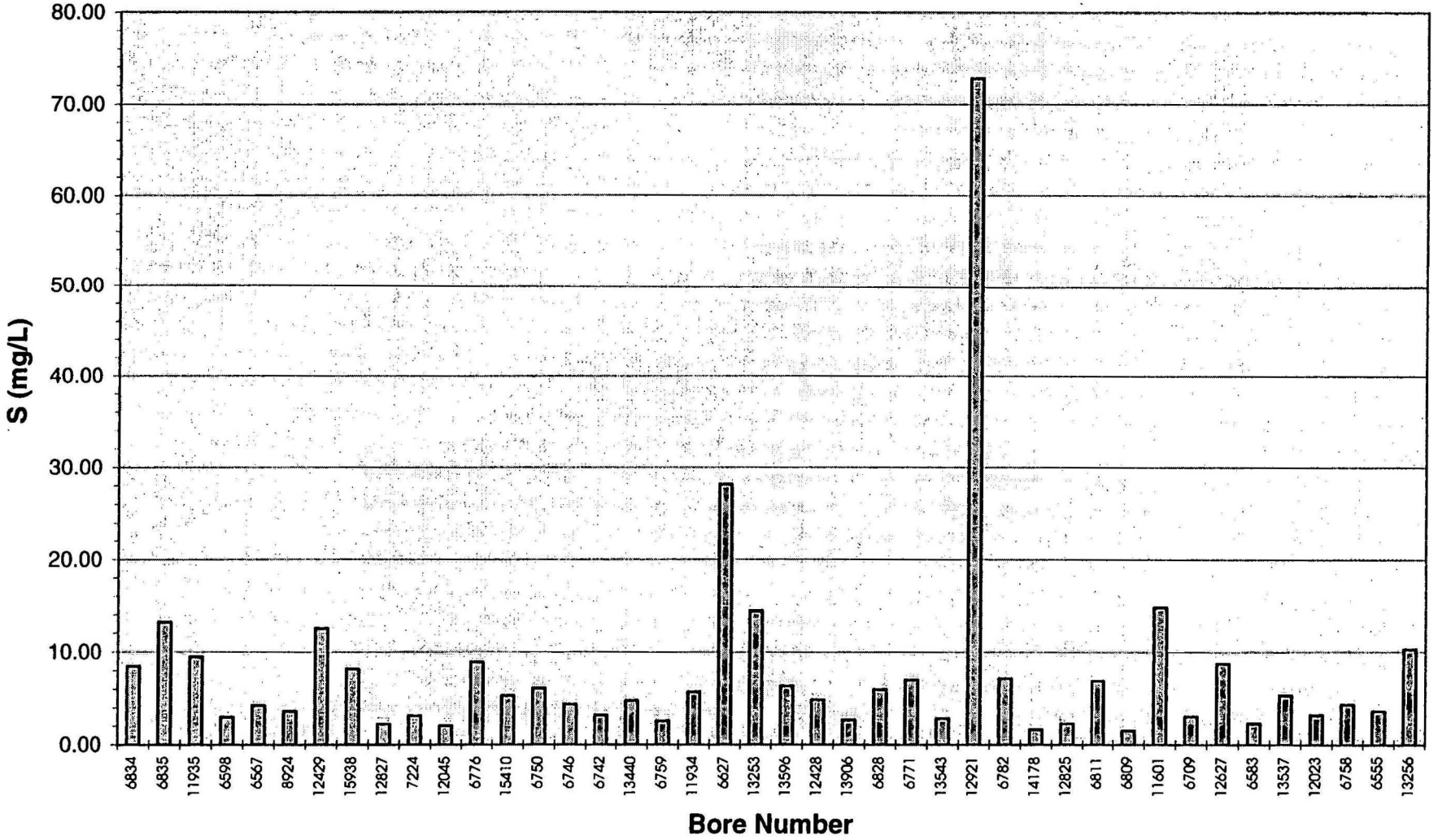


Fig 5.21 Piccadilly Valley: April-May 1994 Groundwater - Sulphate Concentrations

Health Drinking Water Guideline Value 500mg/L
Aesthetic Drinking Water Guideline Value 250 mg/L

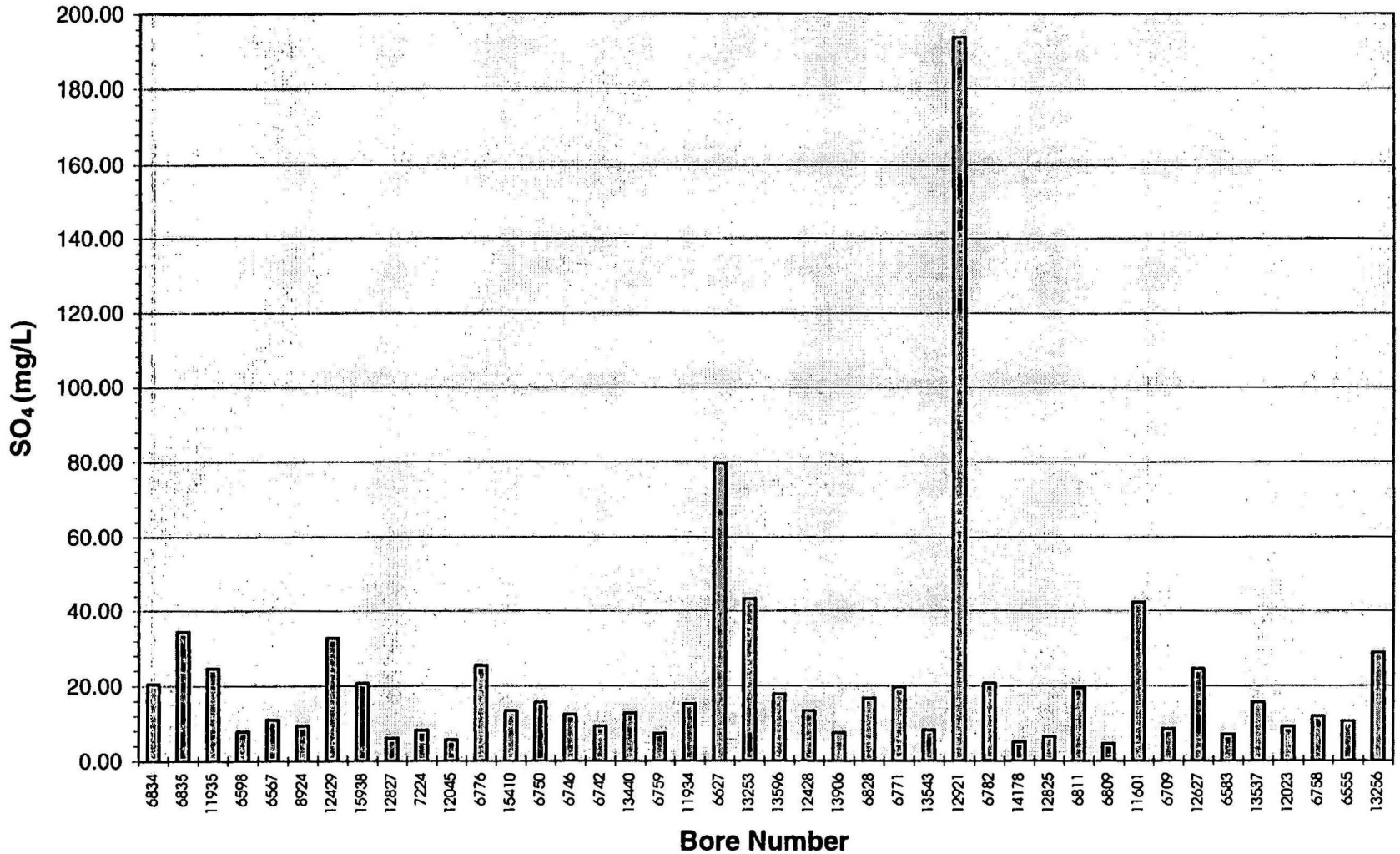


Fig 5.22 Piccadilly Valley: April-May 1994 Groundwater - Bicarbonate Concentrations

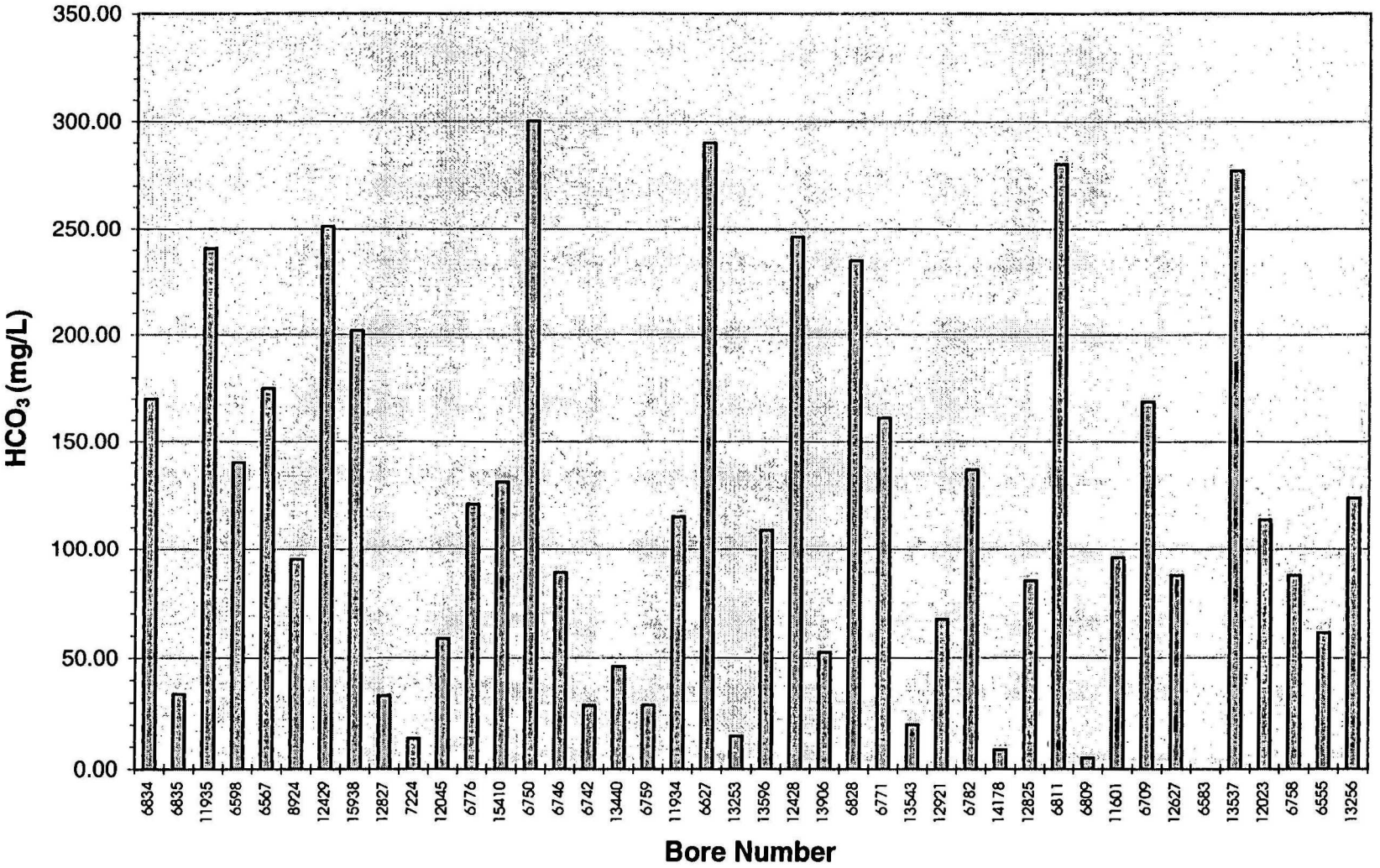


Fig 5.23 Piccadilly Valley: April-May 1994 Groundwater - Chloride Concentrations

Aesthetic Drinking Water Guideline Value 250 mg/L

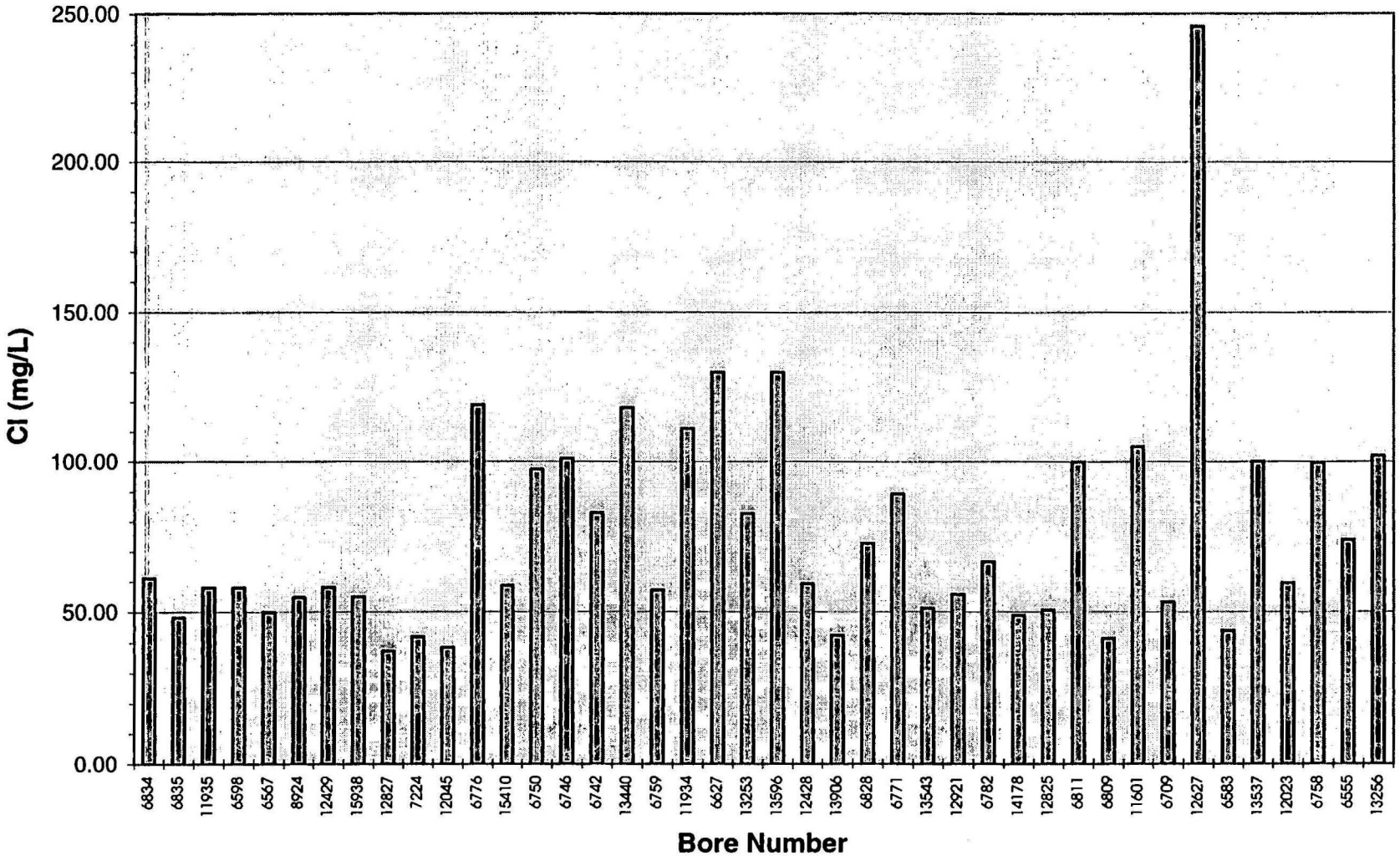


Fig 5.24 Piccadilly Valley: April-May 1994 Groundwater Sodium vs Chloride Concentrations

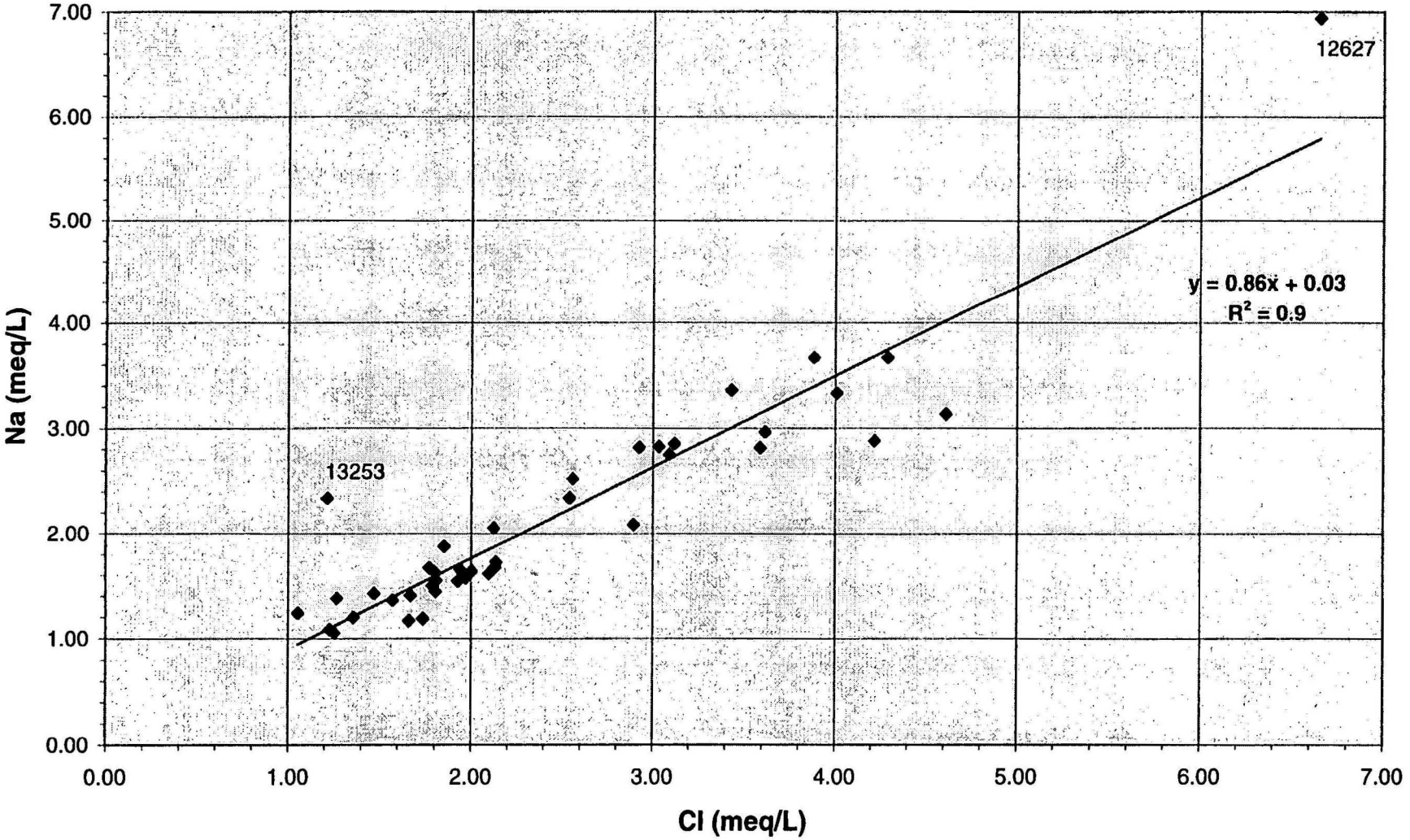
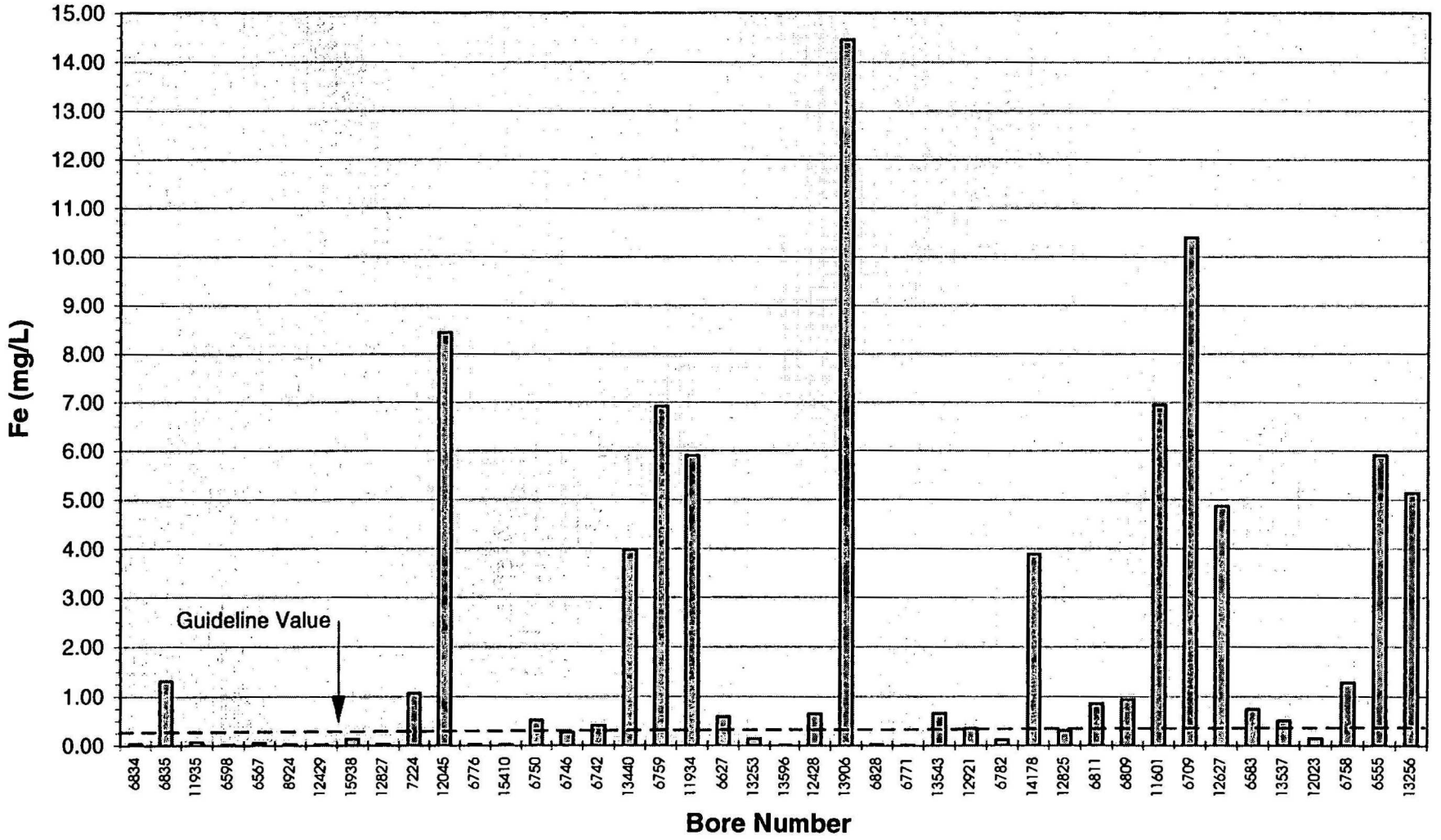


Fig 5.25 Piccadilly Valley: April-May 1994 Groundwater - Iron Concentrations

Aesthetic Drinking Water Guideline Value 0.03 mg/L



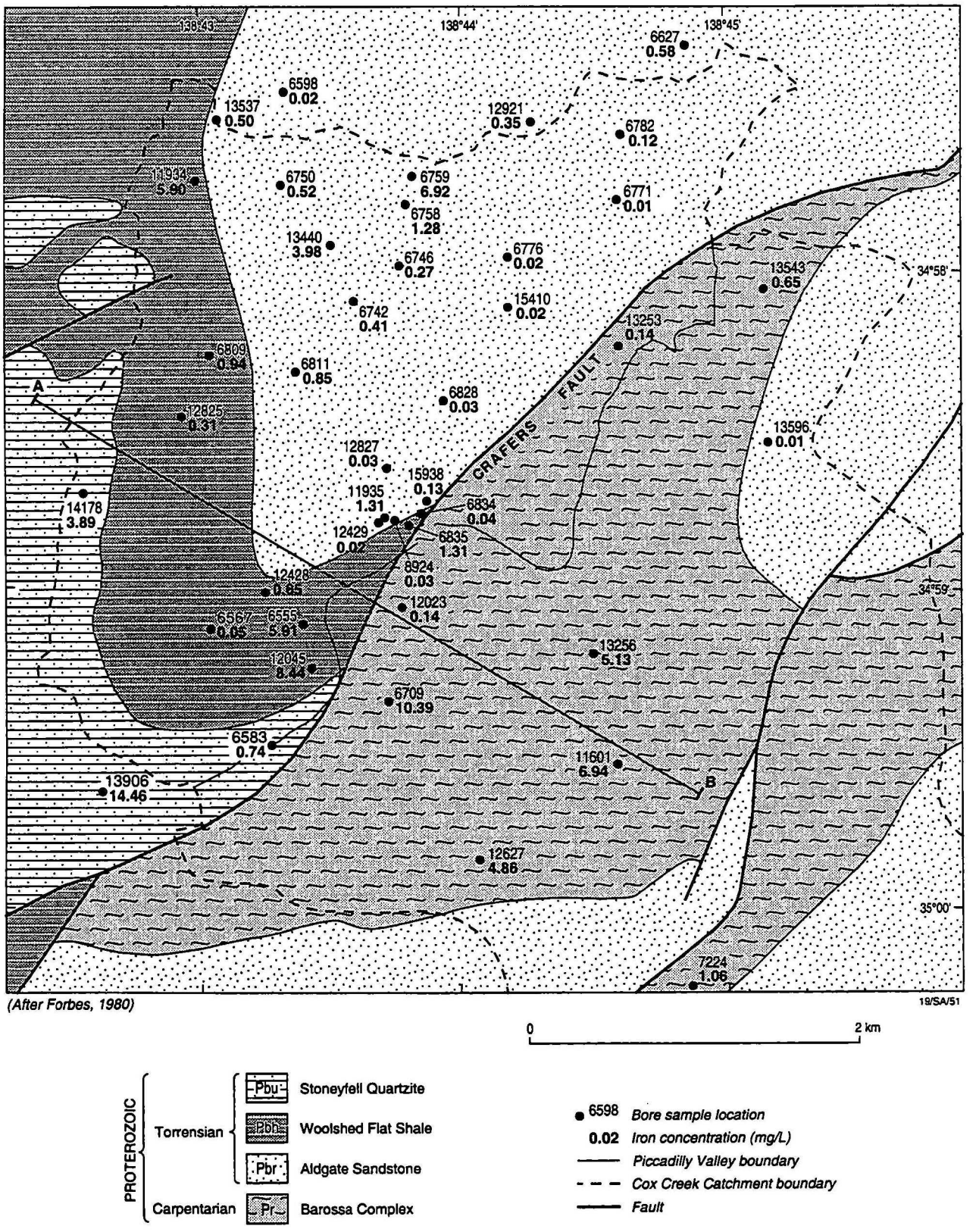


Figure 5.26 Distribution of iron concentrations in Piccadilly Valley Groundwaters

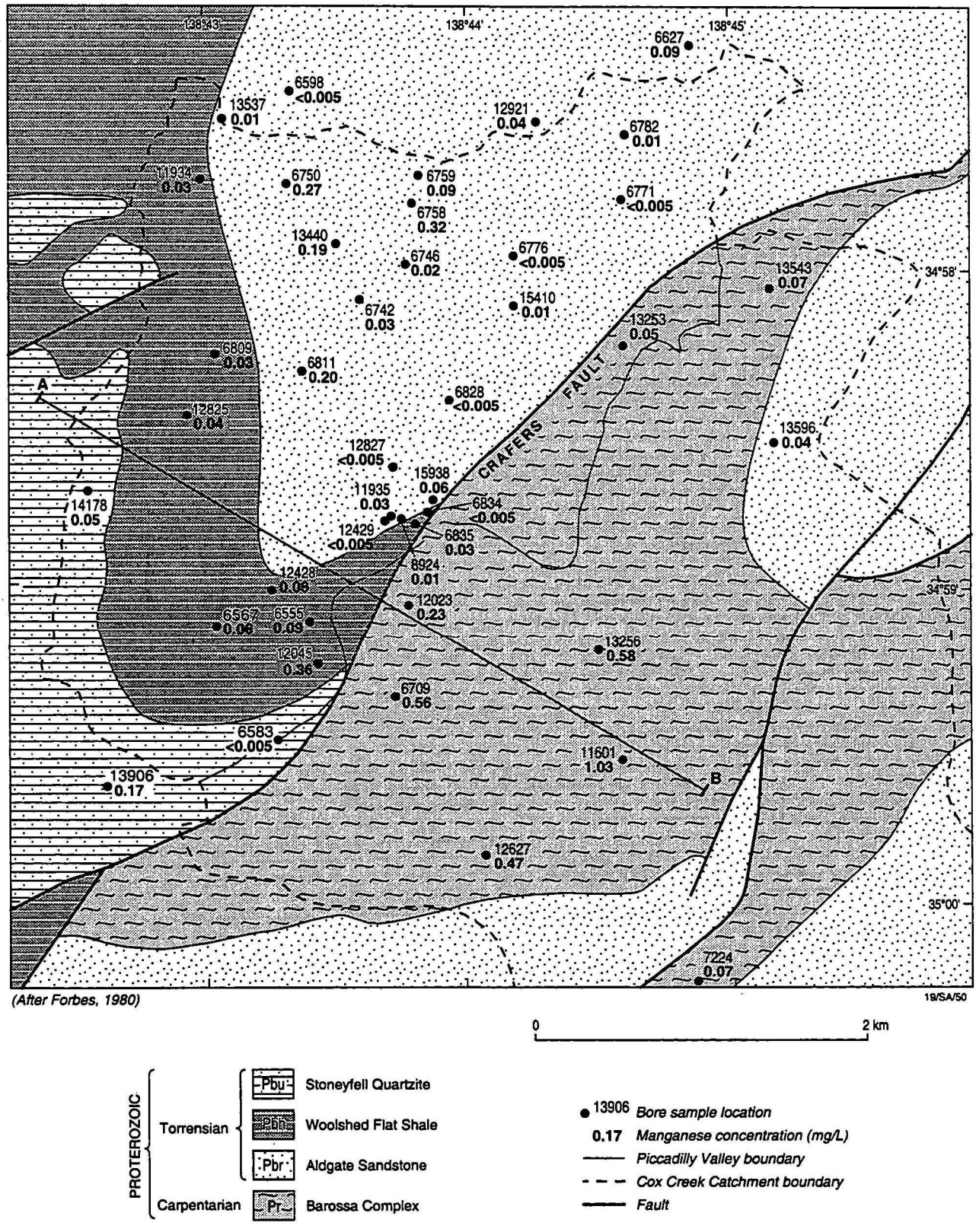


Figure 5.28 Distribution of manganese concentrations in Piccadilly Valley Groundwaters

Fig 5.27 Piccadily Valley: April-May 1994 Groundwater - Manganese Concentrations

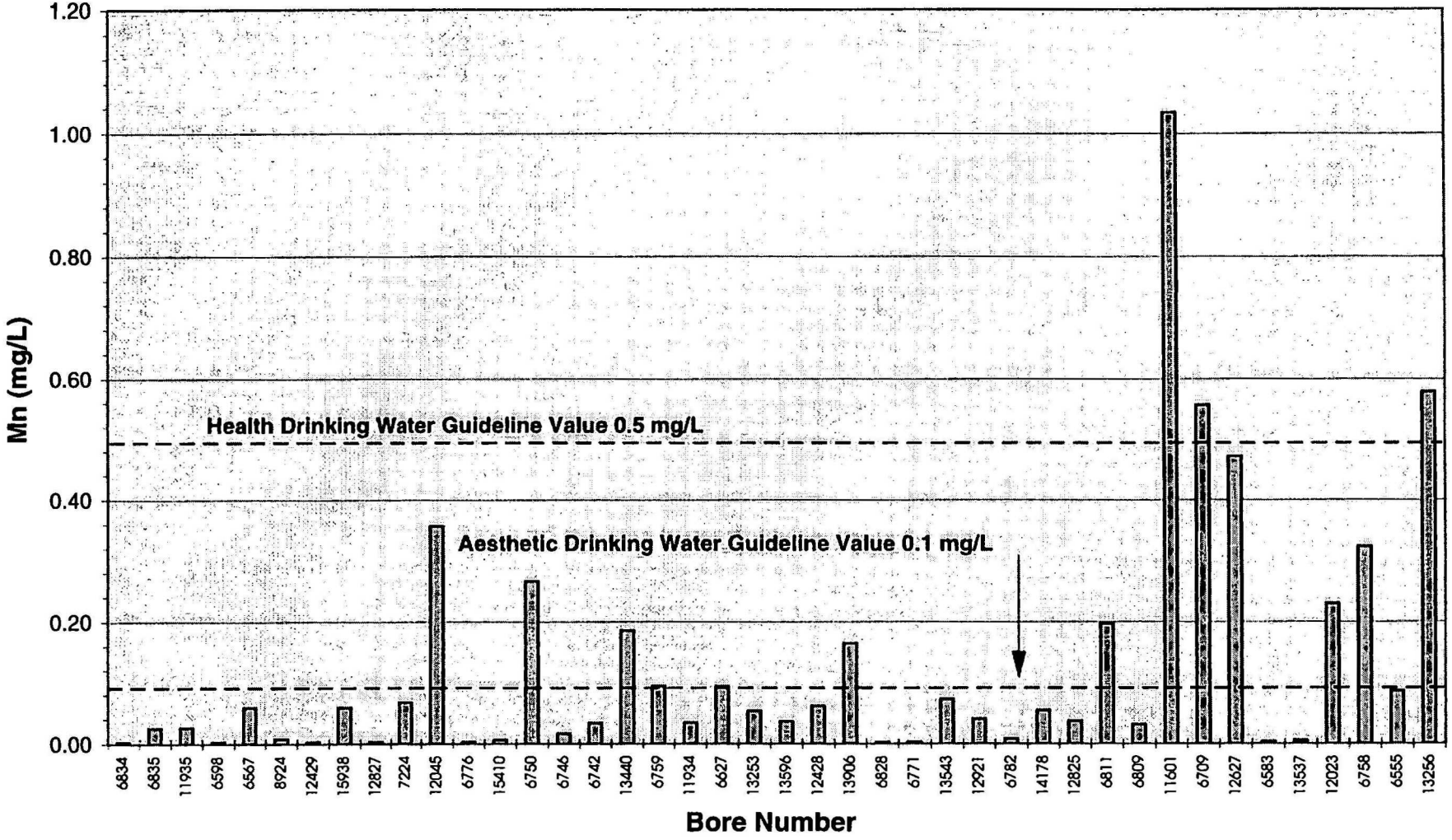


Fig 5.29 Piccadilly Valley: April-May 1994 Groundwater Manganese Concentration vs Dissolved Oxygen

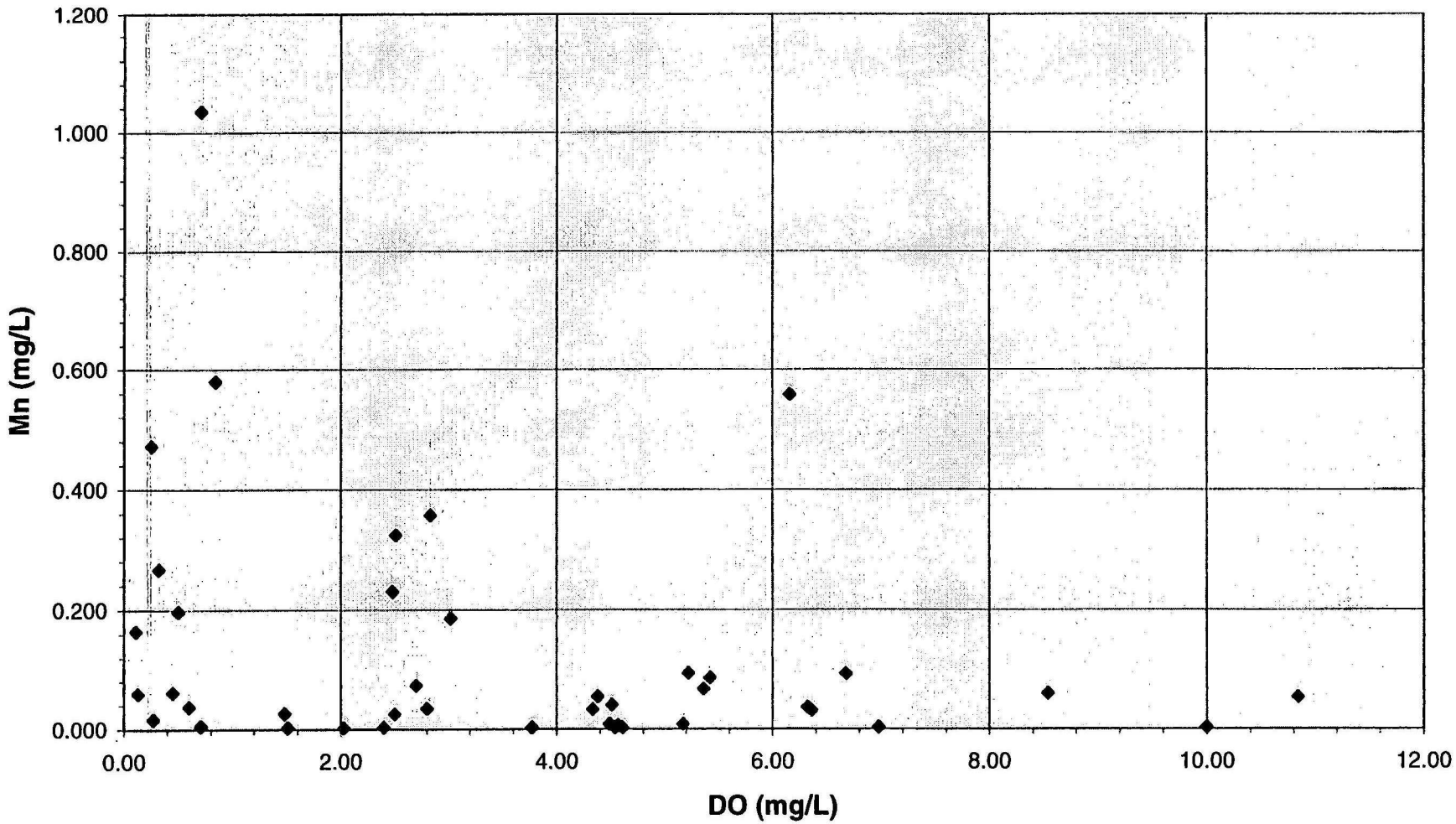
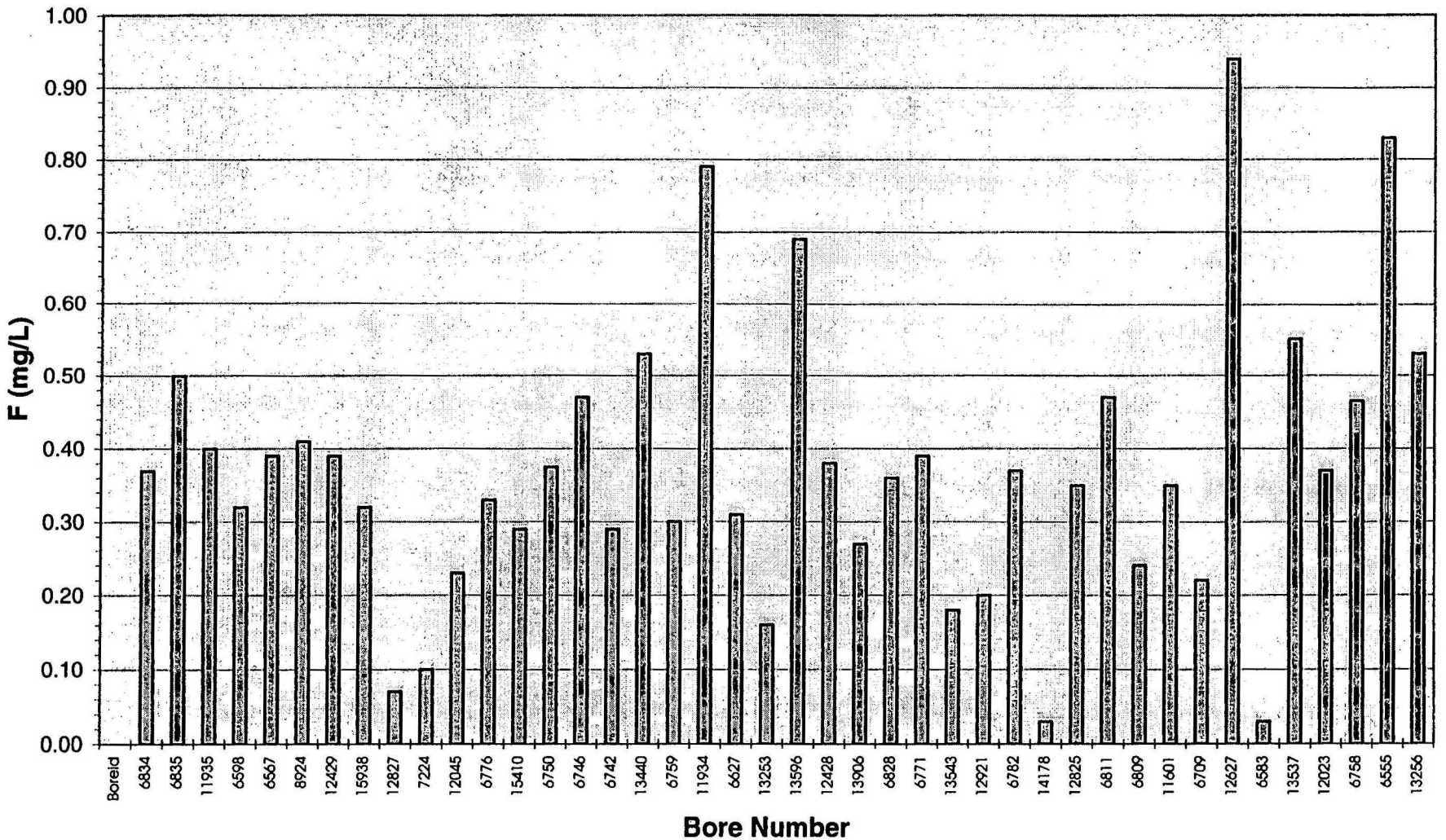


Fig 5.30 Piccadilly Valley: April-May 1994 Groundwater - Fluoride Concentrations



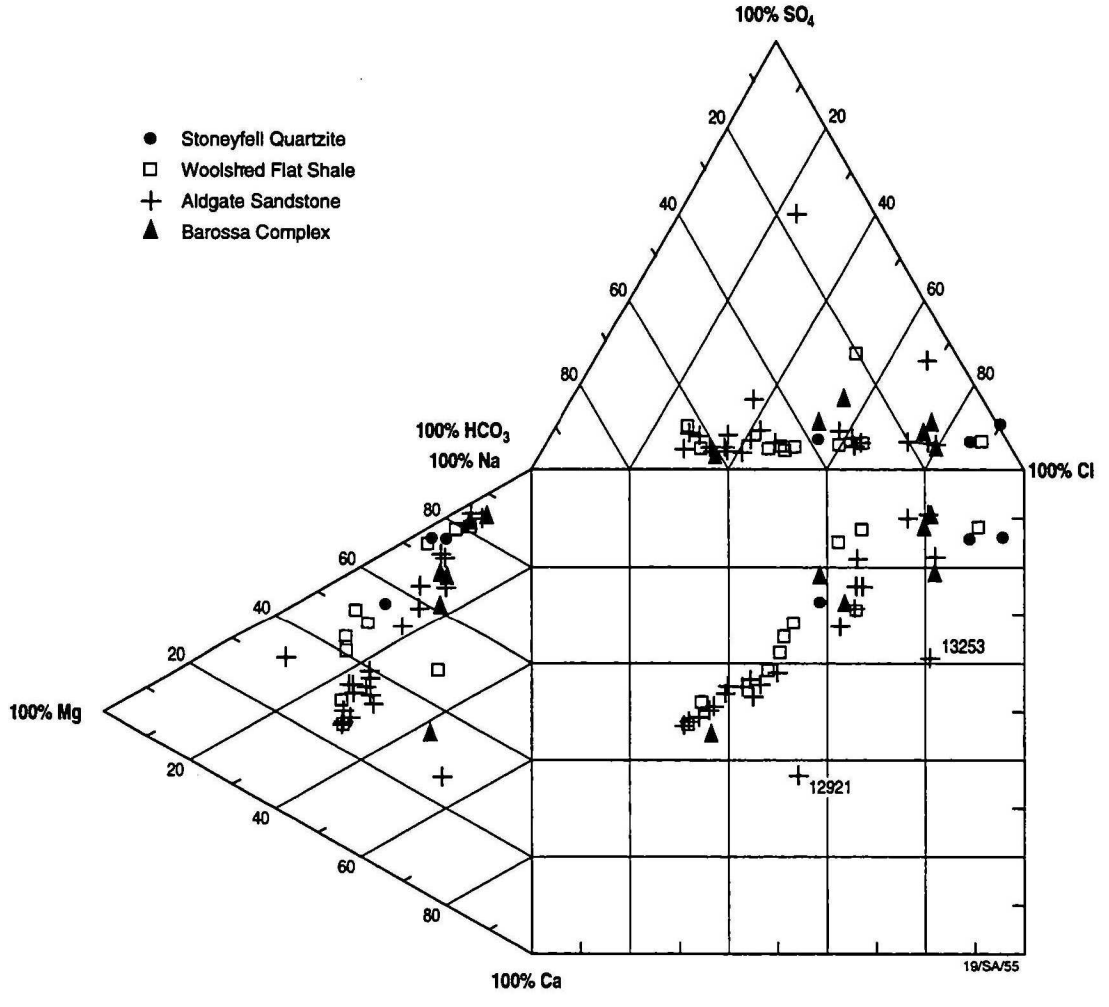


Fig 5.31 Durov diagram for Piccadilly Valley groundwaters

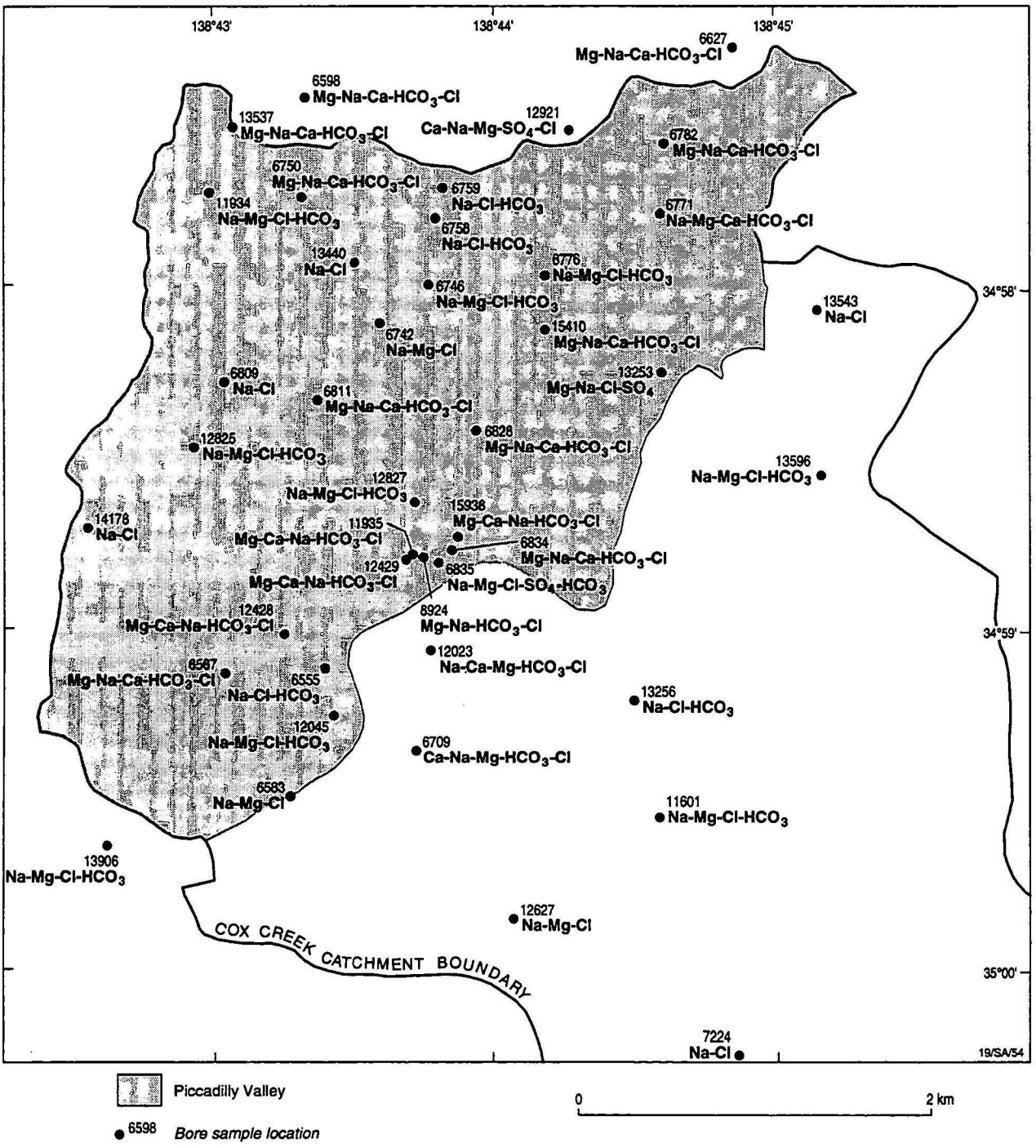


Figure 5.32 Distribution of hydrochemical facies in Piccadilly Valley Groundwaters

Fig 5.33 Major Cations vs Total Dissolved Ions (TDI) in Piccadilly Valley Groundwaters

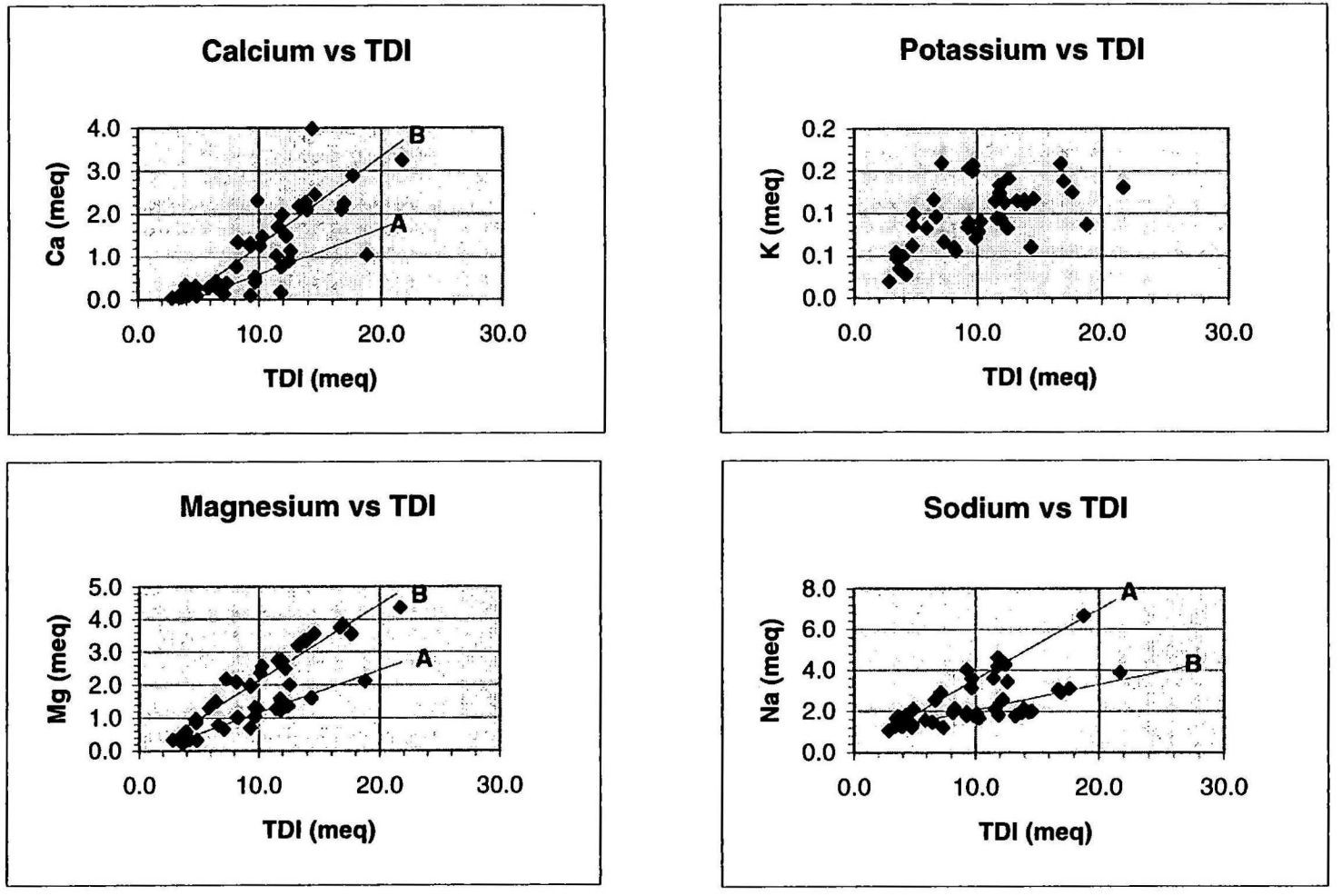
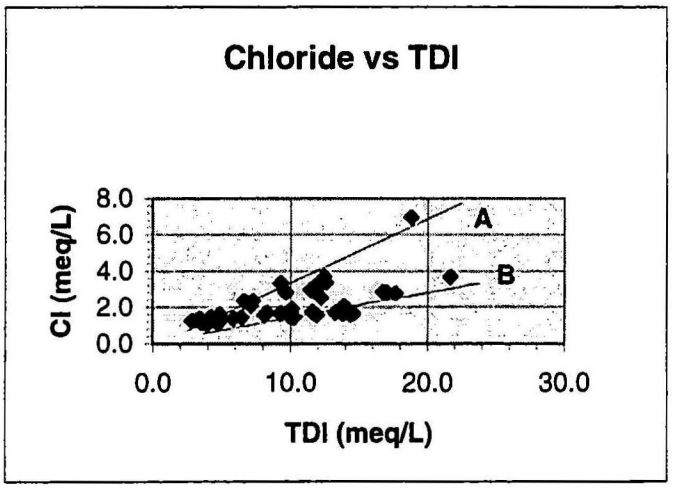
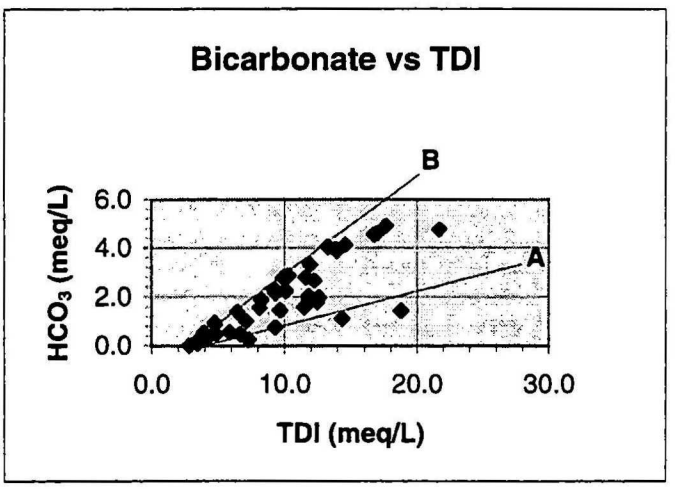
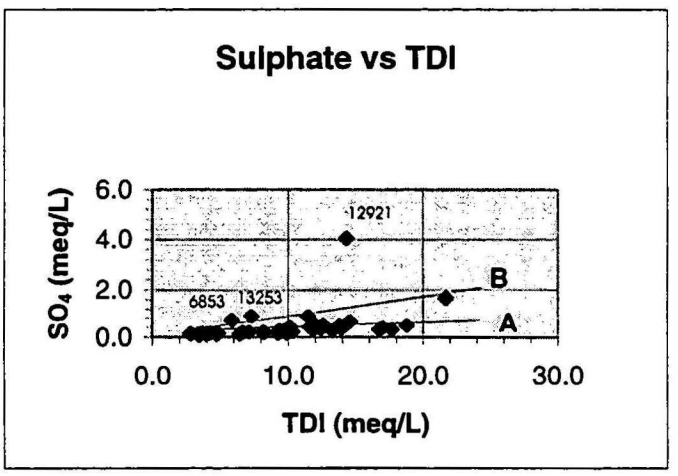


Fig 5.34 Major Anions vs Total Dissolved Ions (TDI) in Piccadilly Valley Groundwaters







6.0 TRACE ELEMENT AND METALS CHEMISTRY

Many elements are, or can be, present in groundwater at concentrations often well below 0.01 mg/L, but sometimes much higher, particularly if the water has been in contact with mineralised rock or ore bodies (Bouwer, 1978). Several minor elements are of great concern because of their toxic effects, even at low concentrations. Over recent years there has been a greater interest in the toxic effects of trace elements on humans and the environment, illustrating the importance of including them in a groundwater quality assessment. The following minor inorganic and trace metals were analysed in this study:

Alkali Metals:	Lithium
Alkali Earth Metals:	Barium Strontium
Metallic Elements:	Aluminium Cadmium Chromium Cobalt Copper Gold Lead Mercury Molybdenum Nickel Silver Tin Vanadium Zinc
Non-Metals:	Antimony Arsenic Boron Selenium
Radioactive Elements:	Uranium

The concentrations of these elements are presented in Tables 6.1 (AGSO Lab data) and 6.2 (AMDEL Lab data) and include the minimum, maximum and median values. Where data exists for an element analysed by both AMDEL and AGSO, the AGSO lab analytical results have been used for data analysis due to the greater reproducibility of AGSO data (as determined by quality assurance/quality control analysis of the data). A brief description and bargraph of the data for each element are given together

Table 6.1: April-May 1994 Piccadilly Valley Groundwaters
Trace Element and Metals Chemistry - AGSO Lab

Bore Number	Li (mg/L)	Ba (mg/L)	Sr (mg/L)	Al (mg/L)	Cu (mg/L)	Zn (mg/L)	B (mg/L)
6834	0.015	0.069	0.078	0.003	0.003	0.114	0.037
6835	0.018	0.111	0.025	0.012	0.003	0.045	0.037
11935	0.012	0.119	0.129	0.003	0.003	0.081	0.029
6598	0.003	0.020	0.044	0.003	0.003	0.035	0.027
6567	0.011	0.083	0.073	0.002	0.003	0.031	0.030
8924	0.011	0.088	0.041	0.057	0.003	0.020	0.025
12429	0.014	0.120	0.134	0.003	0.003	0.044	0.026
15938	0.013	0.064	0.128	0.003	0.003	0.120	0.024
12827	0.003	0.018	0.013	0.003	0.003	0.018	0.022
7224	0.003	0.068	0.003	0.008	0.006	0.065	0.025
12045	0.003	0.022	0.024	0.017	0.003	0.061	0.048
6776	0.012	0.054	0.060	0.003	0.003	0.041	0.030
15410	0.009	0.033	0.068	0.003	0.003	0.147	0.024
6750	0.013	0.126	0.177	0.003	0.003	0.042	0.141
6746	0.010	0.054	0.029	0.003	0.003	0.095	0.021
6742	0.008	0.037	0.040	0.014	0.003	0.032	0.028
13440	0.006	0.061	0.003	0.016	0.003	0.050	0.031
6759	0.003	0.024	0.003	0.017	0.003	0.050	0.040
11934	0.023	0.019	0.003	0.012	0.003	0.343	0.037
6627	0.003	0.039	0.164	0.006	0.003	0.108	0.041
13253	0.003	0.050	0.070	0.010	0.024	0.035	0.025
13596	0.003	0.032	0.023	0.003	0.003	0.032	0.018
12428	0.011	0.168	0.123	0.003	0.003	0.076	0.052
13906	0.003	0.024	0.012	0.026	0.003	0.470	0.060
6828	0.009	0.022	0.106	0.003	0.003	0.058	0.037
6771	0.010	0.040	0.081	0.003	0.003	0.023	0.034
13543	0.003	0.039	0.003	0.007	0.003	0.018	0.034
12921	0.003	0.020	1.824	0.003	0.003	0.045	0.037
6782	0.013	0.038	0.072	0.003	0.003	0.025	0.037
14178	0.003	0.037	0.003	0.103	0.003	0.029	0.086
12825	0.015	0.031	0.032	0.016	0.003	0.081	0.050
6811	0.016	0.048	0.104	0.003	0.003	0.045	0.047
6809	0.003	0.009	0.003	0.024	0.116	0.099	0.033
11601	0.003	0.085	0.044	0.015	0.003	0.075	0.056
6709	0.003	0.148	0.039	0.019	0.003	0.084	0.061
12627	0.011	0.120	0.063	0.017	0.006	0.137	0.045
6583	0.003	0.012	0.003	0.236	0.029	0.045	0.043
13537	0.013	0.007	0.107	0.003	0.003	0.047	0.045
12023	0.005	0.013	0.016	0.003	0.003	0.030	0.036
6758	0.015	0.080	0.014	0.003	0.005	0.924	0.037
6555	0.018	0.0025	0.003	0.014	0.006	0.513	0.048
13256	0.003	0.083	0.026	0.010	0.003	0.056	0.069
Limit of Detection	0.005	0.005	0.005	0.005	0.005	0.005	0.005
Minimum	0.003	0.003	0.003	0.002	0.003	0.018	0.018
Maximum	0.023	0.168	1.824	0.236	0.116	0.924	0.141
Median	0.009	0.040	0.041	0.004	0.003	0.050	0.037

Table 6.2: April-May 1994 Piccadilly Valley Groundwaters
Trace Element and Metals Chemistry - AMDEL Lab

Bore Number	Al (µg/L)	Cd (µg/L)	Cr (µg/L)	Co (µg/L)	Cu (µg/L)	Au (µg/L)	Pb (µg/L)	Hg (µg/L)	Mo (µg/L)	Ni (µg/L)	Ag (µg/L)	Sn (µg/L)	V (µg/L)	Zn (µg/L)	Sb (µg/L)	As (µg/L)	Se (µg/L)	U (µg/L)	Fe (µg/L)	Mn (µg/L)
6834	111	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.20	0.4	0.5	109	0.30	1.4	7.0	0.1	21	7
6835	24	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.05	0.1	0.5	61	0.40	0.1	1.0	0.1	1555	25
11935	3	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.10	0.4	0.5	69	0.40	0.4	2.0	0.1	25	25
6598	12	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.05	0.1	0.5	59	0.30	0.2	0.5	0.1	7	2
6567	55.5	0.25	0.5	0.5	2.5	0.05	0.5	0.05	42.50	0.5	0.05	0.1	0.5	29.5	0.35	0.2	0.5	0.1	21.5	43
8924	91	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	2.0	0.05	0.6	3.0	38	0.30	0.8	2.0	0.6	16	13
12429	208	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.10	0.2	2.0	42	0.20	0.2	2.0	0.2	48	2
15938	4	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.05	0.1	0.5	132	0.20	1.0	2.0	0.1	100	40
12827	37	0.25	0.5	0.5	3	0.05	0.5	0.05	0.50	0.5	0.20	0.1	1.0	32	0.10	0.2	0.5	0.1	3	4
7224	11	0.25	0.5	0.5	8	0.05	0.5	0.05	0.25	2.0	0.05	0.1	0.5	85	0.10	0.2	0.5	0.1	1200	42
12045	15	0.25	0.5	0.5	5	0.05	0.5	0.05	0.25	5.0	0.30	0.1	0.5	78	0.10	4.0	0.5	0.1	8920	370
6776	95	0.25	0.5	0.5	3	0.05	0.5	0.05	0.50	3.0	0.05	0.2	0.5	43	0.10	0.1	4.0	0.1	11	8
15410	3	0.25	0.5	0.5	2	0.05	0.5	0.05	0.25	1.0	0.05	0.1	0.5	112	0.10	0.1	0.5	0.1	8	5
6750	69.5	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.05	0.1	0.5	36	0.05	3.7	0.5	0.1	615	265
6746	17	0.25	0.5	3.0	5	0.05	6.0	0.05	0.50	2.0	0.05	0.3	3.0	90	0.05	1.0	0.5	0.5	250	18
6742	22	0.25	0.5	3.0	3	0.05	2.0	0.05	0.25	2.0	0.05	0.1	4.0	42	0.05	0.2	0.5	0.1	480	23
13440	27	0.25	0.5	5.0	0.5	0.05	0.5	0.05	0.25	2.0	0.05	0.1	2.0	78	0.05	0.2	0.5	0.1	4540	160
6759	41	0.25	0.5	4.0	0.5	0.05	0.5	0.05	0.25	1.0	0.05	0.1	0.5	70	0.05	0.1	0.5	0.1	8000	65
11934	53	0.25	0.5	4.0	0.5	0.05	0.5	0.05	0.25	1.0	0.05	0.1	1.0	380	0.05	0.6	4.0	0.1	7250	67
6627	2	0.25	0.5	3.0	0.5	0.05	0.5	0.05	0.50	0.5	0.05	0.1	0.5	90	0.05	0.6	0.5	0.5	610	71
13253	216	0.25	0.5	4.0	23	0.05	0.5	0.05	0.25	23.0	0.05	0.1	0.5	43	0.05	0.1	0.5	0.1	120	52
13596	7	0.25	0.5	2.0	0.5	0.05	0.5	0.05	0.25	2.0	0.05	0.1	1.0	36	0.05	0.2	0.5	0.2	8	36
12428	2	0.25	0.5	3.0	0.5	0.05	0.5	0.05	0.25	0.5	0.05	0.1	0.5	67	0.05	0.1	0.5	0.1	630	54
13906	5	0.25	0.5	5.0	3	0.05	0.5	0.05	0.25	1.0	0.05	0.1	1.0	450	0.05	0.4	0.5	0.1	9000	120
6828	67	0.25	0.5	3.0	2	0.05	5.0	0.05	0.25	0.5	0.20	0.1	0.5	90	0.05	0.2	2.0	0.1	6	9
6771	5	0.25	0.5	2.0	1	0.05	1.0	0.05	0.25	0.5	0.10	0.1	0.5	31	0.05	0.1	1.0	0.1	3	3
13543	130	0.25	0.5	4.0	0.5	0.05	1.0	0.05	0.25	2.0	0.50	0.1	0.5	27	0.05	0.1	0.5	0.1	660	40
12921	220	0.25	0.5	2.0	0.5	0.05	0.5	0.05	0.25	2.0	0.05	0.1	1.0	81	0.05	0.1	0.5	0.1	320	41
6782	4	0.25	0.5	2.0	0.5	0.05	0.5	0.05	0.40	0.5	0.20	83.9	1.0	76	0.10	0.1	2.0	0.1	114.5	15
14178	139	0.25	0.5	3.0	0.5	0.05	0.5	0.05	0.25	0.5	0.10	0.4	2.0	39	0.05	1.0	0.5	0.4	4560	57
12825	359	0.25	0.5	3.0	2	0.05	0.5	0.05	0.25	0.5	0.05	0.1	0.5	97	0.05	0.5	0.5	0.1	260	45
6811	9	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.05	0.1	0.5	38	0.05	4.2	0.5	0.1	920	160
6809	126	0.25	0.5	0.5	107	0.05	0.5	0.05	0.25	0.5	0.05	0.9	0.5	108	0.20	0.1	0.5	0.1	1030	33
11601	12	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.05	0.3	0.5	112	0.05	1.0	0.5	1.4	8420	1030
6709	29	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.05	0.1	0.5	76	0.05	2.0	2.0	0.5	12030	550
12627	78	0.25	0.5	0.5	2	0.05	0.5	0.05	0.25	0.5	0.05	0.4	0.5	147	0.05	2.4	0.5	0.1	5900	440
6583	250	0.25	0.5	0.5	18	0.05	0.5	0.05	0.25	0.5	0.05	0.1	0.5	54	0.05	0.1	0.5	0.1	700	22
13537	34	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.05	0.1	0.5	74	0.05	0.2	0.5	0.2	500	44
12023	8	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.05	40.0	0.5	33	0.05	0.7	0.5	0.1	50	270
6758	16	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.05	0.1	0.5	995	0.05	0.1	0.5	0.1	1320	300
6555	2	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.05	0.1	0.5	480	0.05	1.6	0.5	0.6	6830	80
13256	1	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.05	0.1	0.5	94	0.05	1.6	0.5	0.1	5570	560
Limit of Detection	1	0.5	1	1.0	1	0.1	1.0	0.1	0.50	1.0	0.10	0.1	1.0	1	0.10	0.2	1.0	0.1	1	1
Minimum	1	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.05	0.05	0.5	27	0.05	0.1	0.5	0.05	3	2
Maximum	359	0.25	0.5	5	107	0.05	6	0.05	42.5	23	0.5	83.85	4	995	0.4	4.2	7	1.4	12030	1030
Median	25.5	0.25	0.5	0.5	0.5	0.05	0.5	0.05	0.25	0.5	0.05	0.05	0.5	75	0.05	0.2	0.5	0.1	555	42.5

with the 1996 NH&MRC/ARMCANZ guideline values for drinking water where appropriate. The reference used for descriptive information is Hem (1989). For those samples in which the concentration was less than the limit of detection, a value of half the detection limit has been substituted for statistical purposes and graphing.

Lithium

Lithium is an alkali metal usually sourced from igneous rocks, evaporites and natural brines. Lithium ions substitute for magnesium in some minerals. When lithium is brought into solution by weathering reactions, it tends to remain in the dissolved state. It can be toxic to plants at concentrations above 0.06 mg/L.

Lithium concentrations in groundwater samples from the Piccadilly Valley (Fig 6.1) ranged from <0.005 to a maximum of 0.023 mg/L (found in bore 11934). The median value was 0.009 mg/L. Lithium was detectable in 60% (25/42) of the bores. There are no drinking water guideline values for lithium.

Barium

Barium is an alkaline earth metal and is abundant in igneous rocks. The concentration of barium in natural water tends to be controlled by barite ($BaSO_4$) solubility, and adsorption by metal oxides or hydroxides. Ingestion of soluble barium compounds may affect the gastrointestinal tract and central nervous system. Barium salts are considered to be muscle stimulants, especially of the heart. (ANZECC, 1992)

Barium concentrations in groundwater samples from the Piccadilly Valley (Fig 6.2) ranged from 0.007 to 0.168 mg/L with a median value of 0.04 mg/L. Barium was detected in all of the bores sampled in concentrations well below the health drinking water guideline value of 0.7 mg/L. The source is most likely to be barite, a fairly common mineral which historically has been mined in the Piccadilly Valley.

Strontium

Strontium is an alkaline earth metal and its chemistry is similar to that of calcium. Strontium is a fairly common element, replacing calcium or potassium in igneous-rock minerals.

Strontium concentrations in Piccadilly Valley Groundwaters (Fig 6.3) ranged from <0.005 to 1.824 mg/L with a median value of 0.041 mg/L. The concentration of strontium in bore 12921 is much higher than the other bores. As the sulphate concentrations were also elevated in this bore, the most likely source of strontium is strontium sulphate (celestite). Strontium was detected in 79% (33/42) of the bores sampled; there are no guideline values for strontium.

Aluminium

Although aluminium is the third most abundant element in the Earth's crust, it rarely occurs in solution in natural waters at concentrations greater than 1 mg/L, except at low pH. Aluminium occurs in substantial amounts in many silicate igneous rock minerals such as feldspars, feldspathoids, micas and amphiboles. Clays are the most common sedimentary aluminium enriched minerals. Aluminium is not essential to humans and has been associated with Alzheimer's disease (ANZECC, 1992). No health-based guideline value is currently established; however, the aesthetic drinking water guideline value has been set at 0.2 mg/L.

Aluminium concentrations in Piccadilly Valley groundwaters (Fig 6.4) ranged from <0.005 to a maximum of 0.236 mg/L (found in bore 6583). The median value was <0.005 mg/L. Aluminium was detected in 52% (22/42) of the bore samples. Bore 6583 was the only bore to exceed the aesthetic drinking water guideline value; this bore is located in the Stonyfell Quartzite and had a relatively low pH of 4.74, which would increase the solubility of aluminium.

Cadmium

Cadmium is a rather rare element in the earth's crust and is always found in association with zinc ore minerals at levels around 0.5% of the zinc levels (Hart, 1982). Cadmium at very low concentrations can be toxic to humans, livestock and crops. The drinking water guideline value is 2 µg/L. Cadmium concentrations in groundwater samples from the Piccadilly Valley were all below the detection limit of 0.5 µg/L.

Chromium

Chromium is found at low levels in almost all biological material and in man is an essential element acting as a co-factor with insulin to maintain normal glucose metabolism (Hart, 1982). Chromium can also be toxic to humans and aquatic organisms and as a result the health drinking water guideline value has been set at 50 µg/L. Commercially chromium is extracted from chromium ores, of which the most important is chromite. Generally, the levels of chromium found in natural waters are low due to the low solubility of chromium compounds. Anthropogenic sources of chromium include the metallurgical industry, leather tanning industry, pigments and fungicides. Chromium concentrations in the Piccadilly Valley groundwaters sampled were all below the 1 µg/L limit of detection.

Cobalt

Cobalt is essential in plant and animal nutrition, especially for ruminant animals. Cobalt ions can substitute for part of the iron in ferromagnesian rock minerals and, like iron, cobalt may occur in the 2^+ or 3^+ oxidation states. Co-precipitation or

adsorption of cobalt by oxides of manganese and iron appear to be important factors in controlling the amounts that can occur in solution in natural waters. In uncontaminated natural water concentrations of cobalt are generally no more than a few micrograms per litre.

Cobalt concentrations (Fig 6.5) in Piccadilly Valley groundwaters ranged from <1 to 5.0 µg/L with a median value of <1 µg/L. Seventeen of 42 bores sampled (41%) contained detectable concentrations of cobalt. There are no drinking water guideline values for cobalt.

Copper

Copper is an essential element in plant and animal metabolism. It occurs naturally in the Earth's crust as free native metal or in copper minerals. Copper in groundwater can have anthropogenic sources linked with industrial or agricultural activity, such as from inorganic copper compounds used extensively as fungicides.

In general, the concentrations of copper in surface and groundwater are near or below predictions based on pH-Eh diagrams. The lower concentrations are readily explainable as results of co-precipitation by oxides or adsorption on mineral surfaces. Naturally occurring concentrations of copper in Australian groundwaters have been reported to be as high as 12 mg/L (Hart, 1982).

Copper in water has an unpleasant, astringent taste and when concentrations exceed 1 mg/L, may stain laundry and plumbing fixtures. Copper poisoning is rare in humans; the dose usually considered lethal being 15g in a single dose (ANZECC, 1992). Copper concentrations in groundwater samples from the Piccadilly Valley (Fig 6.6) ranged from <0.005 to 0.116 mg/L with a median value of <0.005 mg/L. Copper was detected in 17% (7/42) of the bores. No samples exceeded the aesthetic drinking water guideline value of 1.0 mg/L or the health guideline value of 2.0 mg/L.

Gold

Gold was not detectable in groundwater samples from the Piccadilly Valley (limit of detection 0.1 µg/L).

Lead

Lead is widely dispersed in sedimentary rocks. Its mobility is low due to the low solubility of lead hydroxy carbonates and phosphate. The adsorption of lead on organic and inorganic sediment surfaces and the co-precipitation of lead with manganese oxide also tend to maintain low concentrations in surface and groundwater. The main anthropogenic source of lead to the environment is petrol. Reticulation systems incorporating lead pipes and fittings are the principal sources of lead in drinking water. Lead tends to accumulate in the bones and eventually may cause lead toxication.

Lead concentrations in Piccadilly Valley groundwaters (Fig 6.7) ranged from <1 to 6 µg/L with a median value of <1 µg/L. Lead was detected in 12% (5/42) of the bores at concentrations below the guideline value of 10 µg/L.

Mercury

Mercury exists in natural water systems in its most stable form as a free metal. Sources of mercury include the natural degassing of the earth's crust. Anthropogenic sources include industrial emissions and spills, pre-1970's biocides and mercury fungicides. Mercury can concentrate in man and animal tissues, and there be converted into organo-mercury complexes (particularly methylmercury) which are extremely toxic. Mercury was not detected in the groundwaters sampled from the Piccadilly Valley (limit of detection 0.1 µg/L). The health drinking water guideline value is 1 µg/L.

Molybdenum

Molybdenum is a rare element and is an accessory element in many metal ores. Soluble molybdates may be produced in oxidised sectors of these deposits and may appear in detectable concentrations in stream water, sediments, groundwater and vegetation at considerable distances from their source. The solubility controls of molybdenum may include precipitation with metals and adsorption. It is an essential element in animal and plant nutrition. Anthropogenic sources of molybdenum include molybdenum mining, fossil fuels and fertilisers. Molybdenum is an essential element in animal and plant nutrition and may accumulate in vegetation in excessive amounts that cause problems for grazing animals. Its role in human nutrition is not well known.

Molybdenum concentrations in the groundwaters sampled in the Piccadilly Valley (Fig 6.8) ranged from <0.5 to 42.5 µg/L (median concentration <0.5 µg/L). Molybdenum was detected in 14% (6/42) of the bores sampled. The maximum value of 42.5 µg/L (bore 6567) was derived by averaging duplicate samples for the same bore whose values were 83 and 2 µg/L. The value of 83 µg/L for bore 6567 may be in error, making the concentration 2 µg/L. Nonetheless, the averaged value of 42.5 µg/L is below the health drinking water guideline value of 50 µg/L. Molybdenum concentrations are generally less than 10 µg/L in natural waters and it is probable that the concentrations found in this study (assuming a concentration of 2 µg/L for bore 6567) are naturally occurring.

Nickel

Nickel behaves similarly to cobalt in that it may substitute for iron in ferromagnesian igneous-rock minerals and tends to be co-precipitated with iron oxides and especially with manganese oxides. Anthropogenic sources of nickel include stainless steel and

other corrosion-resistant alloys. Nickel is now recognised as an essential trace element for man. Its oral toxicity is very low as it does not accumulate in tissues and is rapidly eliminated from the body. Long term exposure to nickel may result in toxic effects to the kidney and may be carcinogenic.

Nickel concentrations from groundwater samples in the Piccadilly Valley (Fig 6.9) ranged from <1 to 23 µg/L with a median value of <1 µg/L. Nickel was detected in 36% (15/42) of the bores. Bore 13253, with a concentration of 23 µg/L, exceeded the health drinking water guideline value of 20 µg/L. It is possible that the nickel contamination in bore 13253 resulted from a pipe fitted onto the bore through which the water sample was collected.

Silver

Silver is a rare element in crustal rocks. It is a common minor constituent of industrial wastes but is sufficiently valuable to justify intensive efforts to reclaim it. The pH-Eh diagram for silver suggests that metallic silver and silver chloride or sulfide solids are likely to limit the solubility of the element to much less than 10 µg/L. Cases of silver toxicity have been recorded after extremely high doses. The main effects of silver are discolouration of skin, hair and fingernails (ANZECC, 1992).

Silver concentrations from groundwater samples in the Piccadilly Valley (Fig 6.10) ranged from <0.1 to 0.5 µg/L with a median value of <0.1 µg/L. Silver was detected in 24% (10/42) of the bores. All concentrations were well below the health drinking water guideline value of 100 µg/L and are most likely naturally occurring.

Tin

QA/QC results (Appendix C) indicated unreliable tin analyses, therefore the data will not be discussed.

Vanadium

Vanadium can be associated with uranium in certain ore deposits and is also found in plants, coal and petroleum. Combustion of the latter may release the element to the environment. The aqueous geochemistry of vanadium is complicated with the dominant form being V^{5+} forming anionic complexes with oxygen and hydroxide. It has a greater solubility in oxidising alkaline environments.

Vanadium concentrations in groundwater samples from the Piccadilly Valley (Fig 6.11) ranged from <1 to 4 µg/L with a median value of <1 µg/L. Vanadium was detected in 29% (12/42) of the bores in concentrations presumed to be naturally occurring. There is no drinking water guideline value for vanadium.

Zinc

Zinc has about the same abundance in crustal rocks as copper or nickel, but is more soluble than the other two metals. Zinc is essential in plant and animal metabolism, but water is not a significant dietary source of the element. Factors controlling zinc concentrations in natural water are adsorption, ion exchange or co-precipitation processes. Anthropogenic sources of zinc include pigments, metallurgy (including galvanisation) and pesticides.

Zinc concentrations in groundwater samples from the Piccadilly Valley (Fig 6.12) ranged from 0.018 to 0.924 mg/L with a median value of 0.05 mg/L. Zinc was detected in all samples at concentrations well below the aesthetic guideline value of 3.0 mg/L and are presumably naturally occurring.

Antimony

Antimony is naturally found in lodes containing sulfo-arsenides and sulfo-antimonides as a reduction product of these minerals and is often associated with silver. Antimony has a chemistry similar to that of arsenic, but it is not nearly as abundant. The concentrations of antimony that occur in natural waters can be expected to be very low and few data are available for groundwater samples. Antimony is a possible carcinogen to humans and may cause foetal damage.

Antimony concentrations in groundwater samples from the Piccadilly Valley (Fig 6.13) ranged from <0.1 to 0.4 µg/L with a median value of <0.1 µg/L. Antimony was detected in 36% (15/42) of the bores at concentrations well below the drinking water guideline value of 3 µg/L.

Arsenic

Arsenic naturally occurs in hydrothermal veins associated with arsenides and sulphides of silver, nickel and cobalt. It is also found in some metamorphosed dolomitic rocks. Anthropogenic sources of arsenic include mining, industrial and agricultural wastes from cattle and sheep dips and wood preservatives.

The transformation of arsenic species in natural waters is dependent upon the environmental conditions, particularly pH and redox conditions, and the presence of arsenic-transforming mircroorganisms. Australian freshwaters generally contain less than 10 µg/L of arsenic, although some Australian groundwaters have been reported to contain up to 12,000 µg/L (Hart, 1982). Arsenic is considered to be a human carcinogen.

Arsenic concentrations in groundwater samples from the Piccadilly Valley (Fig 6.14) ranged from <0.2 to 4.2 µg/L with a median value of <0.2 µg/L. Arsenic was detected in 69% (29/42) of the bores sampled at concentrations below the health drinking water guideline value of 7 µg/L. The concentrations are most likely naturally occurring.

Boron

The most widely distributed mineral of igneous rocks in which boron is an essential constituent is tourmaline, which is typically a constituent of granitic rocks and pegmatites. Boron may also be present as an accessory constituent of biotite and amphiboles and is also common in evaporite deposits. Boron may be present in sewage and industrial wastes. Concentrations are generally below 1 mg/L in both surface and groundwater. Excessive intake of boron by humans may cause a variety of physiological distress symptoms (ANZECC, 1992). Small amounts of boron are essential to plant growth; however, concentrations greater than 1 mg/L in irrigation water may be toxic to some plants.

Boron concentrations in groundwater samples from the Piccadilly Valley (Fig 6.15) ranged from 0.018 to 0.141 mg/L with a median value of 0.037 mg/L. Boron was detected in all of the samples at concentrations well below the health drinking water guideline value of 0.3 mg/L.

Selenium

The chemistry of selenium is similar to that of sulphur, but selenium is a much less common element. Selenium is often associated with iron and uranium ore deposits, sulphide minerals or as selenides of silver, copper, lead, mercury or nickel. Most selenium is used in the manufacture of photochemical cells, glass, steel, electronic components, explosives, animal and poultry feeds, fungicides and pigments. The main anthropogenic source of selenium to the environment is the burning of fossil fuels.

Selenium concentrations in surface waters are generally less than 0.1 µg/L. Groundwaters can sometimes contain elevated selenium concentrations; levels as high as 330 µg/L have been reported in wells situated in a seleniferous area of South Dakota (Hart, 1982). Long term exposure to high selenium levels may result in gastrointestinal disturbance, discolouration of the skin and bad teeth (ANZECC, 1992).

Selenium concentrations in groundwater samples from the Piccadilly Valley (Fig 6.16) ranged from <1 to 7 µg/L with a median value of <1 µg/L. Selenium was detected in 29% (12/42) of the bores sampled at concentrations below the health drinking water guideline value of 10 µg/L.

Uranium

Uranium, a radioactive element, is composed of several isotopes of which uranium-238 is predominant. It is naturally occurring in various rocks such as granites, pegmatites, in hydrothermal veins and in sedimentary clastic deposits. Uranium is present in concentrations between 0.1 and 10 µg/L in most natural water. Concentrations greater than 1 mg/L can occur in water associated with uranium-ore

deposits. Excessive radiation from radioactive materials is carcinogenic and as a result the health drinking water guideline value for uranium has been set at 20 µg/L.

Uranium concentrations in groundwater samples from the Piccadilly Valley (Fig 6.17) ranged from <0.1 to 1.4 µg/L with a median value of 0.1 µg/L. Uranium was detected in 60% (25/42) of the bores sampled in concentrations well below the guideline value of 20 µg/L.

Fig 6.1 Piccadilly Valley: April-May 1994 Groundwater - Lithium Concentrations (AGSO Lab)

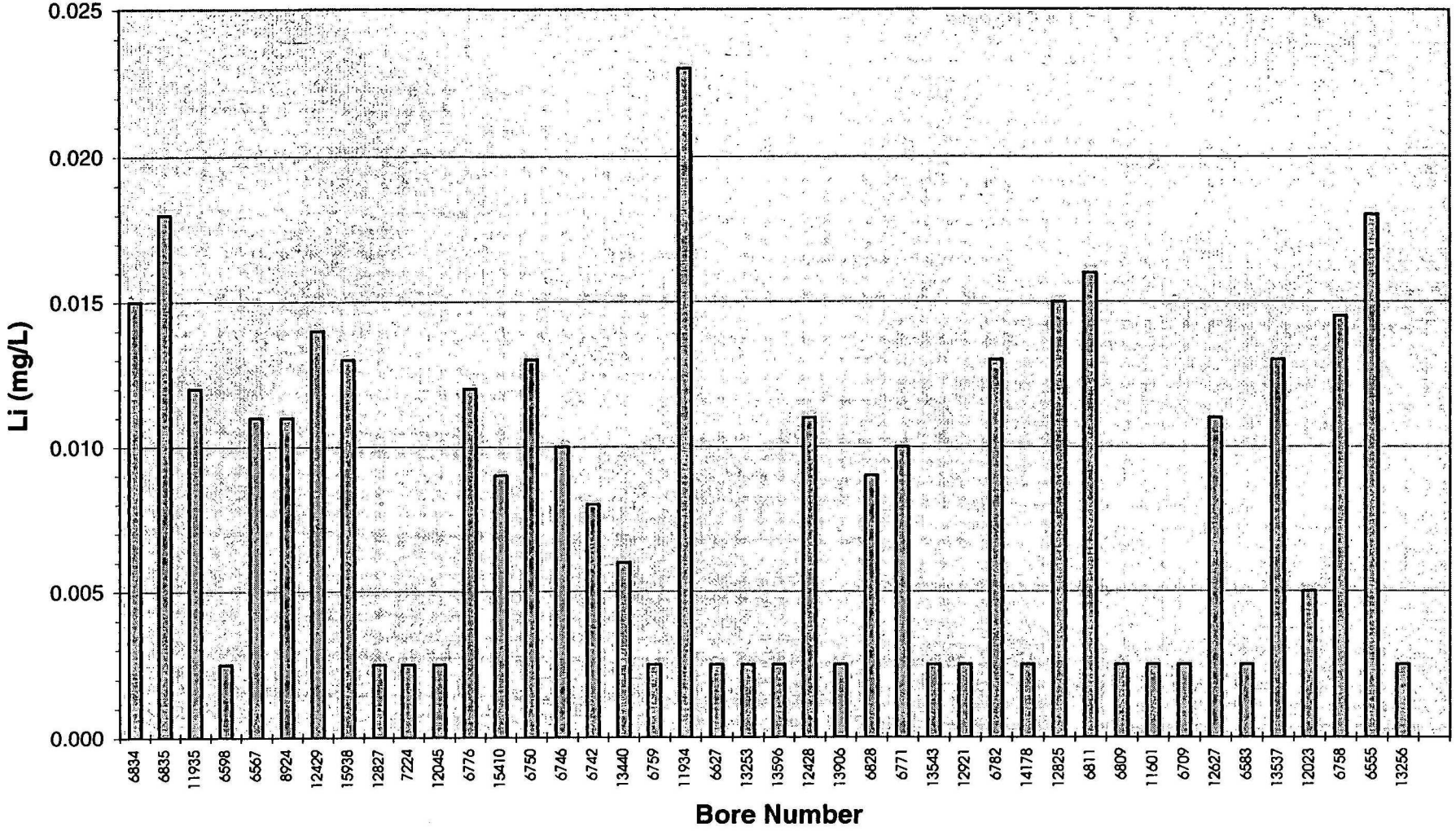


Fig 6.2 Piccadilly Valley: April-May 1994 Groundwater - Barium Concentrations (AGSO Lab)

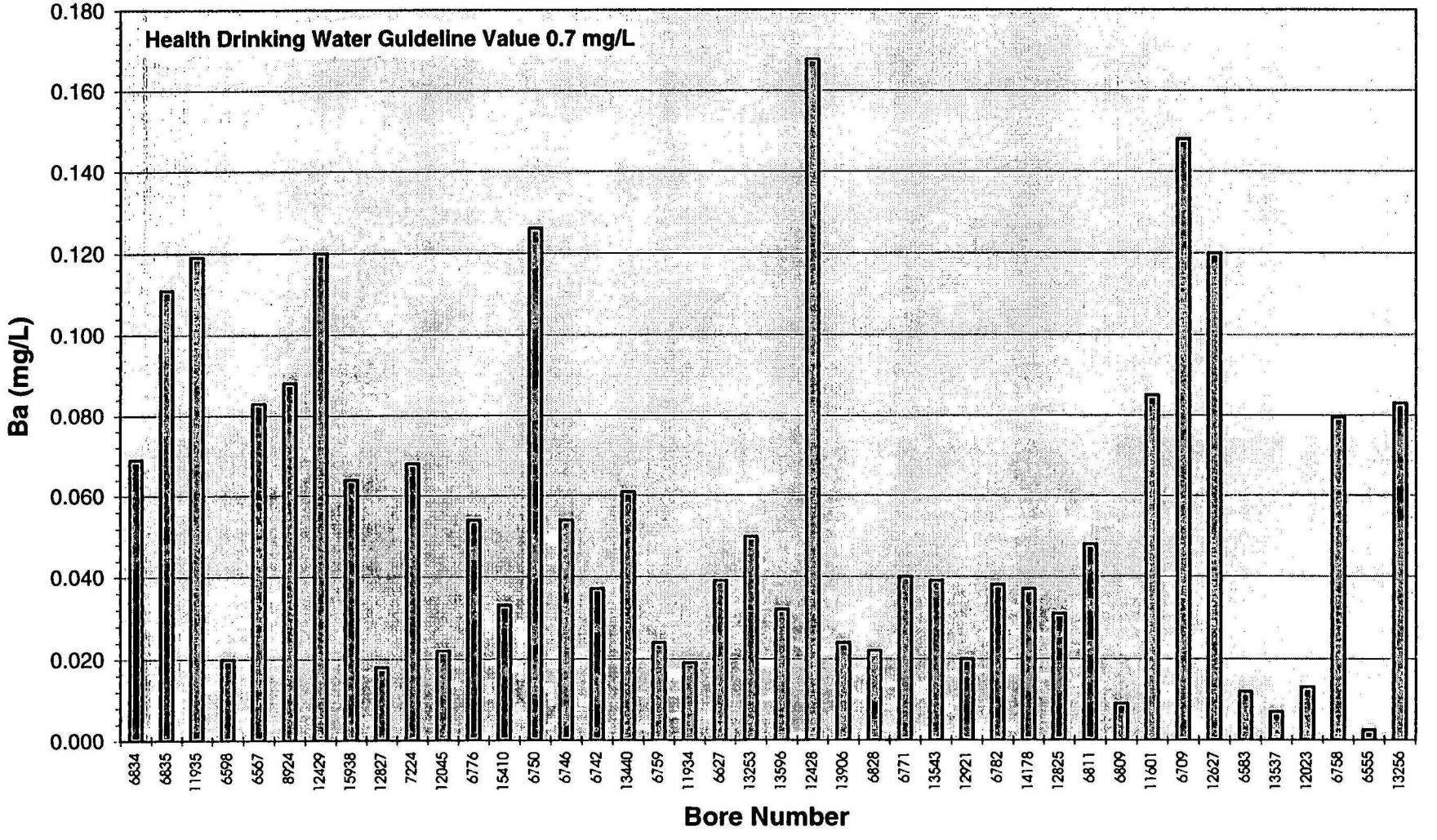


Fig 6.3 Piccadilly Valley: April-May 1994 Groundwater - Strontium Concentrations (AGSO Lab)

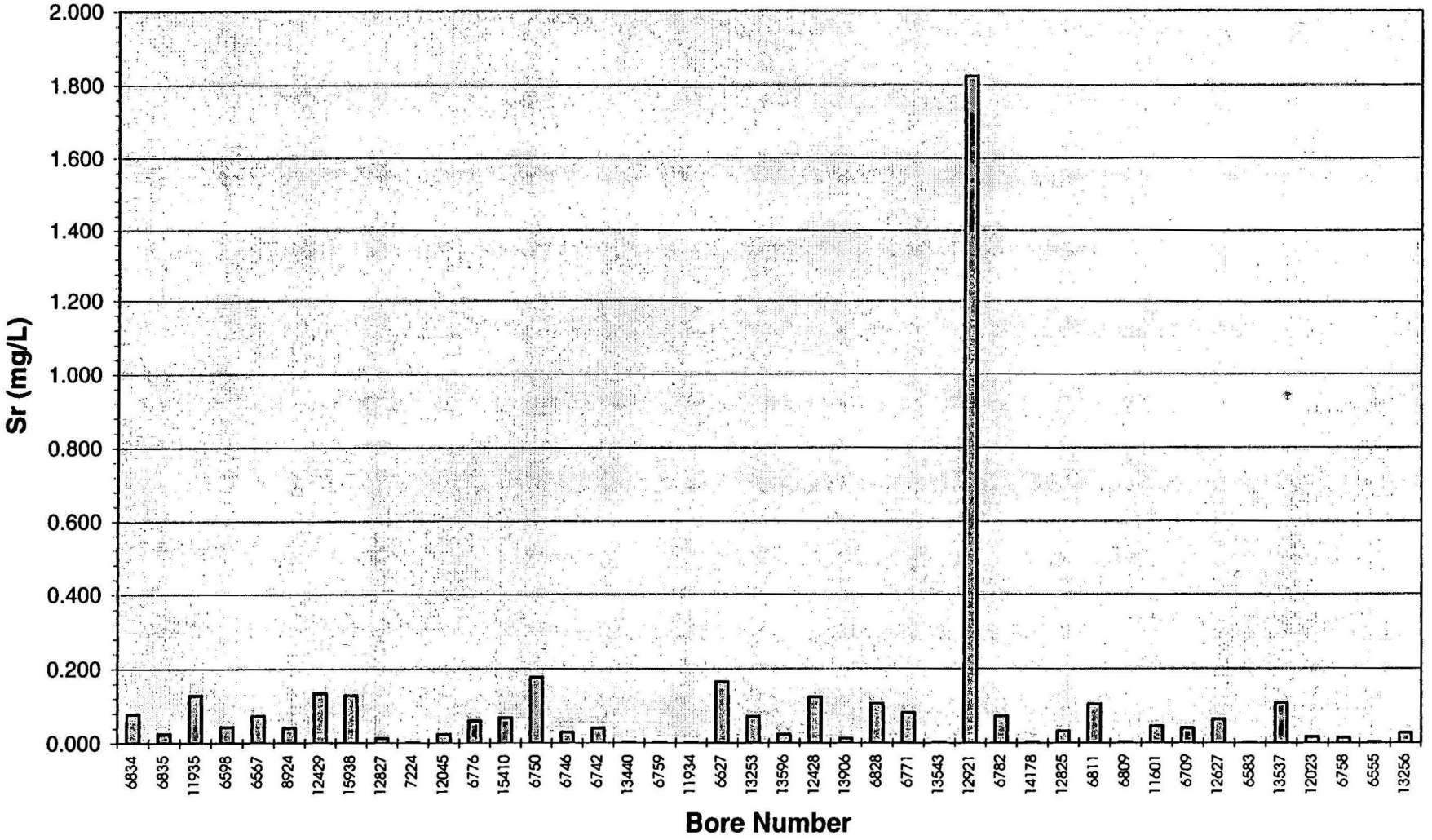


Fig 6.4 Piccadilly Valley: April-May 1994 Groundwater - Aluminium Concentrations (AGSO Lab)

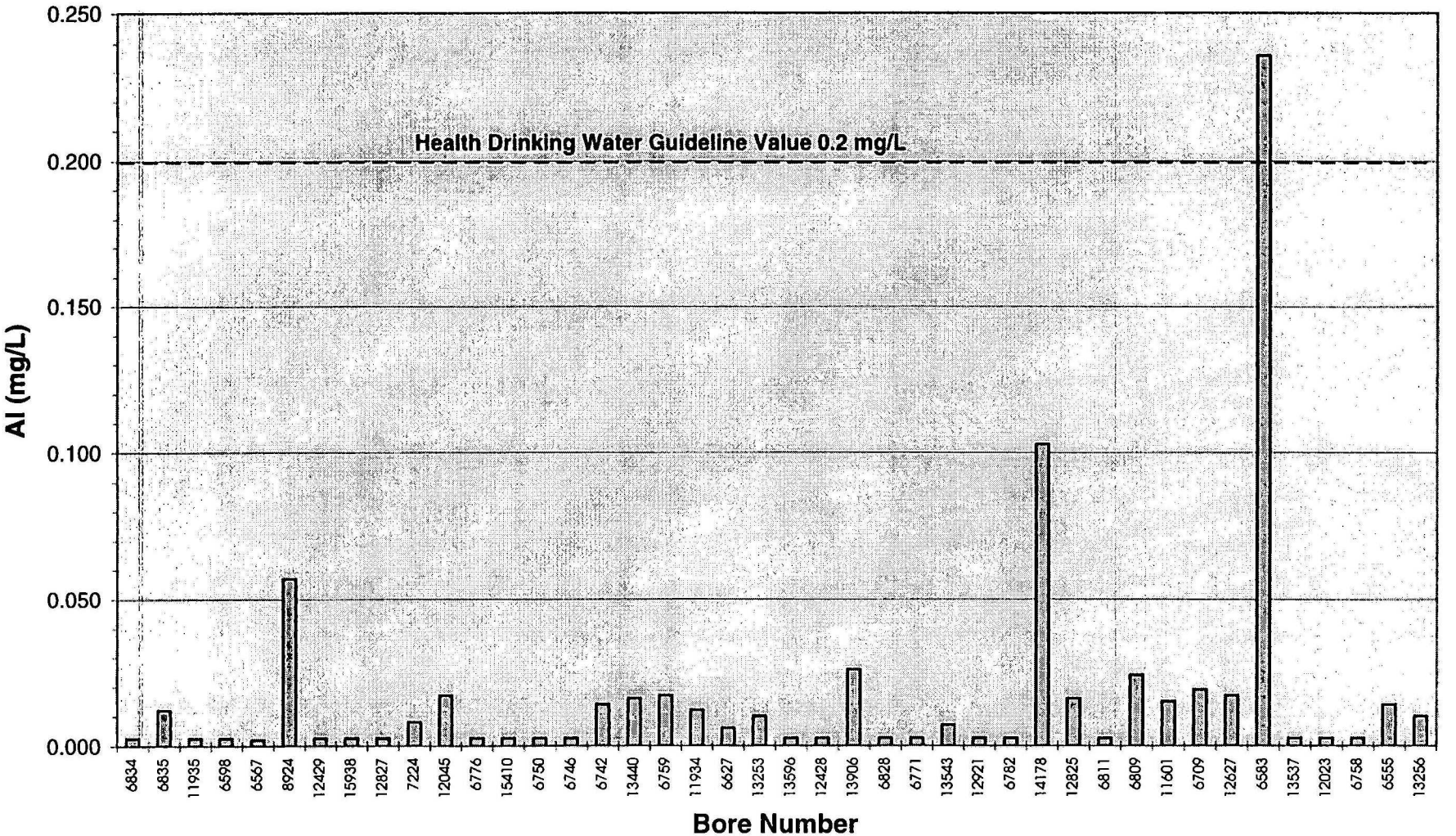


Fig 6.5 Piccadilly Valley: April-May 1994 Groundwater - Cobalt Concentrations (AMDEL Lab)

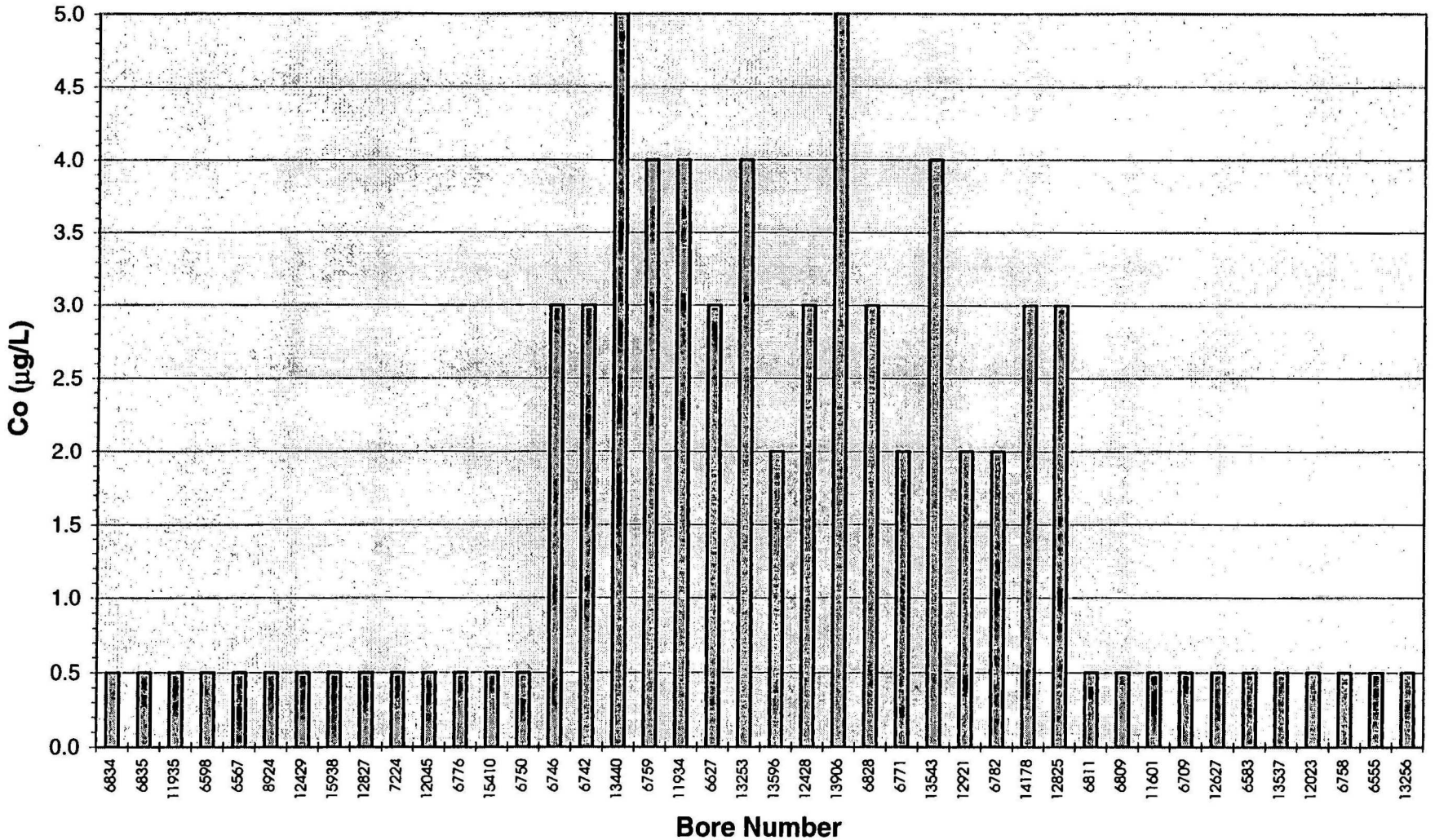


Fig 6.6 Piccadilly Valley: April-May 1994 Groundwater - Copper Concentrations (AGSO Lab)

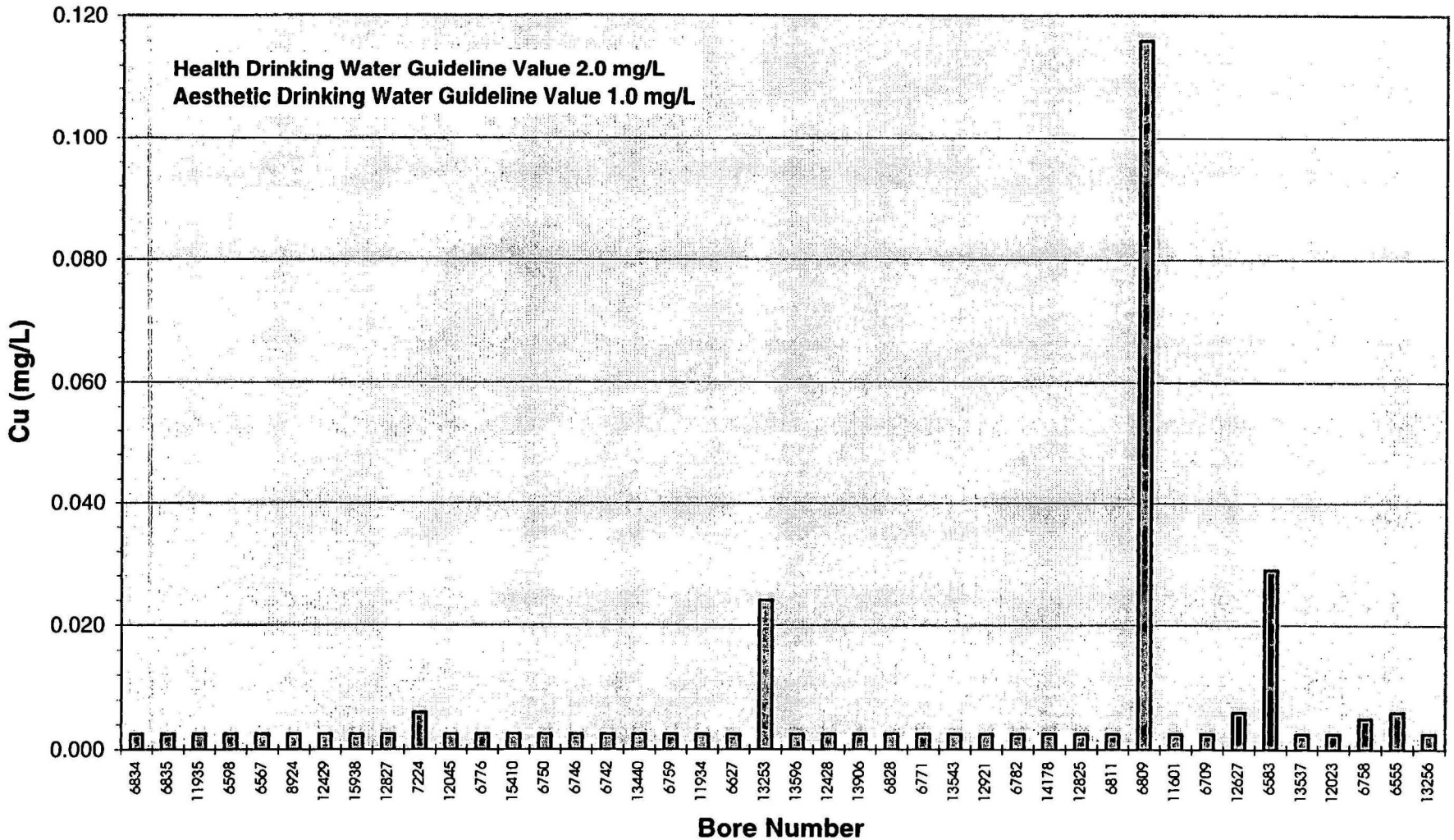


Fig 6.7 Piccadilly Valley: April-May 1994 Groundwater - Lead Concentrations (AMDEL Lab)

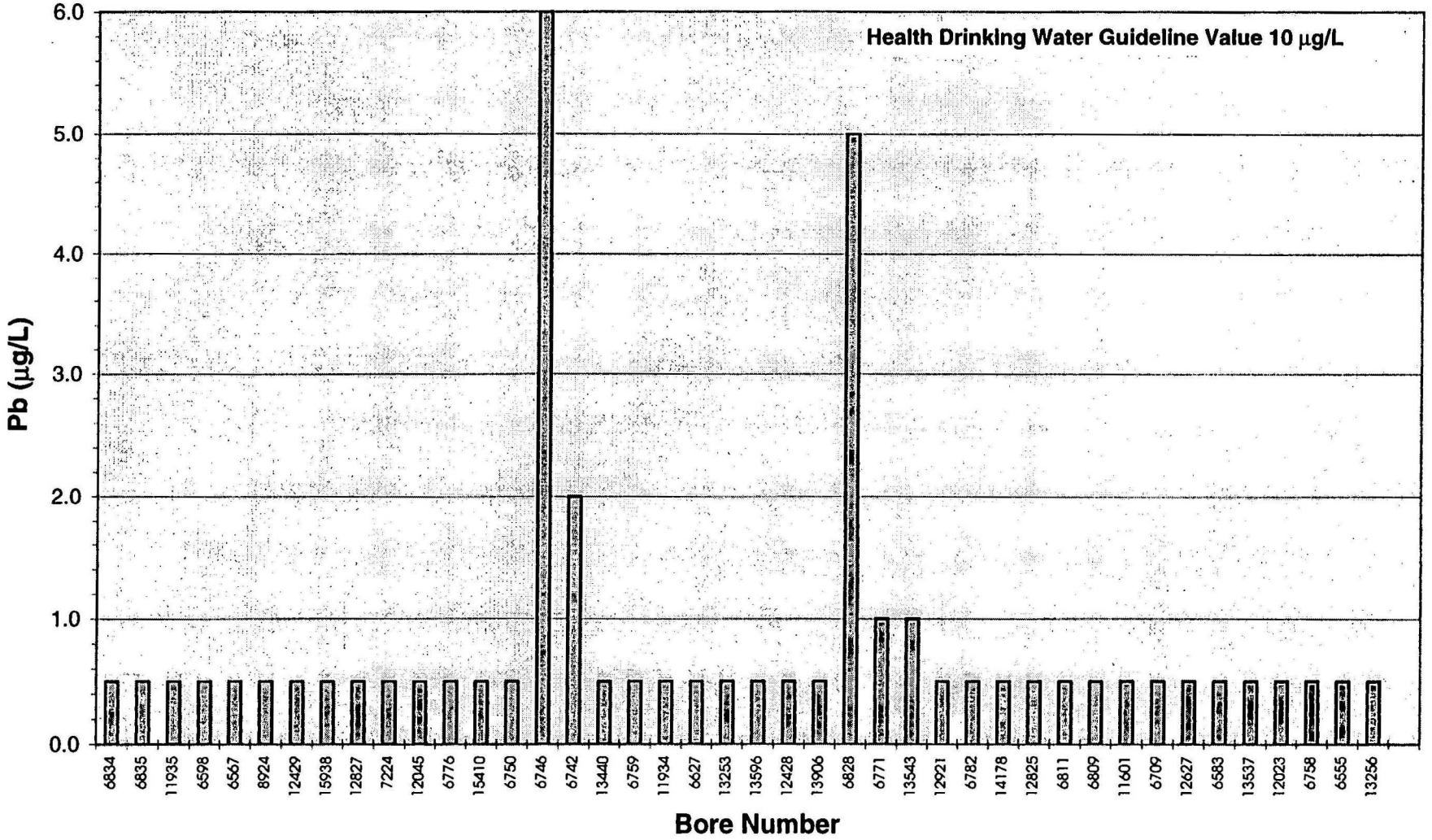


Fig 6.8 Piccadilly Valley: April-May 1994 Groundwater - Molybdenum Concentrations (AMDEL Lab)

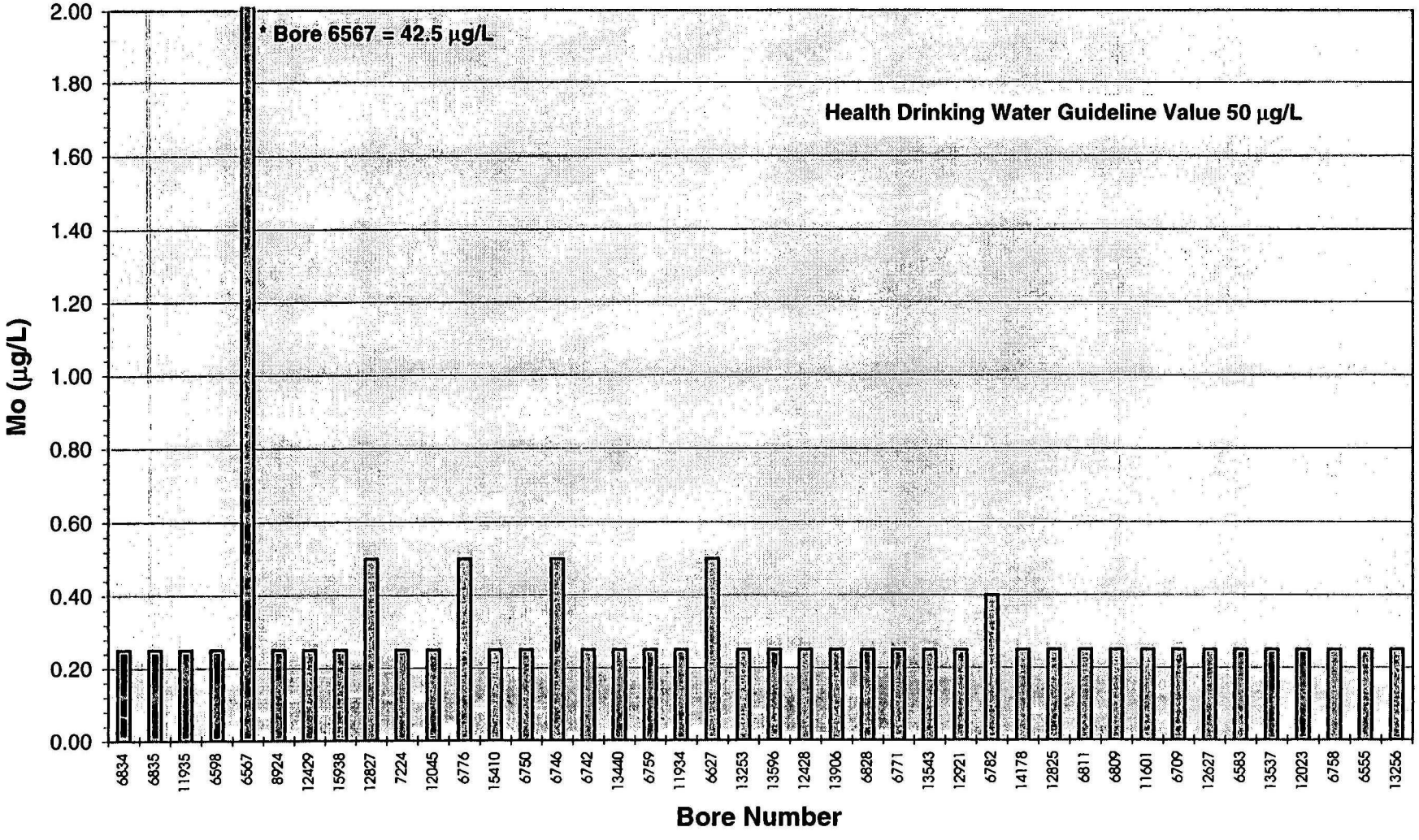


Fig 6.9 Piccadilly Valley: April-May 1994 Groundwater - Nickel Concentrations (AMDEL Lab)

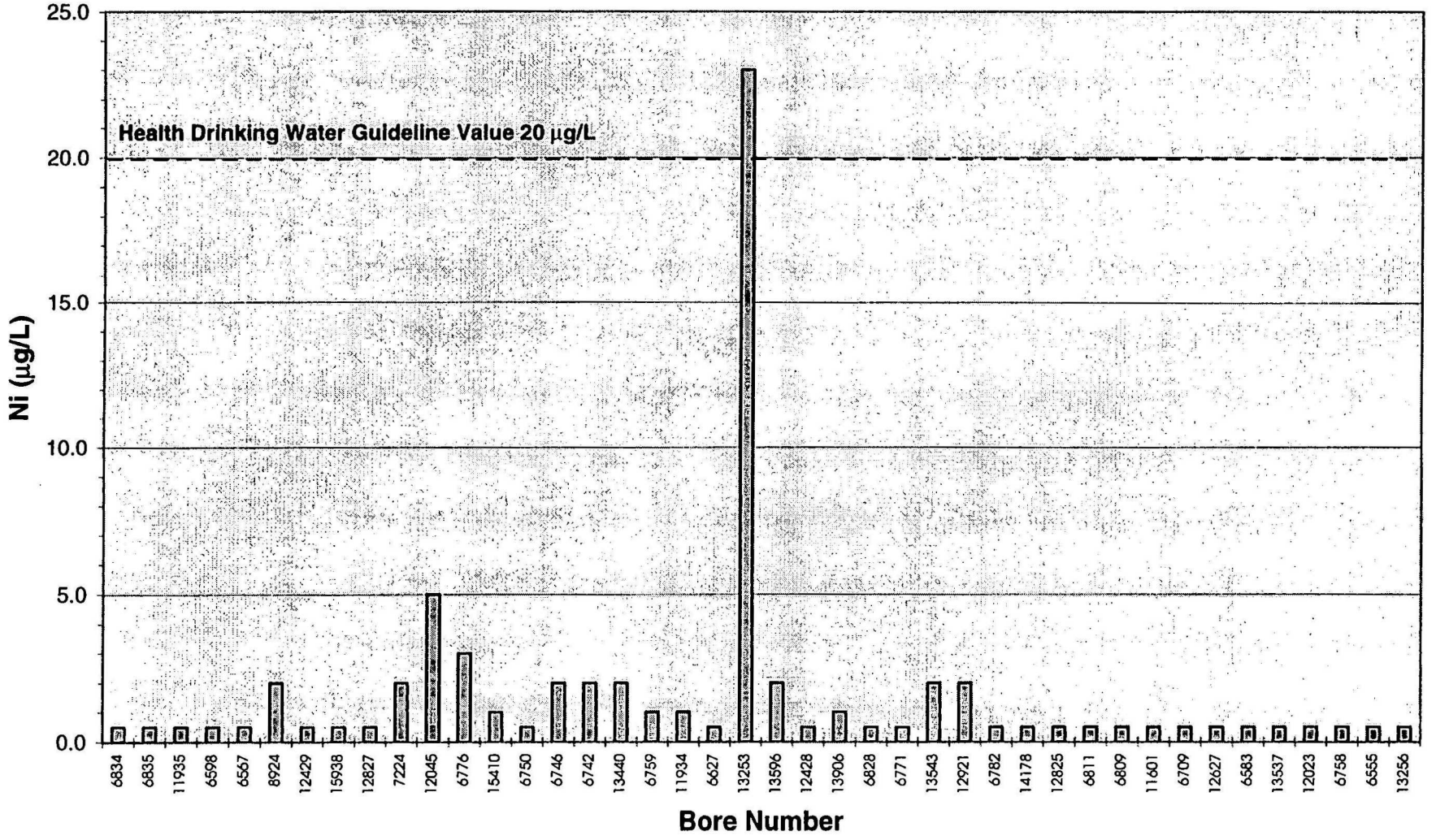


Fig 6.10 Piccadilly Valley: April-May 1994 Groundwater - Silver Concentrations (AMDEL Lab)

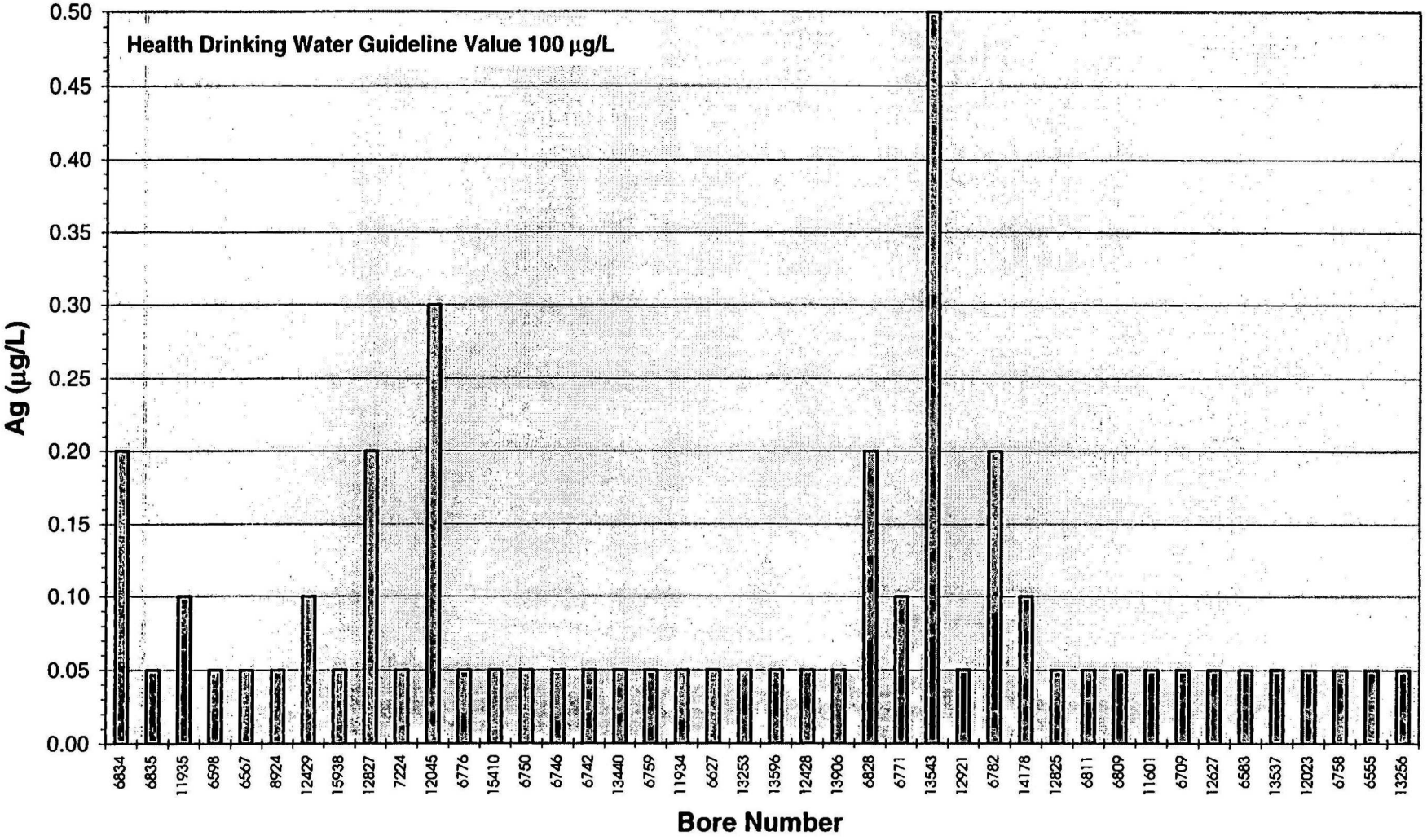


Fig 6.11 Piccadilly Valley: April-May 1994 Groundwater - Vanadium Concentrations (AMDEL Lab)

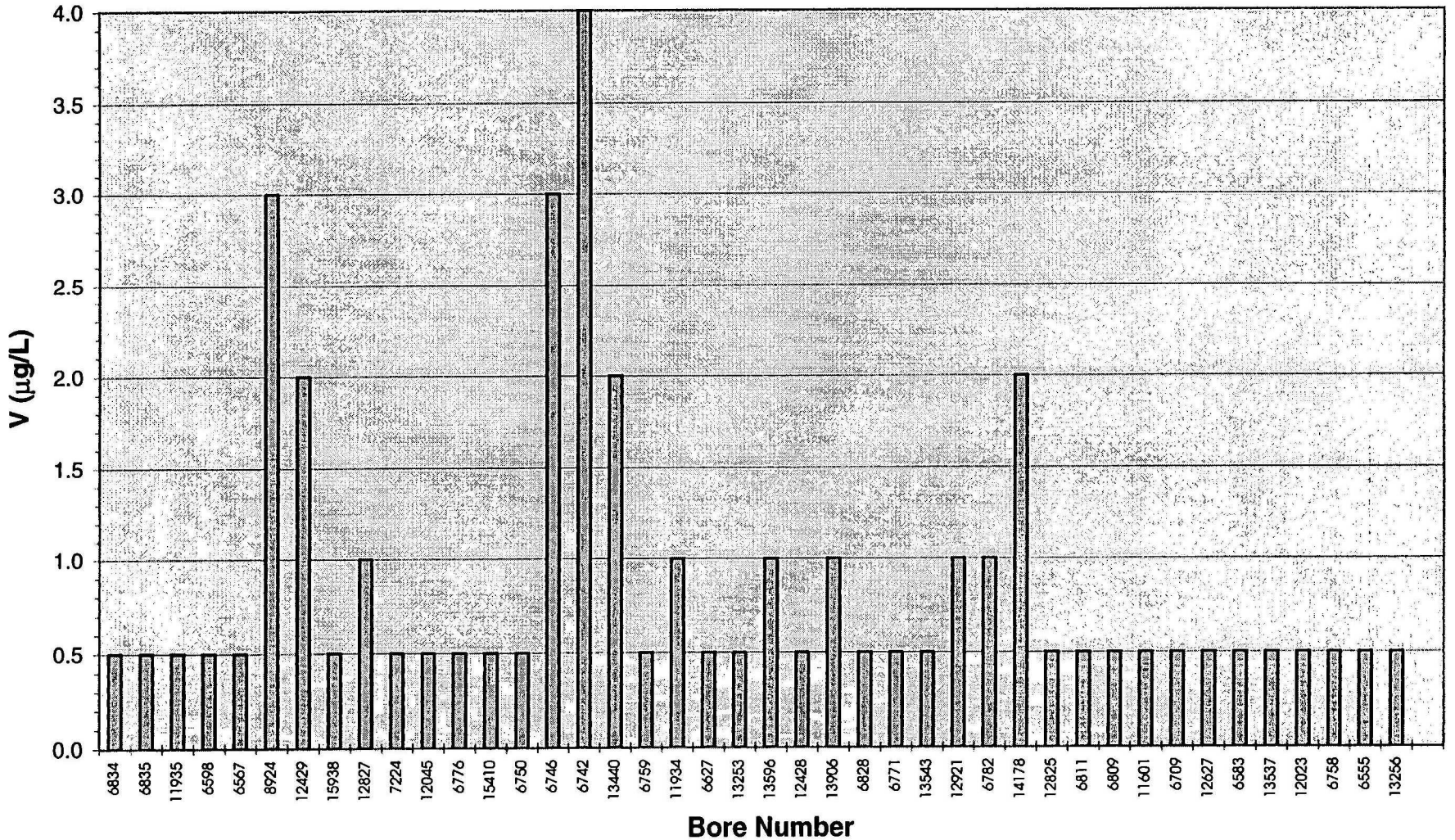


Fig 6.12 Piccadilly Valley: April-May 1994 Groundwater - Zinc Concentrations (AGSO LAB)

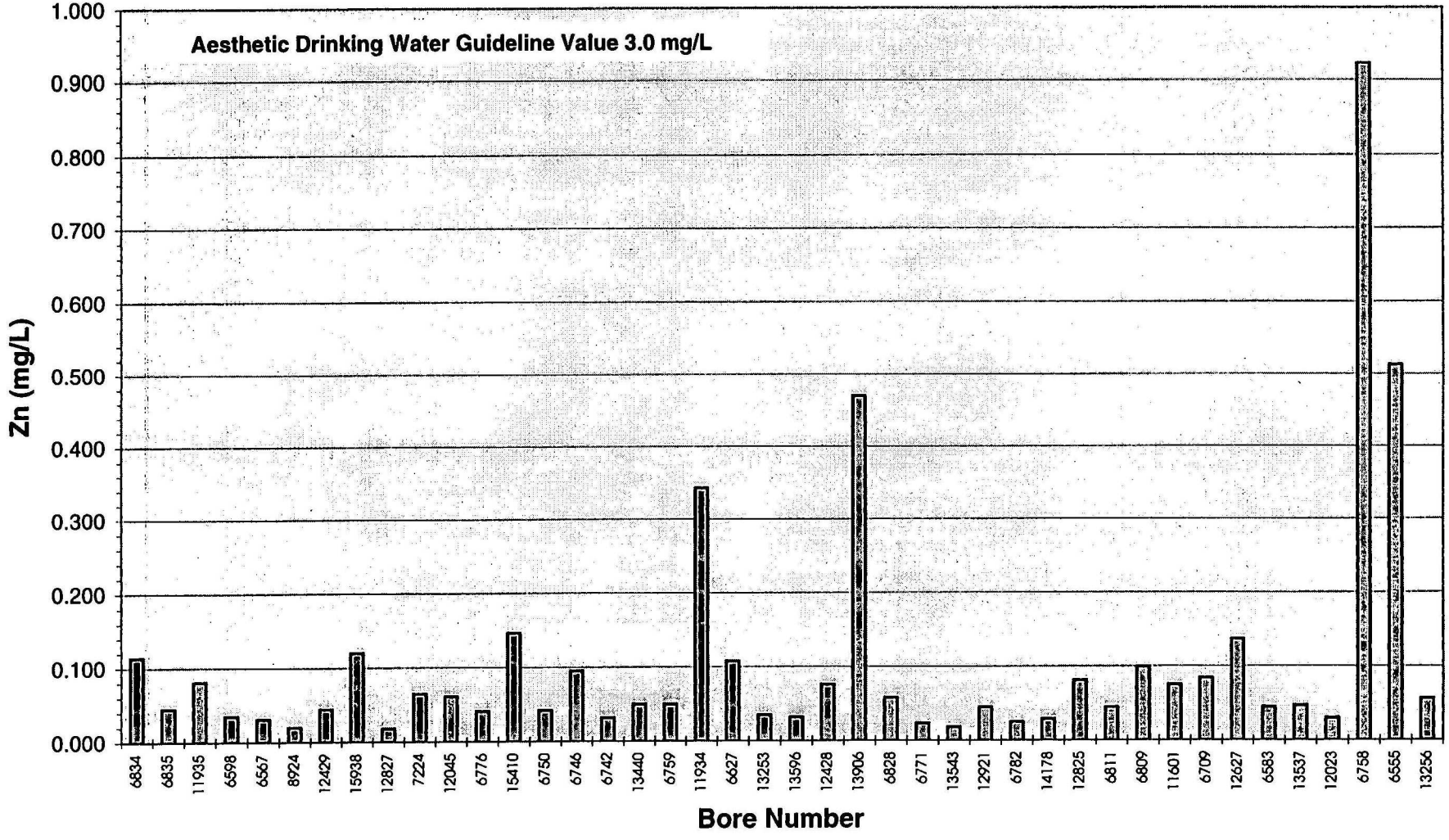


Fig 6.13 Piccadilly Valley: April-May 1994 Groundwater - Antimony Concentrations (AMDEL LAB)

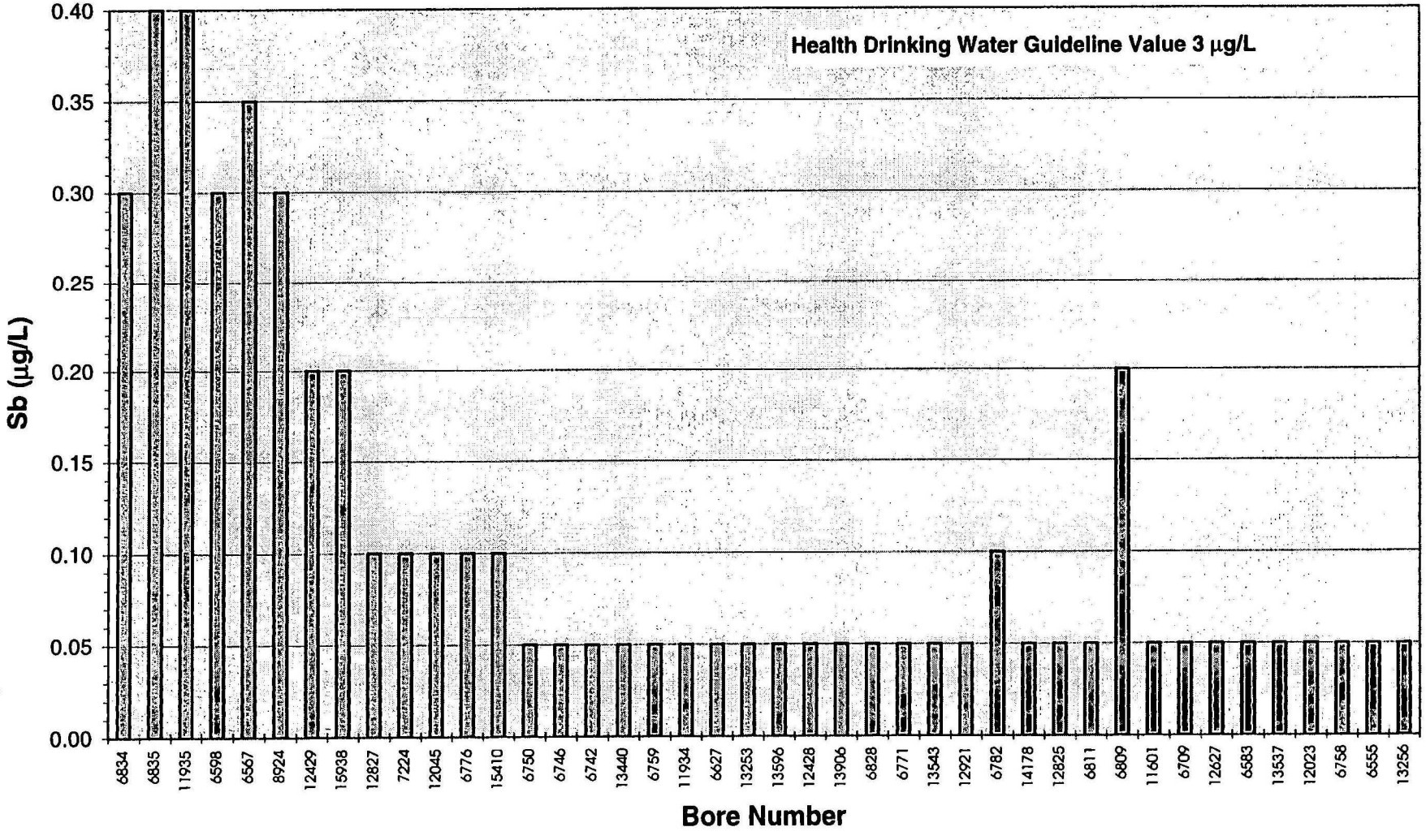


Fig 6.14 Piccadilly Valley: April-May 1994 Groundwater - Arsenic Concentrations (AMDEL Lab)

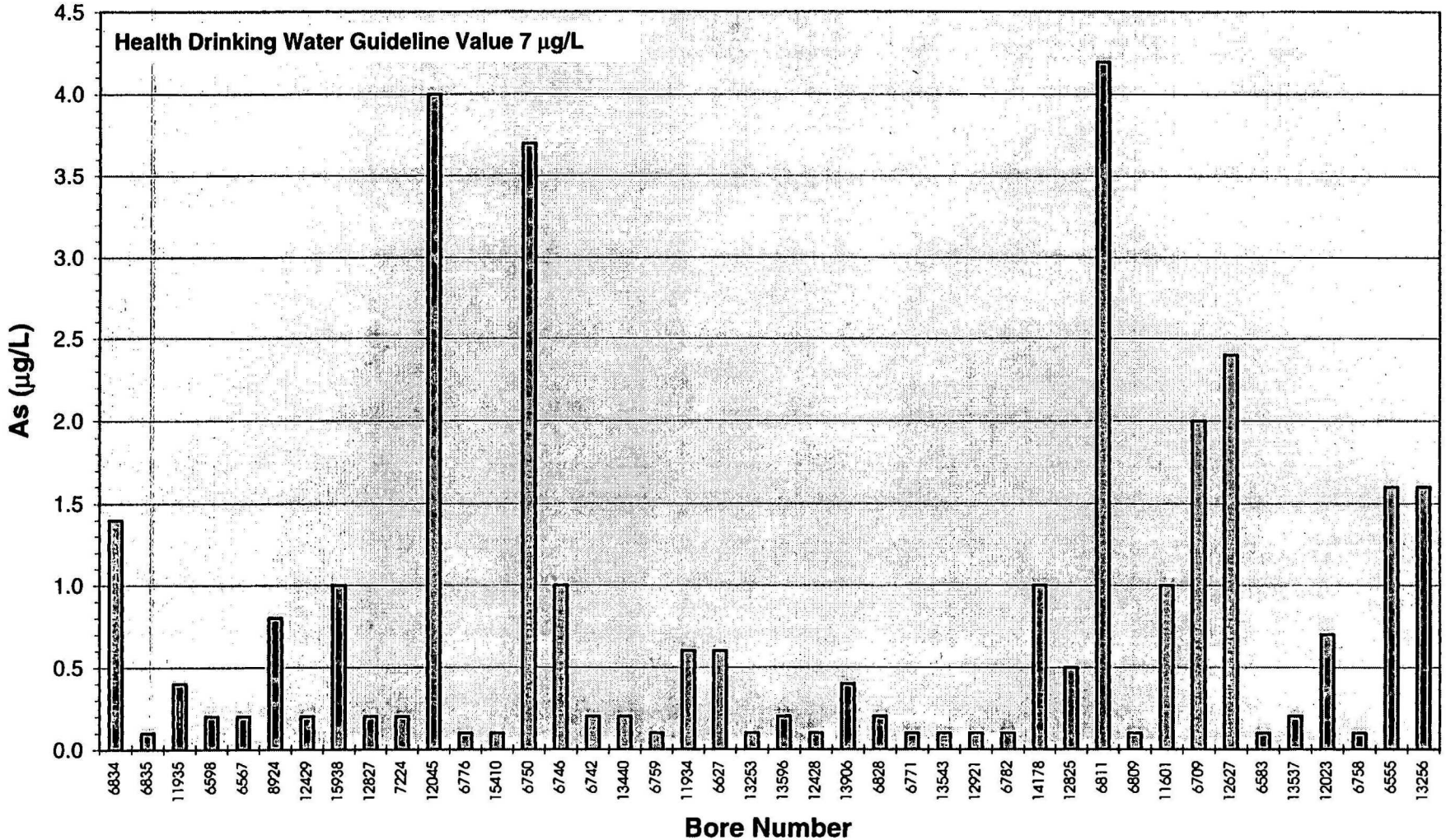


Fig 6.15 Piccadilly Valley: April-May 1994 Groundwater - Boron Concentrations (AGSO Lab)

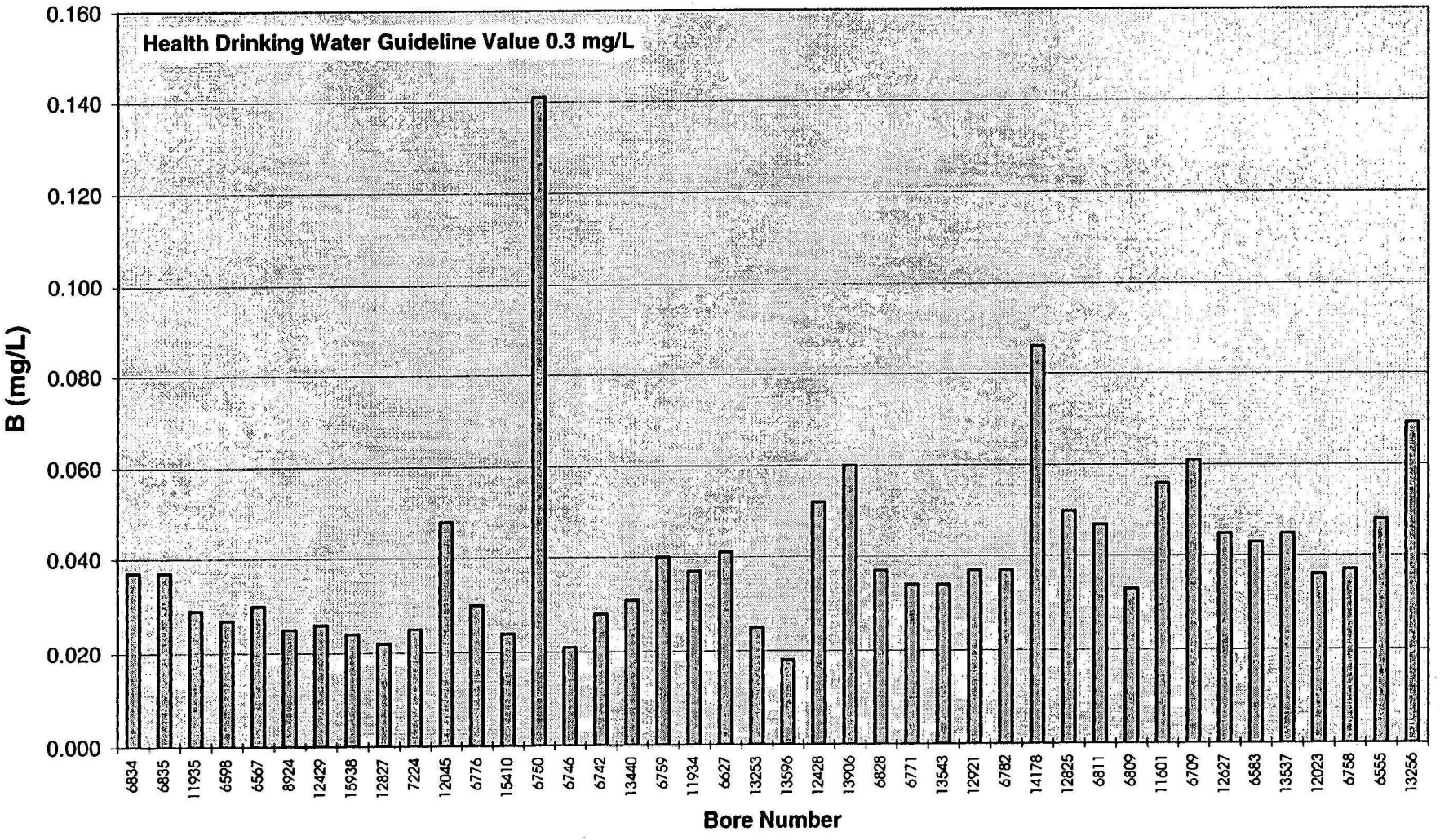


Fig 6.16 Piccadilly Valley: April-May 1994 Groundwater - Selenium Concentrations (AMDEL Lab)

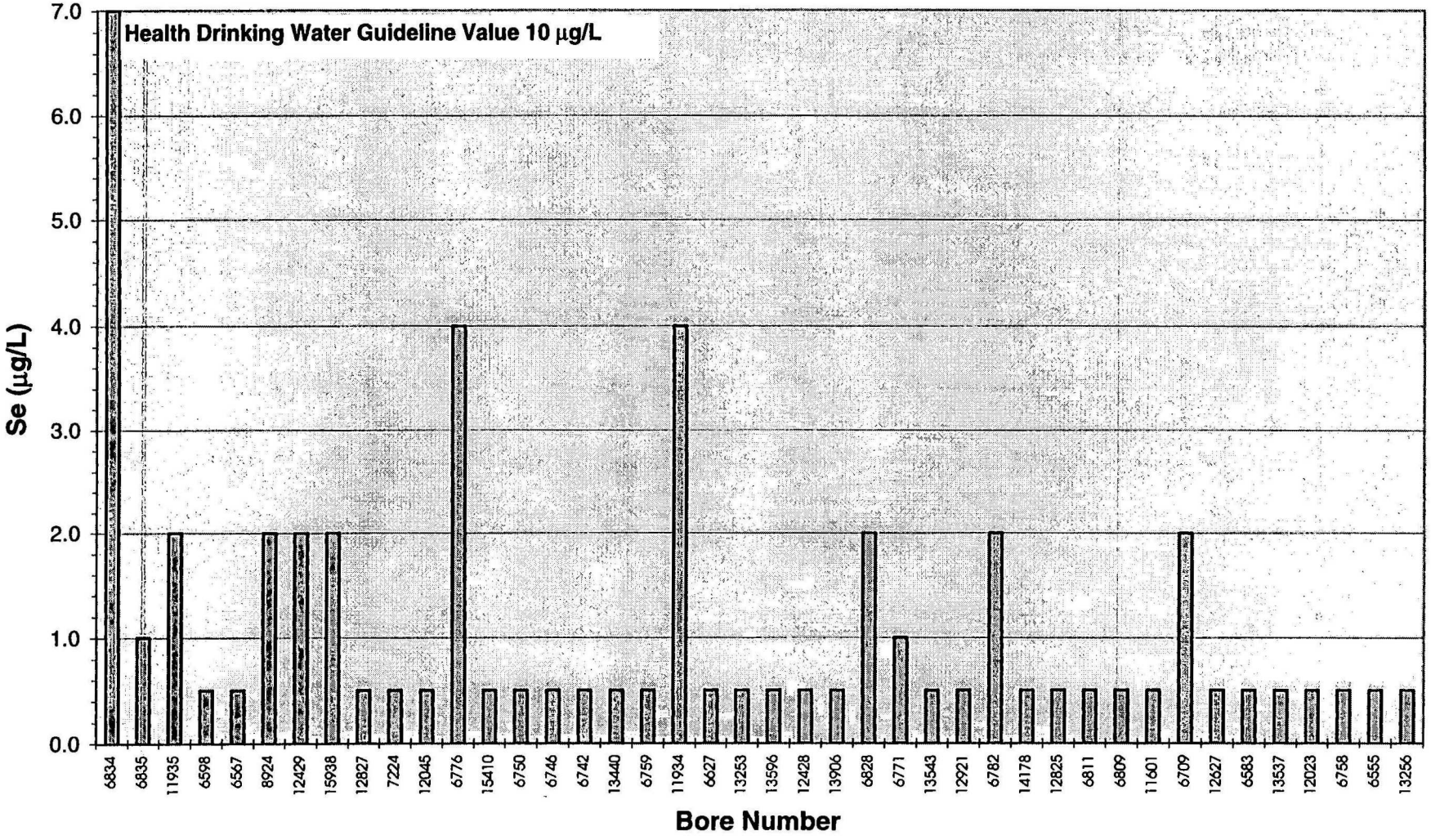
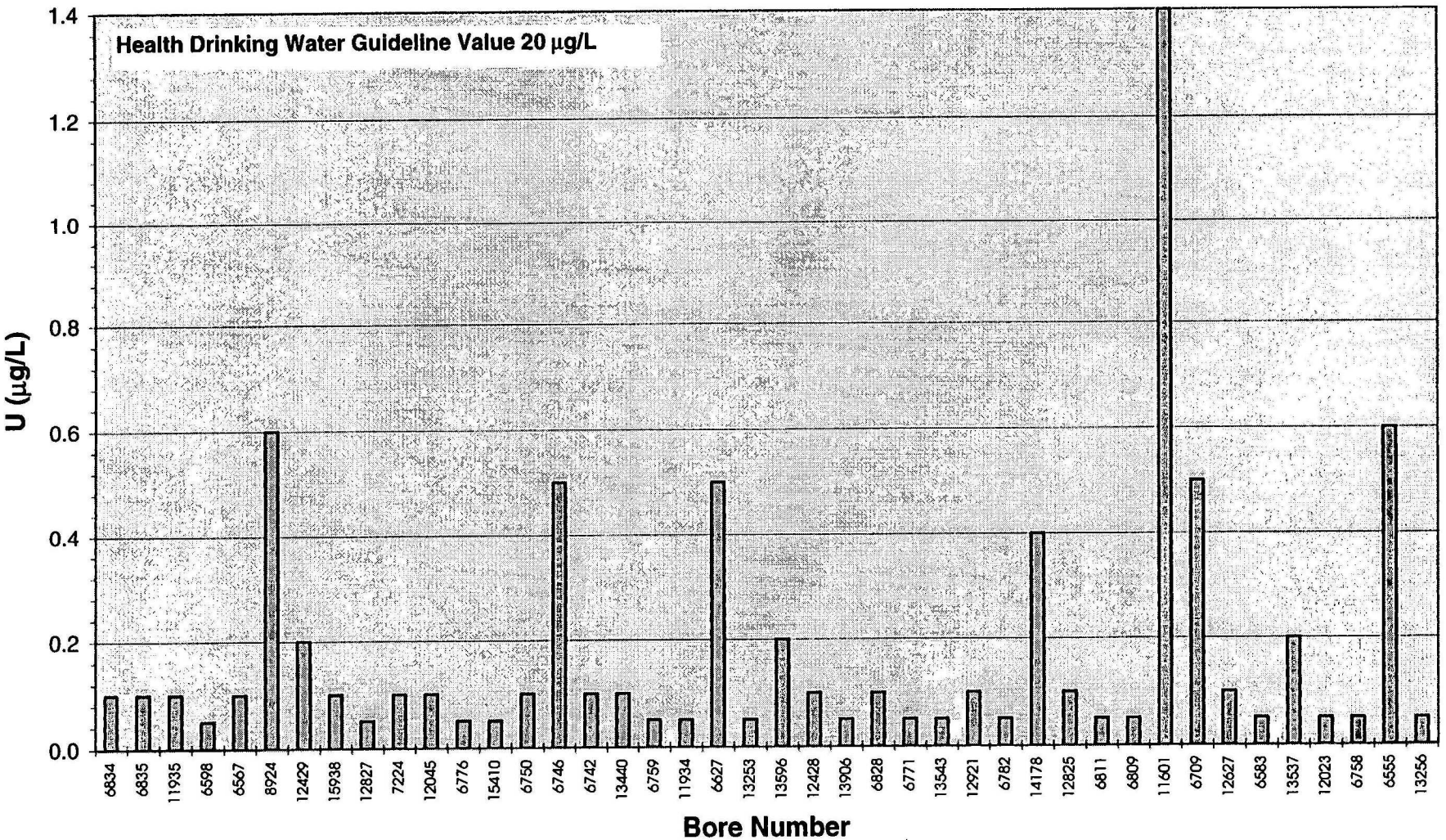


Fig 6.17 Piccadilly Valley: April-May 1994 Groundwater - Uranium Concentrations (AMDEL Lab)



7.0 NUTRIENTS

The nutrients analysed for in this study were dissolved organic carbon, ammonium, nitrite, nitrate, total oxidised nitrogen, total nitrogen, orthophosphate, acid hydrolysed phosphate and total phosphate. The data is presented in Table 7.1 and includes the maximum, minimum and median values for each parameter. For those samples in which the concentration was less than the limit of detection, a value of half the detection limit has been substituted for statistical purposes and graphing.

7.1 DISSOLVED ORGANIC CARBON (DOC)

The dependence of living matter on water in the hydrologic cycle ensures that all natural water contains organic material. Organic matter, even in small amounts, can have significant effects on the chemical properties of aqueous systems by forming complexes that affect metal solubilities, participating in redox reactions and serving as nutrients for microbiota that mediate chemical processes (Hem, 1989).

With the exception of bore 6834, which had a DOC concentration of 1.1 mg/L, the DOC concentrations in this study were below the 1.0 mg/L limit of detection and are at the lower end of the range found in several Australian catchments.

7.2 NITROGEN

Nitrogen is widely present in the environment in many chemical forms exhibiting different environmental behaviours. Nitrate, for example, is highly soluble and very mobile, which makes it highly susceptible to leaching through the soil with infiltrating water. The risk of nitrate contamination to groundwater is especially significant in areas of intense agricultural activity because of the combination of irrigation water and high fertilisation rates.

Nitrogen is an important component of all proteins and, hence is found in all foods and animal wastes. Consequently, there are many sources of nitrogen, natural and anthropogenic, that can contribute to groundwater contamination (Hallberg and Keeney, 1993). The most common forms of nitrogen in groundwater are ammonium, nitrite, nitrate and organic nitrogen.

Table 7.1: April-May 1994 Piccadilly Valley Groundwaters Nutrient Chemistry

Bore Number	DOC (mg/L)	NH_4-N (mg/L)	NO_2-N (mg/L)	NO_3-N (mg/L)	Total Oxidised Nitrogen-N (mg/L)	Total Nitrogen-N (mg/L)	Ortho PO_4-P (mg/L)	Acid Hydrolysed PO_4-P (mg/L)	Total PO_4-P (mg/L)
6834	1.1	0.01	0.005	1.00	1.00	1.10	0.05	0.05	0.05
6835	0.5	0.03	0.005	0.78	0.79	0.85	0.004	0.011	0.015
11935	0.5	0.005	0.005	1.80	1.80	1.80	0.038	0.038	0.038
6598	0.5	0.02	0.005	1.20	1.20	1.50	0.041	0.041	0.041
6567	0.5	0.02	0.005	2.20	2.20	2.20	0.015	0.015	0.016
8924	0.5	0.01	0.005	10.00	10.00	10.00	0.01	0.01	0.015
12429	0.5	0.01	0.005	2.70	2.70	2.70	0.057	0.057	0.057
15938	0.5	0.02	0.005	0.62	0.62	0.65	0.027	0.029	0.032
12827	0.5	0.02	0.005	1.40	1.40	1.70	0.013	0.014	0.017
7224	0.5	0.02	0.005	2.00	2.00	2.00	0.002	0.004	0.012
12045	0.5	0.03	0.005	0.01	0.01	1.10	0.003	0.004	0.008
6776	0.5	0.02	0.005	2.40	2.40	2.40	0.047	0.047	0.047
15410	0.5	0.04	0.005	3.30	3.30	3.30	0.029	0.029	0.029
6750	0.5	0.03	0.005	0.0008	0.0008	0.025	0.027	0.060	0.063
6746	0.5	0.005	0.005	0.22	0.22	0.28	0.015	0.015	0.021
6742	0.5	0.01	0.005	6.00	6.00	6.00	0.026	0.035	0.041
13440	0.5	0.02	0.005	0.16	0.16	0.21	0.003	0.005	0.010
6759	0.5	0.11	0.030	0.74	0.77	0.91	0.002	0.005	0.008
11934	0.5	0.01	0.005	0.019	0.019	0.05	0.047	0.290	0.290
6627	0.5	0.02	0.005	0.10	0.10	0.11	0.008	0.014	0.017
13253	0.5	0.01	0.005	15.00	15.00	15.00	0.016	0.022	0.026
13596	0.5	0.01	0.005	1.00	1.00	1.20	0.740	0.780	0.810
12428	0.5	0.02	0.005	0.004	0.004	0.02	0.046	0.069	0.072
13906	0.5	0.06	0.005	0.033	0.033	0.10	0.007	0.007	0.008
6828	0.5	0.01	0.005	2.60	2.60	2.50	0.061	0.061	0.061
6771	0.5	0.005	0.005	1.50	1.50	1.60	0.043	0.043	0.043
13543	0.5	0.005	0.005	0.71	0.71	0.75	0.002	0.004	0.007
12921	0.5	0.01	0.005	0.30	0.30	0.32	0.008	0.008	0.011
6782	0.5	0.04	0.005	3.05	3.05	3.40	0.034	0.034	0.038
14178	0.5	0.02	0.005	0.57	0.57	0.71	0.002	0.004	0.007
12825	0.5	0.07	0.005	0.13	0.13	0.25	0.006	0.007	0.029
6811	0.5	0.02	0.005	0.0005	0.0005	0.01	0.036	0.087	0.099
6809	0.5	0.10	0.005	6.60	6.60	7.40	0.001	0.003	0.007
11601	0.5	0.02	0.005	0.0005	0.0005	0.11	0.140	0.130	0.150
6709	0.5	0.03	0.005	0.017	0.017	0.04	0.008	0.008	0.009
12627	0.5	0.01	0.005	0.0005	0.0005	0.05	0.022	0.220	0.221
6583	0.5	0.01	0.005	0.38	0.38	0.41	0.001	0.003	0.005
13537	0.5	0.02	0.005	0.015	0.015	0.02	0.017	0.026	0.030
12023	0.5	0.005	0.005	1.10	1.10	0.89	0.120	0.120	0.100
6758	0.5	0.008	0.005	0.28	0.28	0.33	0.005	0.006	0.012
6555	0.5	0.03	0.005	0.16	0.16	0.36	0.008	0.072	0.093
13256	0.5	0.01	0.005	0.0005	0.0005	0.04	0.011	0.200	0.230
Limit of Detection	1.0	0.010	0.010	0.0010	0.0010	0.001	0.002	0.002	0.002
Minimum	0.5	0.005	0.005	0.0005	0.0005	0.01	0.001	0.003	0.005
Maximum	1.1	0.11	0.03	15	15	15	0.74	0.78	0.81
Median	0.5	0.020	0.005	0.665	0.665	0.80	0.016	0.028	0.030

7.2.1 Ammonium (NH_4-N)

Sources of ammonia in groundwater include natural precipitation, geological deposits, fertilisers, plant residues and waste water (including domestic sewage). Ammonium is quickly lost in the nitrogen cycle through nitrification, immobilisation and mineralisation (Hallberg and Keeney, 1993). Its concentration is generally low in groundwaters because it adsorbs to soil particles and clays and is not readily leached from soils. The concentrations of ammonium present in natural or polluted waters are generally not physiologically damaging (ANZECC, 1992).

The concentrations of ammonium found in Piccadilly Valley groundwater samples (Fig 7.1) ranged from <0.01 to 0.11 mg/L with a median value of 0.02 mg/L. No samples were found to exceed the 1996 NH&MRC/ARMCANZ aesthetic drinking water guideline value of 0.4 mg/L ammonium-N.

7.2.2 Nitrite (NO_2 - N)

Nitrite is an intermediate oxidation state of nitrogen, both in the oxidation of ammonia to nitrate and in the reduction of nitrate. It is unstable in oxic water as it is rapidly oxidised to nitrate by nitrifying bacteria or through chemical oxidation. The 1996 NH&MRC/ARMCANZ health drinking water guideline value for nitrite-N is 1.0 mg/L. The major biological effect of nitrite in humans is its involvement in the oxidation of normal haemoglobin to methaemoglobin, which is unable to transport oxygen to the tissues. This condition is called methaemoglobinaemia. Young infants (under three months of age) are more susceptible to methaemoglobin formation than older children and adults. Other susceptible groups include pregnant women and people with a deficiency of methaemoglobin reductase.

With the exception of bore 6759, which had a concentration of 0.03 mg/L nitrite-N, nitrite was not detected. The absence of nitrite is consistent with the generally oxidising conditions measured in the field (median DO value 2.93 mg/L; median Eh value 371 mV).

7.2.3 Nitrate (NO_3-N)

Nitrate is perhaps the most widespread nitrogenous contaminant within groundwater. Elevated nitrate concentrations may occur naturally or arise as a result of livestock wastes, septic tanks and the application of nitrogenous fertilisers. The toxicity of nitrate to humans is mainly due to its reduction to nitrite (which may contribute to methaemoglobin formation). Nitrate may be also be converted to nitrosamines, suspected carcinogens, in the human digestive tract. Adults and children over 3 months of age can generally drink water with up to 100 mg/L nitrate (22.6 mg/L nitrate-N) (1996 NH&MRC/ARMCANZ).

The background concentration for nitrate in the Piccadilly Valley has been reported as 1 mg/L nitrate (or about 0.25 mg/L nitrate-N)(Edwards, 1980). Though no substantiating data was provided, a value of 0.25 mg/L nitrate-N for background concentrations seems quite reasonable and may actually be a conservative estimate. A median value of 0.01 mg/L nitrate-N was obtained from eighty-seven samples collected throughout the Adelaide Hills (predominantly in the Onkaparinga Catchment where the land use is less intensive, excluding the Piccadilly Valley) as part of the AGSO's National Groundwater Quality Assessment Project.

The nitrate-N concentrations found in this study ranged from <0.001 to 15 mg/L nitrate-N (Fig 7.2) with a median value of 0.67 mg/L. Fifteen samples (36% of the bores) were </= to the previously reported background concentration of 0.25 mg/L nitrate-N (Fig 7.3). Twenty-seven samples (64.3% of the bores) exceeded background concentrations which suggests that the land uses in the Piccadilly Valley have impacted on the general quality of the groundwater as measured by nitrate concentrations. Four of the samples which exceeded background concentrations had nitrate-N concentrations >/= 6 mg/L. One sample (bore 13253), located in an recently-cleared orchard, had a concentration of 15 mg/L nitrate-N, which exceeds the 1996 NH&MRC/ARMCANZ health drinking water guideline value of 50 mg/L nitrate (11.3 mg/L nitrate-N). It is probable that the clearing of this orchard, with the subsequent fallowing and tillage of the land, has facilitated the leaching of nitrate to the groundwater. Bore 8924, located adjacent to a market garden in the town of Piccadilly, had a concentration of 10 mg/L nitrate-N, which approaches the health guideline value. As the water from bore 8924 is used for drinking water, it should be monitored. Bore 6809, on land used for viticulture, had a nitrate-N concentration of 6.6 mg/L. Bore 6742 had a concentration of 6.0 mg/L nitrate-N and is located in a market garden.

Because fractures have the capacity to transport water and contaminants rapidly over large distances, there is a degree of uncertainty in specifically correlating the source of contamination with a nearby property or land use. Nonetheless, it is evident that horticultural activity and residential developments are having a measurable impact on the groundwater quality by providing sources of anthropogenic nitrate.

The distribution of nitrate concentrations throughout the study area was fairly erratic (Fig 7.4) and not correlated with land use around the well head or with concentrations of other major ions associated with fertiliser applications such as calcium, magnesium, potassium and chloride. Relatively high concentrations of nitrate were found in bores adjacent to others with low nitrate concentrations. This may be explained by preferential flow paths and by the fact that discrete fracture zones, which are not hydraulically connected, may contain water of different compositions (consistent with the isotopic and hydrochemical interpretations). Generally nitrate concentrations were consistently above background concentrations in the centre of the Piccadilly Valley (Fig 7.5), down gradient from residential areas, where the groundwater table is more shallow and where the land is predominantly used for market gardening.

7.2.3.1 Nitrate, Dissolved Oxygen and TDS

There was a weak (positive) correlation (R^2=0.2) between dissolved oxygen (DO) and nitrate-N concentrations (Fig 7.6). The poor correlation may in part be due to the unreliability of DO measurements from pumps due to air entrainment during pumping. Nonetheless, it is apparent that higher nitrate concentrations (above about 2 mg/L) are associated with higher DO concentrations. This is consistent with the likelihood that greater DO concentrations in the groundwater are inhibiting microbial denitrification. Higher DO concentrations are also consistent with a greater rate of recharge, which would increase the potential for nitrate transport to the aquifer. There was no direct correlation between nitrate concentrations and TDS (Fig 7.7); however, the highest nitrate concentrations were associated with lower TDS values, suggesting that recharge waters (with low TDS concentrations) may be responsible for facilitating nitrate transport to the aquifer. This is confirmed by the tritium data.

7.2.3.2 Nitrate and Tritium Concentrations

Nitrate and tritium concentrations are plotted in Figure 7.8, ordered by decreasing tritium concentration. Four of the most elevated nitrate concentrations (bores 6809, 13253, 8924 and 6742) were found in samples containing tritium concentrations greater than 1.4 TU, which is consistent with modern recharge facilitating the transport of nitrate.

One might expect that water samples containing tritium concentrations less than 1.4 TU would have nitrate concentrations approaching background concentrations due to the minimal input of recharge water; however, 7/25 bores with tritium concentrations less than 1.4 TU had nitrate concentrations above the reported background concentration of 0.25 mg N/L. It is most probable that some modern recharge is transporting nitrate to these bores, and that mixing is occurring between tritiated and non, or low, tritiated water. Another possible explanation is that leaking septic tanks are providing an additional source of nitrate, which is substantiated by the nitrogen-15 isotope (Section 7.2.3.4).

7.2.3.3 Nitrate and Depth Distribution

As nitrate is highly soluble and very mobile, it is highly susceptible to leaching through the soil with infiltrating water (Hallberg and Keeney, 1993). As a result, some of the parameters which may affect nitrate distributions in groundwater are the soil thickness, depth to water table and depth to the aquifer (these parameters have been extracted from records held by the Department of Mines and Energy, South Australia, see Appendix A).

The soil thickness, depth to water table and depth to aquifer (defined by 'first water cut' in drillers logs, which is the top of the casing screen) relationships with nitrate are illustrated in Figures 7.9-7.11. Nitrate concentration did not show any obvious

relationship to any of those parameters; however, some general conclusions can be made. Low concentrations of nitrate (< 1 mg/L) are found throughout the range of depths to water table, soil thicknesses and aquifer depths. Elevated nitrate concentrations (above 1 mg/L) are generally found where the depth to water table is less than 20m, the soil thickness is less than 9m and the depth to aquifer is less than approximately 40m.

7.2.3.4 Nitrogen-15 Isotope

Because of the numerous sources of nitrogen contamination in groundwater systems, distinguishing whether contamination originated from agricultural fertilisers, animal wastes or sewage effluent is often difficult. One method for distinguishing different sources of nitrogen is by the use of stable nitrogen isotopes (Chapelle, 1993).

Nitrogen occurs as two stable isotopes: ^{15}N and ^{14}N. The ratios of these isotopes are reported as $\delta^{15}N$ relative to atmospheric N_2. Many studies have demonstrated that the nitrogen isotopic composition of nitrate dissolved in groundwater can be used to semi-quantitatively differentiate sources of nitrate (Gormly and Spalding 1979; Spalding et al. 1982; Kreitler and Browning 1983; Filpse and Bonner 1985; Kaplan and Magritz 1986; Spalding et al. 1993).

Ranges of $\delta^{15}N$ for nitrogen from different sources are shown in Fig 7.12 (after Chapelle, 1993). In general, nitrogen present in inorganic fertilisers ranges from about -4 to +2 per mil and nitrogen present in animal (and human wastes) ranges from about +9 to +18 per mil.

The nitrogen-15 isotope values from 22 groundwater samples from the Piccadilly Valley ranged from +5.43 to +21.72 with a median value of +10.03 per mil (Table 7.2). The majority of the samples (77%) had $\delta^{15}N$ values above +9 per mil suggesting that human and/or animal wastes are the predominant source of nitrate. As the livestock density is quite low in the Piccadilly Valley, septic tanks or fertilisers containing animal wastes are thought to be the most probable source.

Five samples (12827, 7224, 6742, 13253 and 13543) had $\delta^{15}N$ values ranging from +5.43 to +8.83 per mil, which is indicative of nitrate derived either from the organic matter pool in the soils or a combination of human/animal and inorganic fertiliser nitrogen. As the dissolved organic carbon concentrations in the groundwater samples were low, one would not expect the source of nitrate to be from soil organics. Two of the five samples (13253 and 6742) had markedly elevated nitrate concentrations, suggesting a significant "leakage" of nitrogen from their respective sources.

Table 7.2 April-May 1994 Piccadilly Valley Groundwater Nitrogen-15 Isotopes

Bore Number	Mean NO_3-N (mg/L)	N^{15} ‰
6834	1.23	12.486
6835	1.03	15.878
11935	1.93	9.153
6598	1.38	10.166
6567	2.27	9.569
8924	10.10	9.865
12429	2.43	9.915
15938	0.76	12.230
12827	1.83	8.176
7224	2.09	5.428
6776	2.44	11.094
15410	3.41	9.664
6742	5.10	6.973
6759	0.99	21.722
13253	14.28	7.612
13596	1.24	15.253
6828	2.59	10.531
6771	1.72	11.679
13543	0.93	8.829
6782	3.38	12.560
6809	7.40	9.272
12023	1.26	10.139
Minimum	0.76	5.428
Maximum	14.28	21.722
Median	2.01	10.027

7.2.3.5 Historical Nitrate Data

Prior to this study, little information was available on the groundwater quality in the Piccadilly Valley other than a nitrate study discussed in both Harvey (1979) and Edwards (1980). They reported that of the 54 bores sampled in March and April 1979, five bores exceeded the 30 mg/L nitrate (or 6.8 mg/L nitrate-N) limit for domestic supplies suggested by the South Australian Health Commission at the time. The nitrate concentrations were reported to range from <0.01 to 52 mg/L nitrate (or 11.7 mg/L nitrate-N) with a median value of 1.7 mg/L nitrate (or 0.38 mg/L nitrate-N).

Table 7.3 gives a brief summary of both the 1979 and present nitrate data for comparison and suggests that there has been little increase in nitrate concentrations over the fifteen year period (median concentrations have increased from 0.38 mg/L to 0.67 mg/L nitrate-N). Thirteen of the bores sampled in 1994 were also sampled in 1979. The data from both studies is presented in Table 7.4 for comparison, along with the present day (1994) land use.

Table 7.3: Comparison of 1979 and 1994 Nitrate Studies

	1979 Nitrate Study	1994 Nitrate Study
Number of samples	54	42
Range	<0.01 to 11.7 mg N/L	<0.01 to 15 mg N/L
Median	0.38 mg N/L	0.67 mg N/L
% exceeding 0.25mg N/L	61% (33/54 bores)	64% (27/42 bores)

Table 7.4: A Comparison of 1979 and 1994 Nitrate Data

Bore Number	1979 NO_3-N (mg/L)	1994 NO_3-N (mg/L)	% Change	1994 Land Use
6834	0.18	1.00	82	residential, flowers
6835	2.71	0.78	-193	residential, paddock
8924	5.60	10.00	441	residential, adjacent market garden
6750	<0.01	<0.01	0	market garden
6746	0.03	0.22	19	market garden
6742	1.04	6.00	496	market garden
6759	0.27	0.74	47	residential
6828	1.44	2.60	116	market garden
6771	1.67	1.50	-17	market garden
6782	2.46	3.05	59	Uriadla P.S., adjacent toilet block
6809	7.47	6.60	-87	viticulture
6583	0.31	0.38	7	residential
6758	1.42	0.28	-114	viticulture, residential
Minimum	0.03	0.22		
Maximum	7.47	10.00		
Mean	2.05	2.76		
Median	1.43	1.25		

The data from Table 7.4, plotted in Fig 7.13 (grouped by 1994 land use) indicates that 54% (7/13) samples have shown an increase in nitrate concentration ranging from 19 to 496% between 1979 and 1994 (bores 6834,8924, 6746, 6742, 6759, 6828, 6782). Three of these seven bores (bores 6746, 6742 and 6828) are situated in market gardens and one bore is in a residential area adjacent to a market garden (bore 8924); these bores show the greatest increases in nitrate concentrations. The remaining three bores to show an increase in nitrate concentration are situated in residential areas, one of which is adjacent to the toilet block at Uraidla Primary School (bore 6782), which is likely to be a point source for nitrate, and the remaining two (bores 6759 and 6834) in the town of Piccadilly.

Four of the bores (31%) have shown decreases in nitrate concentrations ranging from 17 to 193% (bores 6835, 6771, 6809 and 6758). One of the bores (6835) is situated in a residential area (Piccadilly) in a grassy paddock which according to records, historically was used for market gardening; this bore shows the largest decrease in nitrate concentration (192.9%). Two bores (6809 and 6758), located on land cultivated for viticulture, showed fairly large decreases in nitrate concentrations.

Viticulture is a fairly recent land use within the Piccadilly Valley and it is probable that the decrease in nitrate concentrations found in these bores has occurred due to a change in land use practice (i.e., for example from market gardening to viticulture). Historical land use information obtained from 1970 aerial photography suggests that this change in land use has occurred. Another bore to show a decrease in nitrate concentration (bore 6771) is located in a market garden.

Two (15 %) of the bores have essentially remained at the same concentrations. One of the bores (6750) lies within a market garden and had nitrate concentrations below the limit of detection. The other bore (6583) lies within a residential area and contained nitrate concentrations just above background levels.

The relative changes in nitrate concentrations appear to be associated with the land use, although the small sample number (13 bores) coupled with the fractured nature of the aquifers and intensive land use, may render these observations to be random occurrence. The greatest increases in nitrate accessions to groundwater were associated with market gardens. Factors contributing to nitrogen accession in market gardening areas are the intensive application of nitrogenous fertilisers and irrigation water, which facilitates the leaching of nitrate. The practices of fallowing the land and soil tillage can also facilitate leaching of nitrate to the groundwater. The land use associated with viticulture showed decreases in nitrate concentrations. Viticulture, in contrast to market gardening, utilises much less fertiliser and irrigation water, and once the land has been planted with vines, it is neither tilled nor left fallow. As a result, less nitrate is likely to be transported to the groundwater in viticultural areas. The land use associated with residential areas has shown increases in nitrate concentration. This is most likely due to the presence of leaking septic tanks and sewerage networks, as well as the application of fertilisers to gardens and lawns in residential areas. As residential areas expand, there will be the potential for increased nitrate accessions to the groundwater.

There can be great variation in nitrate accession to the groundwater within any particular land use. Although the bores associated with market gardening showed the greatest increases in nitrate concentration (bores 6742, 6828 and 8924), one bore (6750) associated with market gardening had a nitrate concentration which remained below the detection limit and another (bore 6771) showed a slight decrease in nitrate concentration over the fifteen year period. The bores which showed no increase in nitrate concentration had water levels, soil thicknesses and DO concentrations comparable to those bores which showed large increases in nitrate concentrations. Additional factors to consider, for which we at present do not have data, are those related to the range of farming practices, fertiliser and irrigation application volumes, vegetative uptake, soil composition and fracture geometry. These variables are likely to influence the amount of recharge which occurs to the aquifer and hence the potential for nitrate accession to the groundwater.

One may conclude from the comparison of 1979 and 1994 data that the changes in nitrate concentrations in groundwater are variable with the increases being as great as 496% and the decreases as much as 193%. Although 54% of the bores have shown an increase in nitrate concentrations, the median nitrate-N value during the fifteen year period (specifically for these thirteen bores) has shown a slight decrease from 1.43 to 1.25 mg/L (or essentially remained about the same). The fact that the median nitrate concentration has not increased for this sub-sample of bores may be due to a shift in land use during recent years from market gardening to viticulture, combined with a greater network coverage of reticulated sewerage in residential areas. Of concern are the large increases in nitrate concentrations observed in bores 8924, 6742, 6828 and 6782.

7.2.4 Total Oxidised Nitrogen

Total oxidised nitrogen is the sum of nitrate and nitrite nitrogen (Fig 7.14) and ranged from <0.001 to 15.0 mg/L with a median value of 0.67 mg/L (as N). As nitrite concentrations were below the detection limit in all but one sample (bore 6759), the nitrate and total oxidised nitrogen concentrations are the same (except for bore 6759 where it was 0.77 mg/L).

7.2.5 Total Nitrogen

Total nitrogen is the sum of all forms of nitrogen and include nitrate, nitrite, ammonia and organic nitrogen. The total nitrogen concentrations (Fig 7.15; median value 0.8 mg/L) are slightly higher than the nitrate concentrations (median value 0.67 mg/L) and indicate that nitrate is the predominant form of nitrogen in the study area.

7.3 PHOSPHOROUS/PHOSPHATE

Phosphorus occurs in natural waters almost solely as phosphates. These are classified as orthophosphates, condensed phosphates (pyro-, meta-, and other poly-phosphates) and organic phosphates. They occur in solution, in particles or detritus, or in the bodies of aquatic organisms (APHA, 1989).

Orthophosphate is the most stable species of phosphate in natural waters. Phosphates are not very mobile in soils or sediments; however, soil erosion may add considerable amounts of suspended phosphate to water. The major solubility controls of phosphorus are related to co-precipitation and adsorption, as well as to uptake by biota (Hem, 1989).

Anthropogenic sources of phosphorus include fertilisers, sewage, animal waste, detergents and other organo phosphorous compounds such as insecticides. Phosphorus occurs naturally in the environment as a rather common element in igneous rocks and shale; nonetheless, concentrations present in solution in natural waters are normally no more than a few tenths of a milligram per litre (Hem, 1989). The range of naturally occurring phosphorus levels in groundwater has not been established. Phosphorus levels in groundwater are generally considered to be elevated when the concentration exceeds about 0.2 mg/L. In some areas natural background concentrations may be higher or lower than this value depending on the geology.

7.3.1 Total Dissolved Phosphate

Total dissolved phosphate (as P) concentrations in the Piccadilly Valley ranged from <0.002 to 0.81 mg/L with a median value of 0.03 mg/L (Fig 7.16). Four samples contained phosphate concentrations greater than 0.2 mg/L. Three of these bores (13596, 12627 and 13256) are located within the Barossa Complex and bore 11934 is located within the Woolshed Flat Shale. As these formations are comprised of igneous rock and shales, which often are rich in phosphatic minerals, the phosphate concentrations may be naturally occurring. Nitrogen-15 isotope data were available for only one of the four bores with elevated phosphate concentrations (bore 13596) and suggests previous impact by human/animal waste. This raises the possibility that the more elevated phosphate concentrations have arisen from anthropogenic sources.

7.3.2 Dissolved Acid Hydrolysable Phosphate

Acid hydrolysis converts dissolved and particulate condensed phosphates to dissolved orthophosphate. The acid hydrolysed phosphate (as P) concentrations (Fig 7.17) ranged from <0.002 to 0.78 mg/L with a median value of 0.03 mg/L. The concentrations were similar to those determined for total phosphate.

7.3.3 Dissolved Orthophosphate

Orthophosphate is the species most commonly found in solution. Concentrations of orthophosphate (Fig 7.18) ranged from <0.002 to 0.74 mg/L with a median value of 0.02 mg/L. The concentrations of orthophosphate are generally lower than the total phosphate concentrations, as the condensed and organically bound fractions of phosphate are not measured in the analytical procedure. Bore 13596, with a concentration of 0.74 mg/L, was the only bore to have a concentration greater than 0.2 mg/L. Proteas are cultivated at this site and the application of orthophosphate fertilisers to proteas is generally contraindicated. Faecal indicator bacteria were not detected in this sample; however, the nitrogen-15 isotope for this bore suggests previous impact by human/animal waste.

Fig 7.1 Piccadilly Valley: April-May 1994 Groundwater Ammonium-N Concentrations

Aesthetic drinking water guideline value 0.4 mg/L

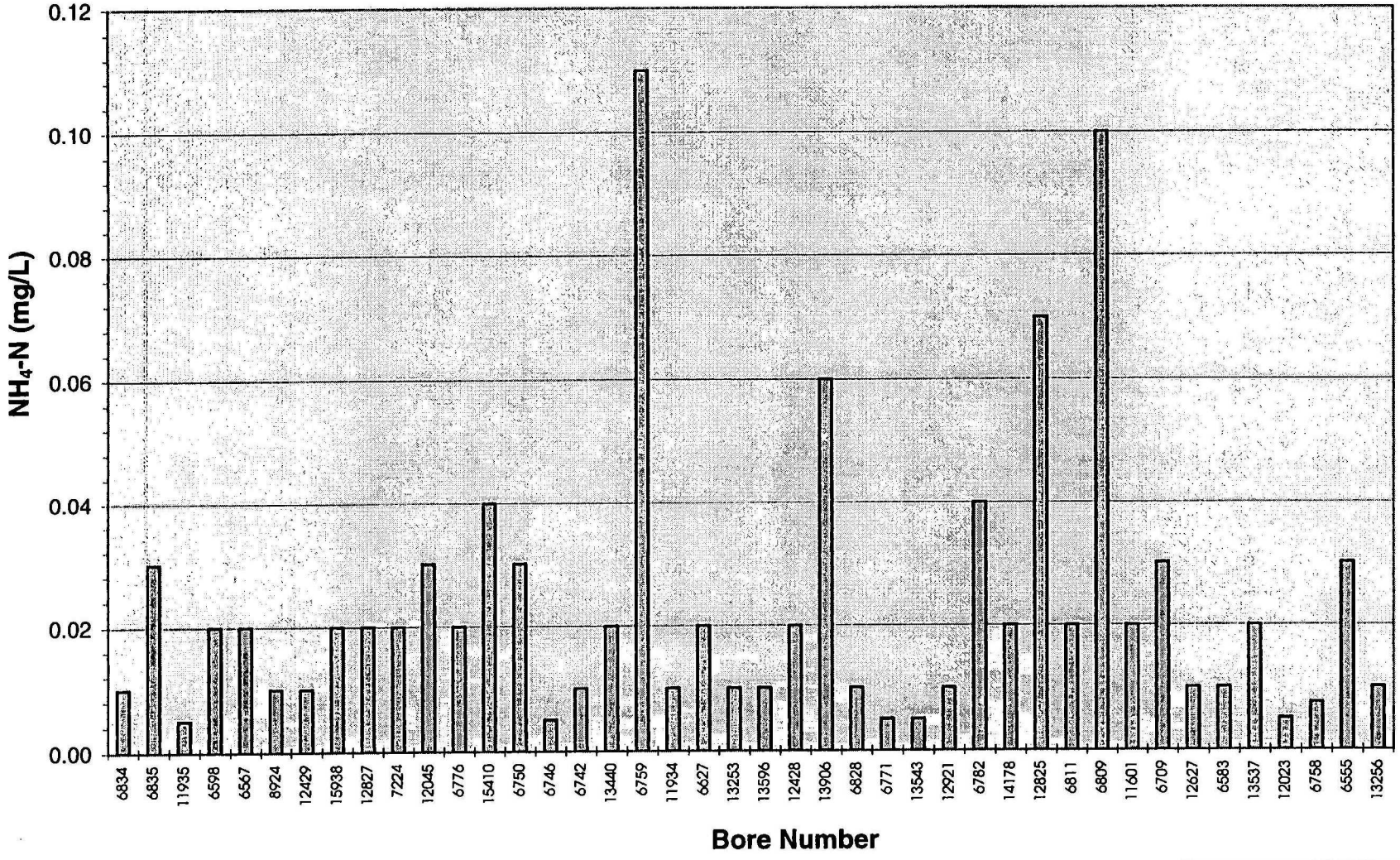


Fig 7.2 Piccadilly Valley: April-May 1994 Groundwater Nitrate-N Concentrations

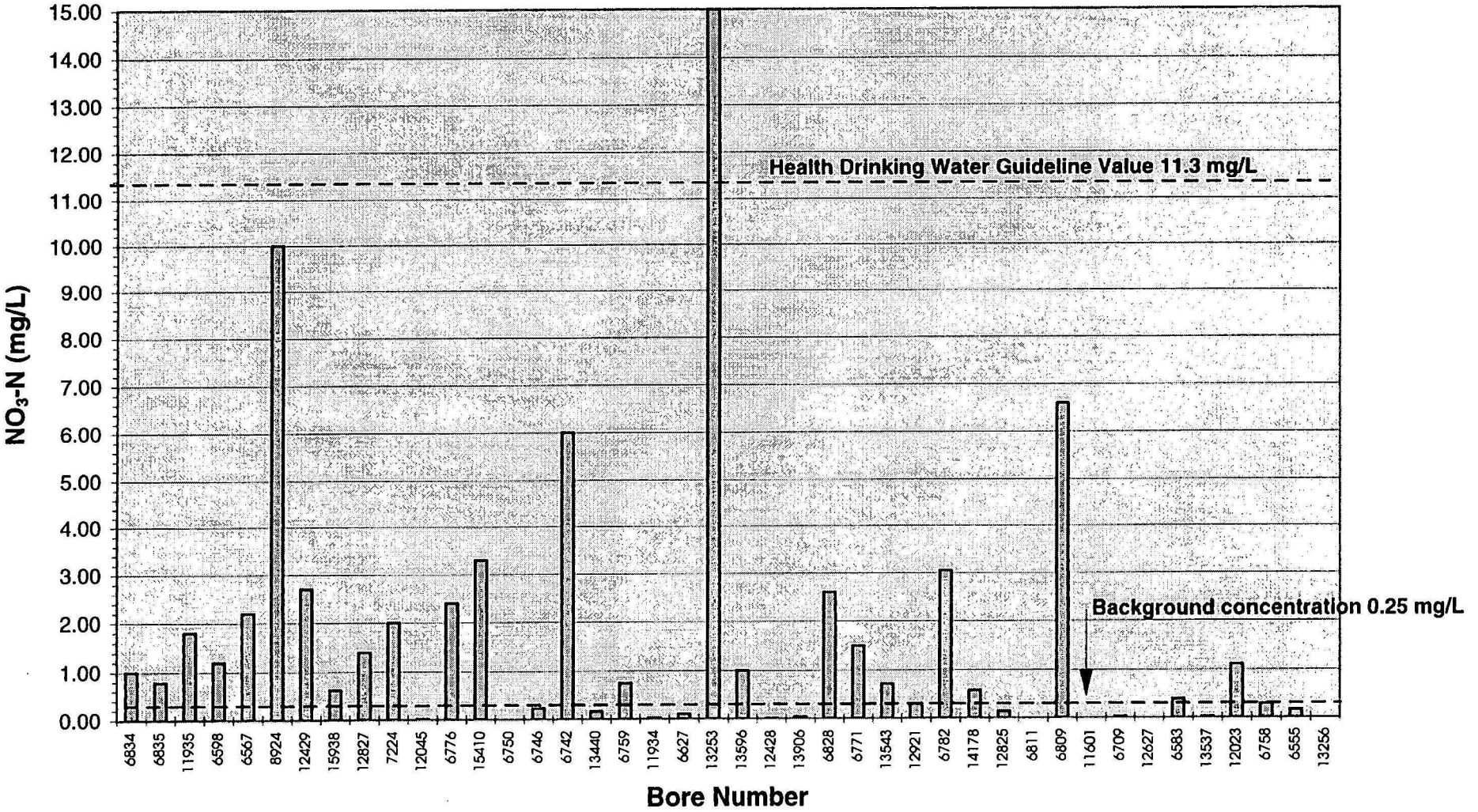
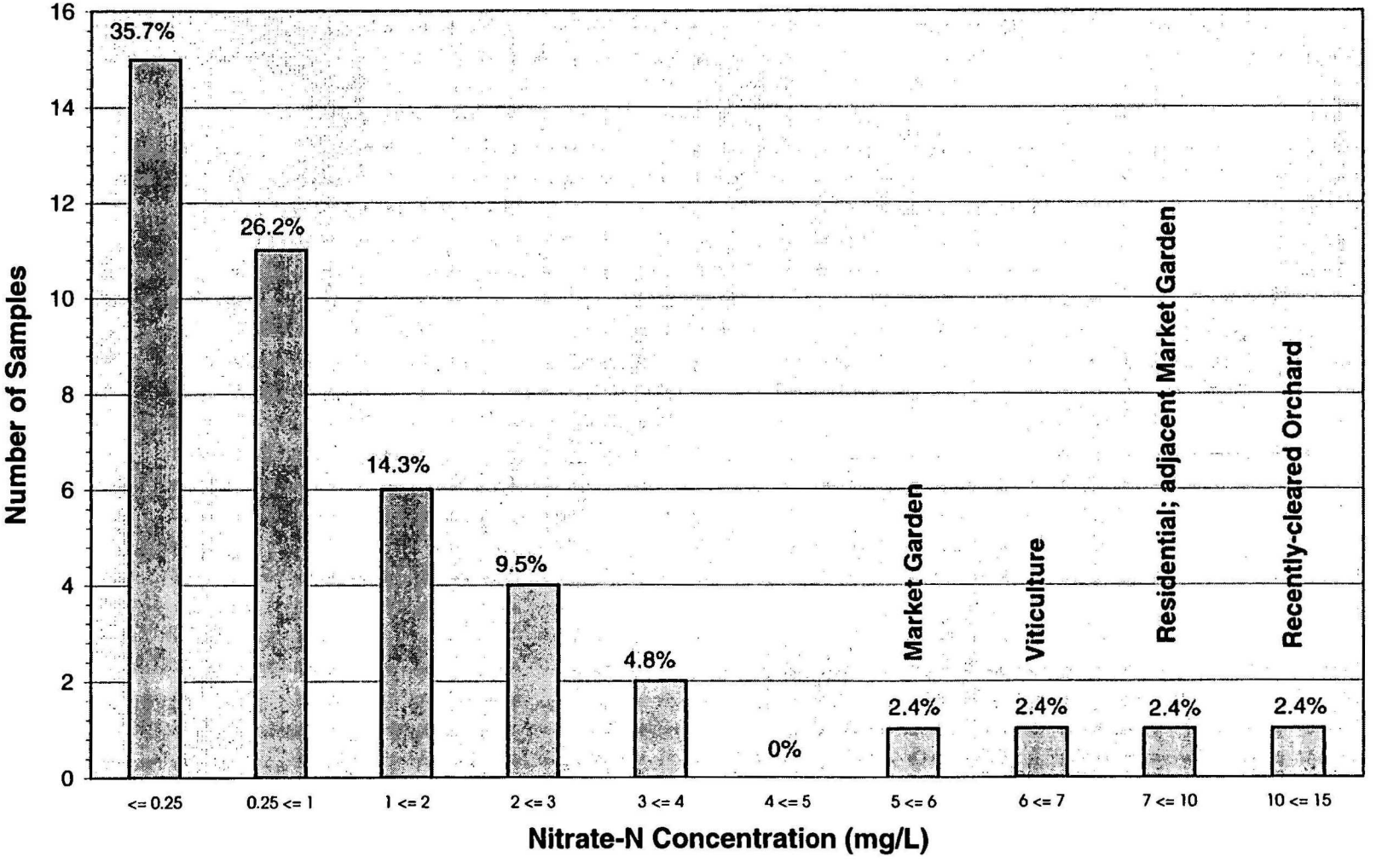


Fig 7.3 Piccadilly Valley: April-May 1994 Groundwater Histogram of Nitrate-N Concentrations



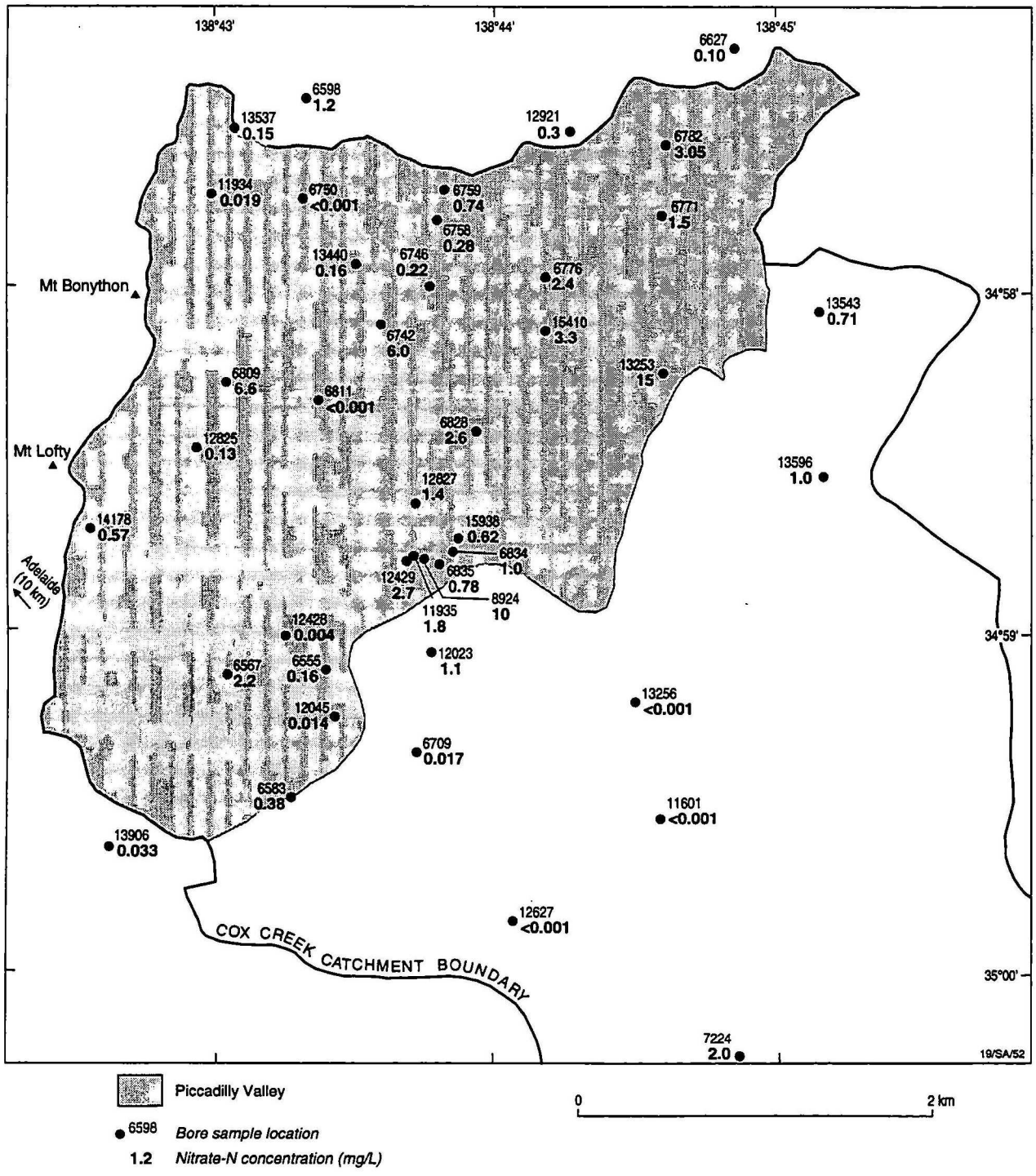


Figure 7.4 Distribution of nitrate-N concentrations in Piccadilly Valley Groundwaters

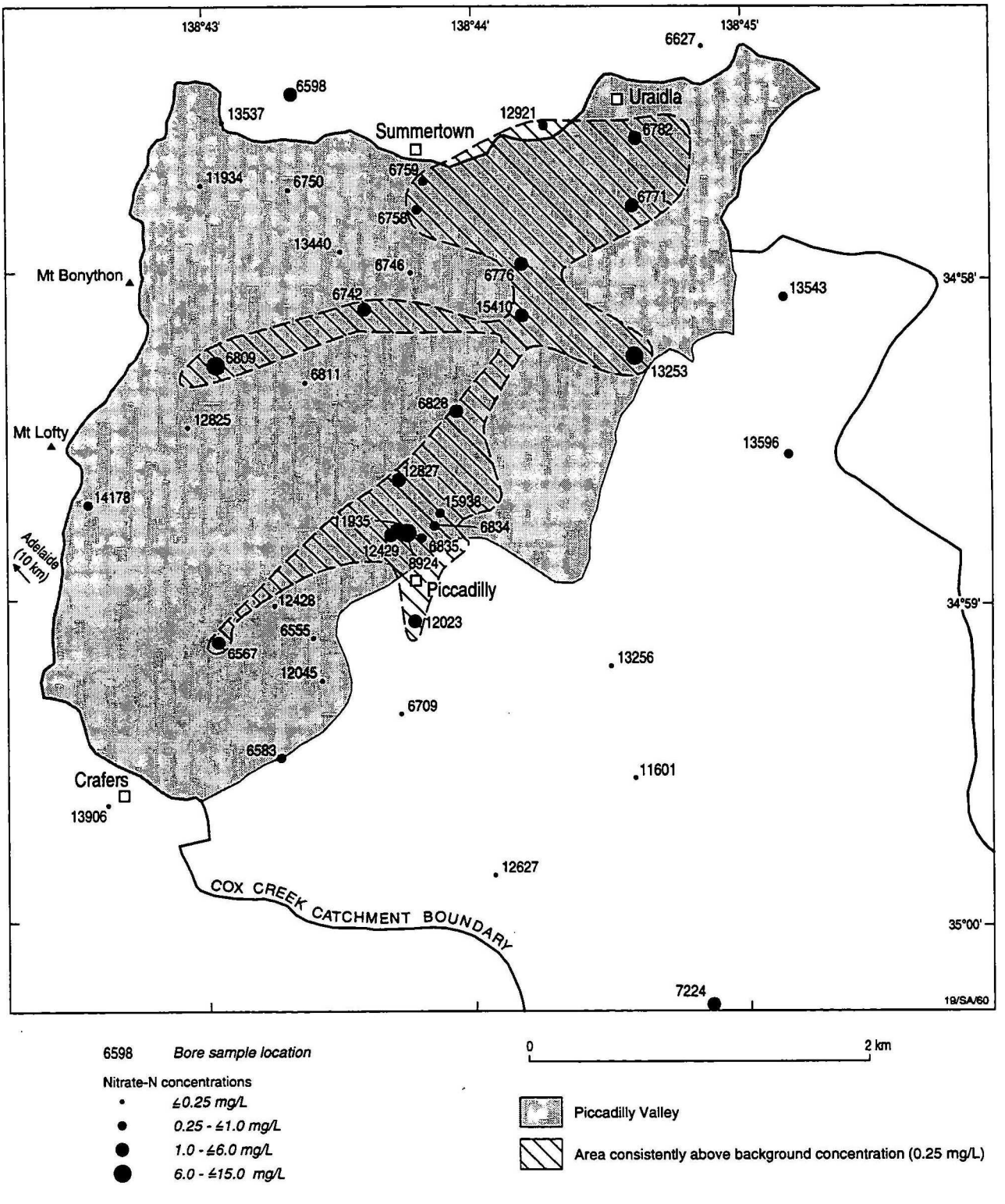


Figure 7.5 Area of elevated nitrate-N concentrations in Piccadilly Valley Groundwaters

Fig 7.6 Piccadilly Valley: April-May 1994 Groundwater Nitrate-N versus Dissolved Oxygen Concentration

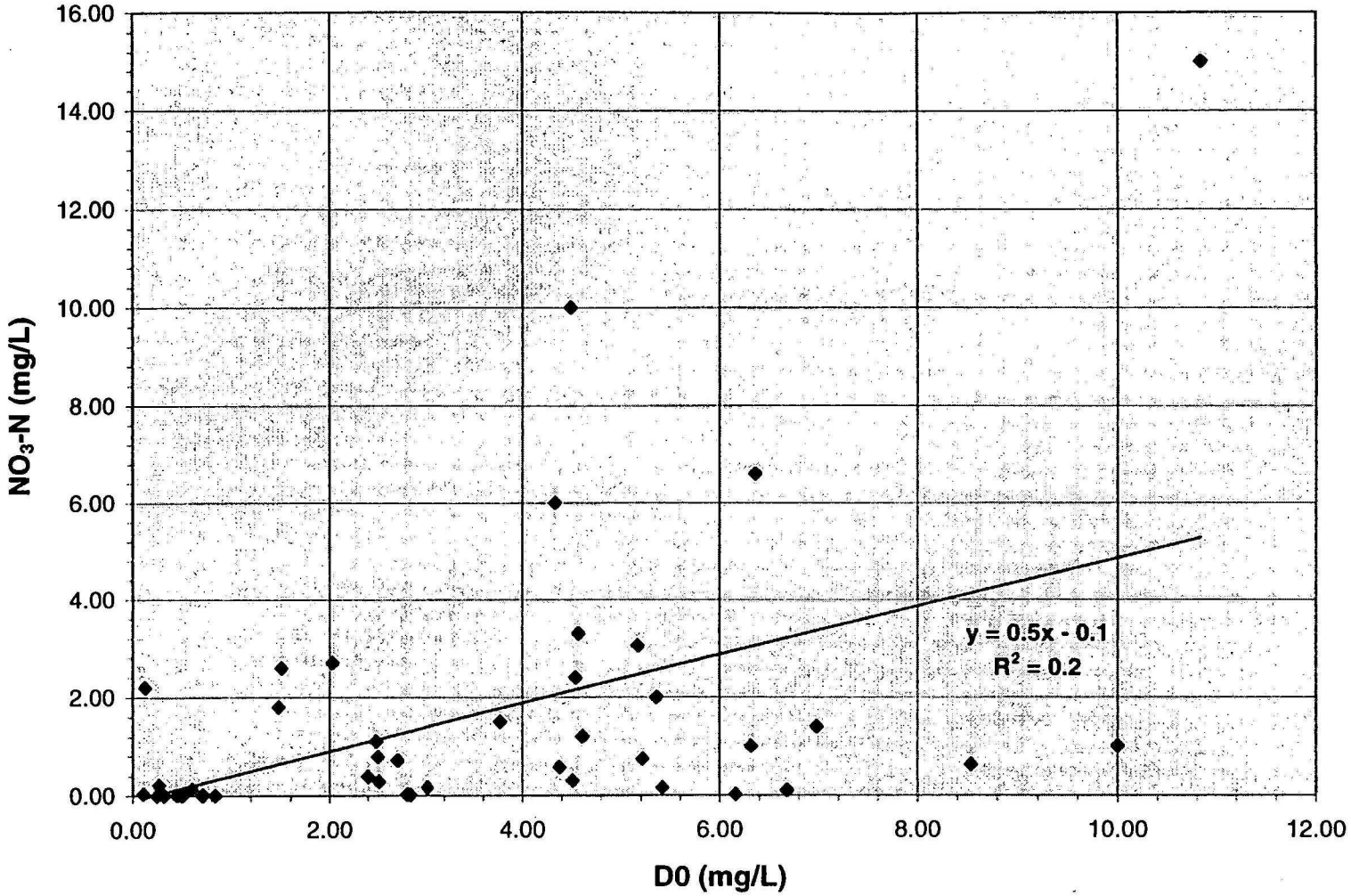


Fig 7.7 Piccadilly Valley: April-May 1994 Groundwater Nitrate-N Concentration vs TDS

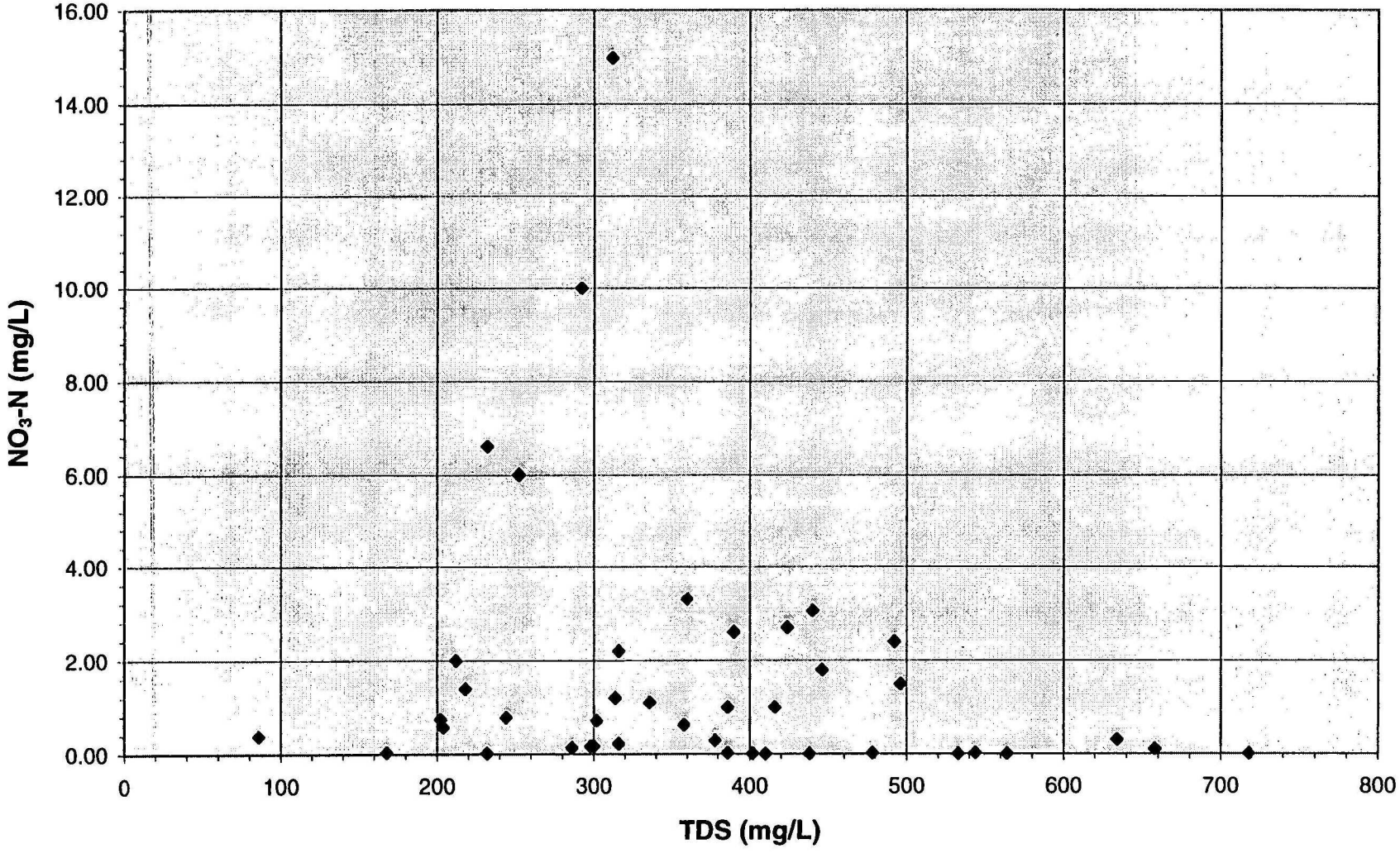
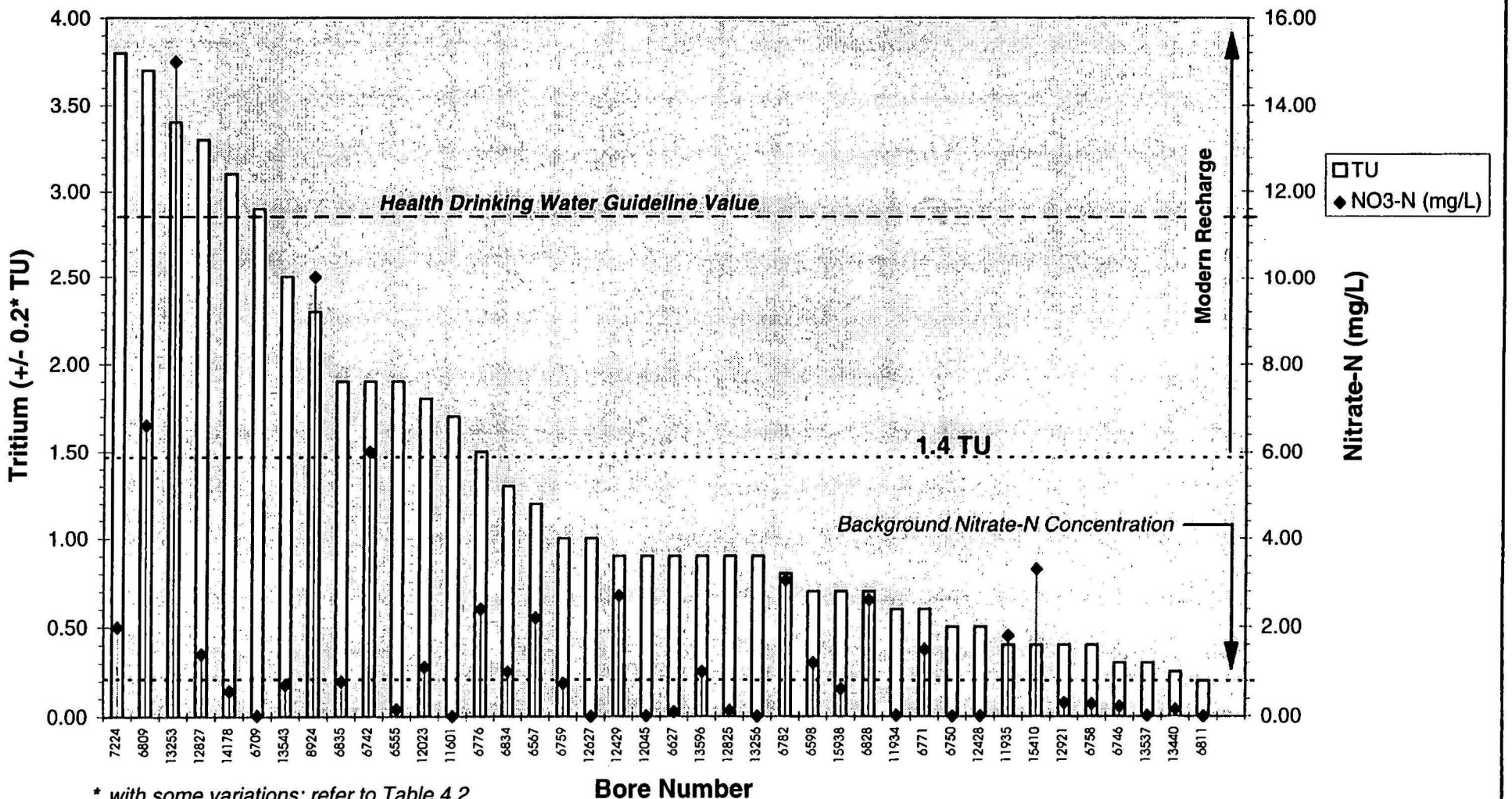


Fig 7.8 Piccadilly Valley: April-May 1994 Groundwater Tritium and Nitrate-N Concentrations



* with some variations; refer to Table 4.2

Fig 7.9 Nitrate-N Concentration vs Soil Thickness

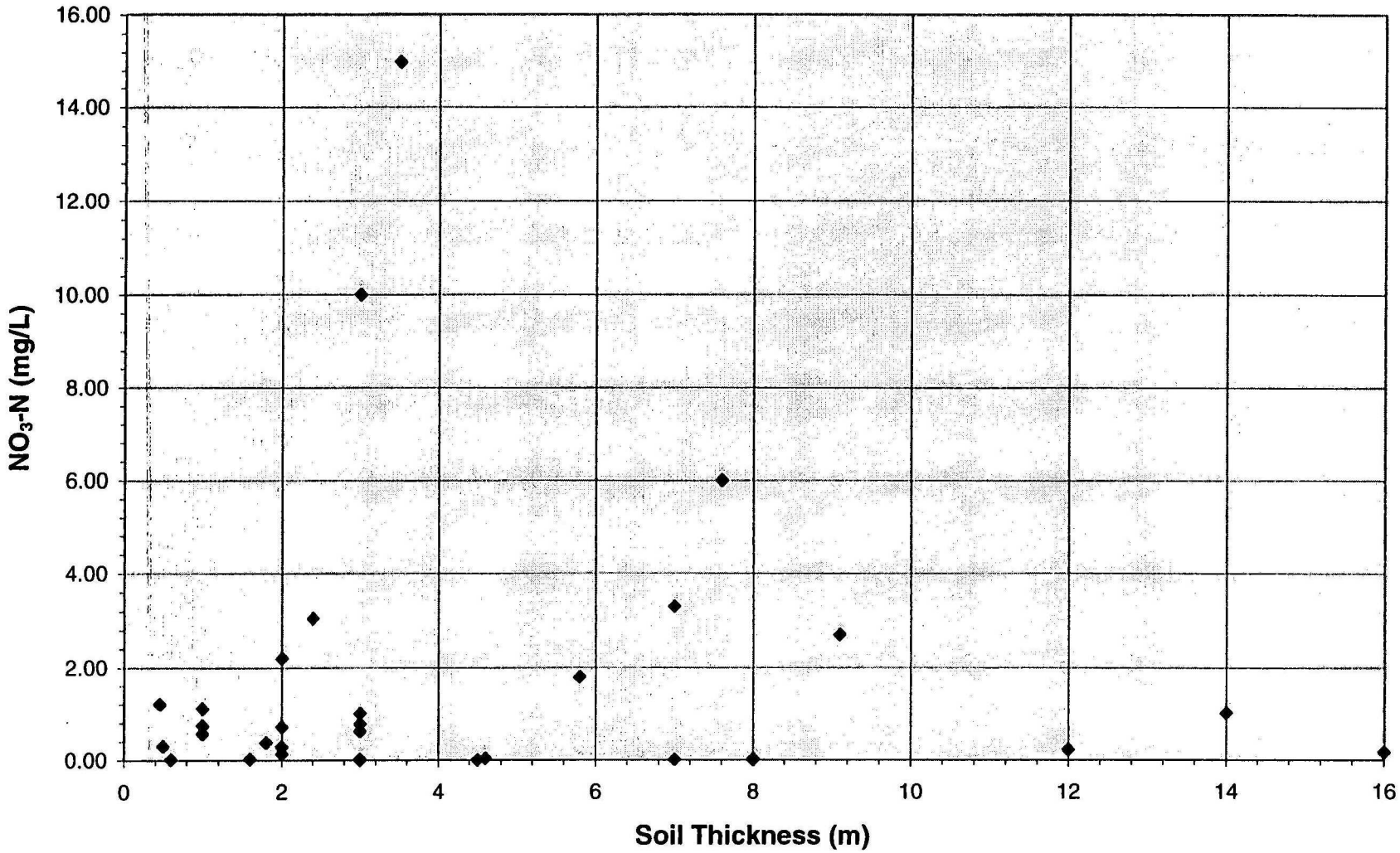


Fig 7.10 Nitrate-N Concentration vs Depth to Water Table

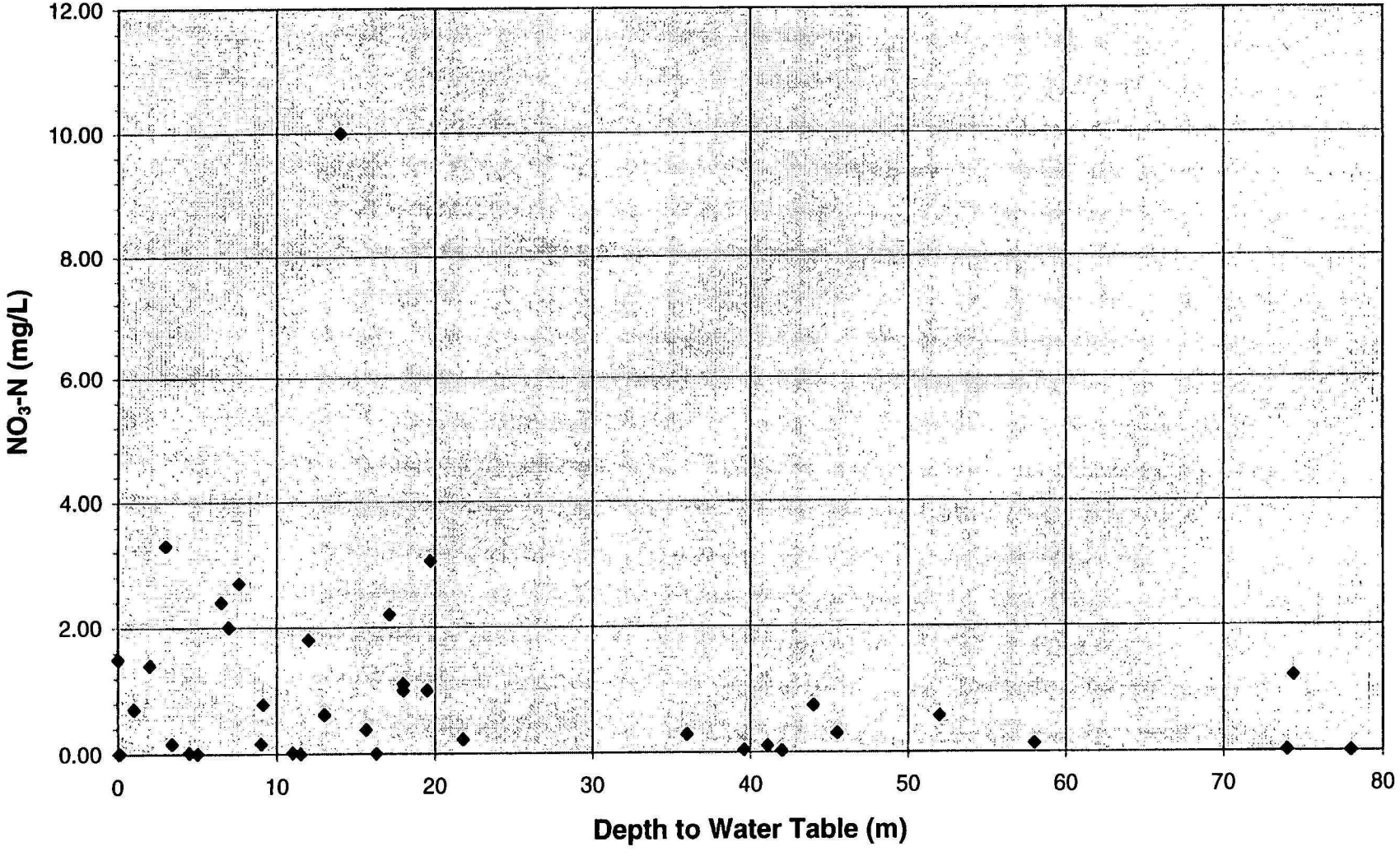
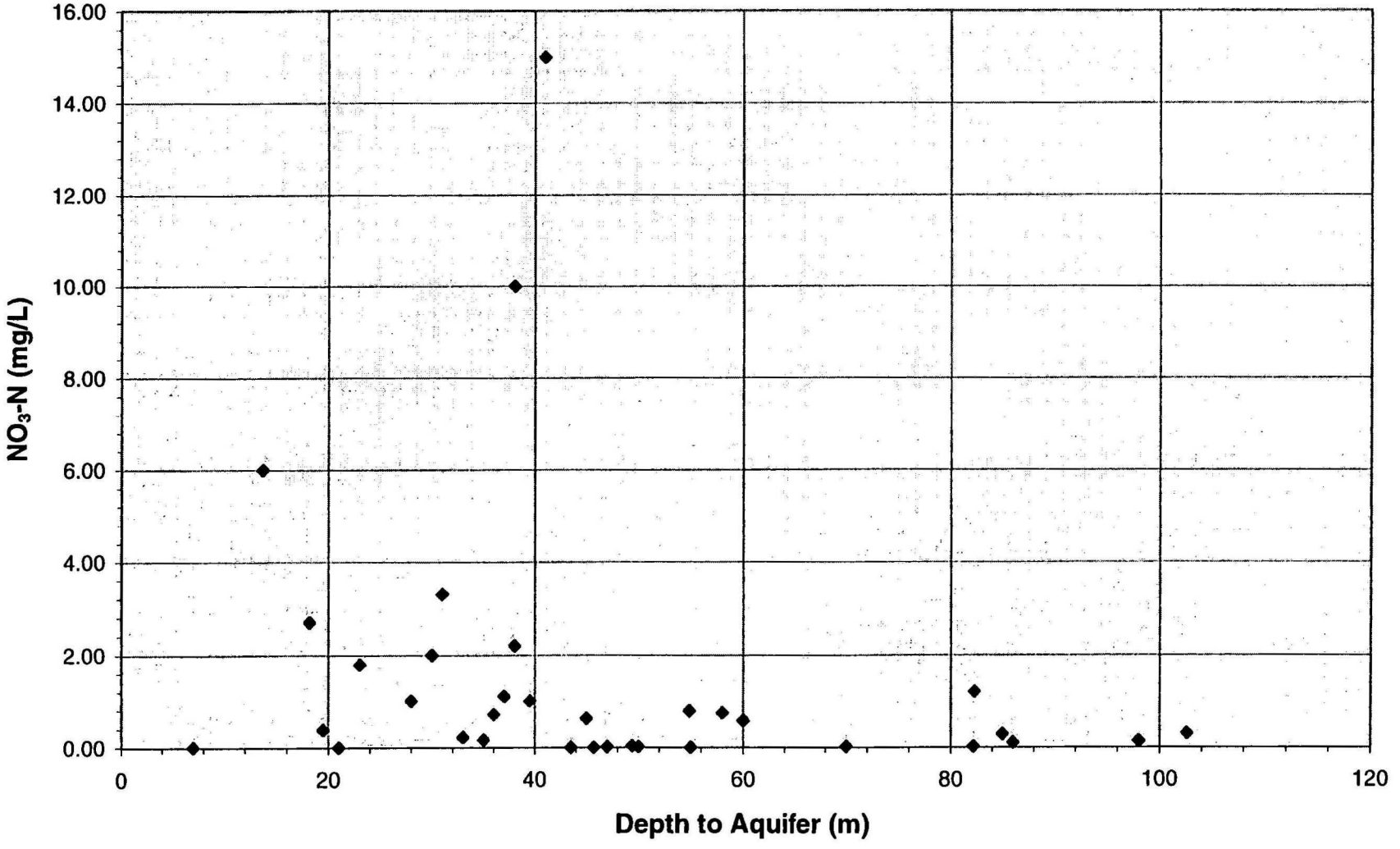
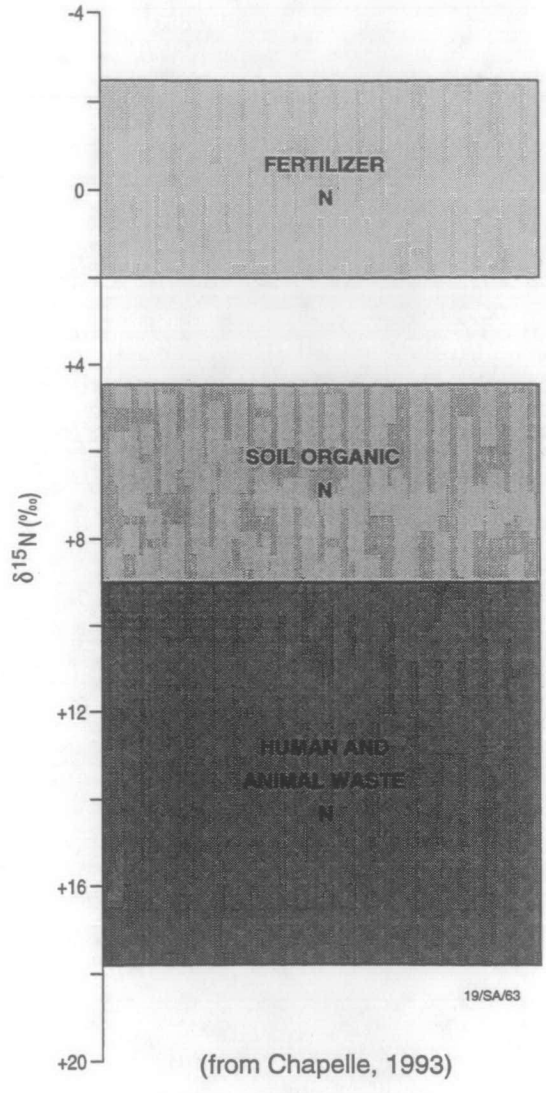


Fig 7.11 Nitrate-N Concentration vs Depth to Aquifer





(from Chapelle, 1993)

Figure 7.12 Ranges for nitrogen-15 values and associated sources

Fig 7.13 Piccadilly Valley: 1979 and 1994 Groundwater Nitrate Concentrations

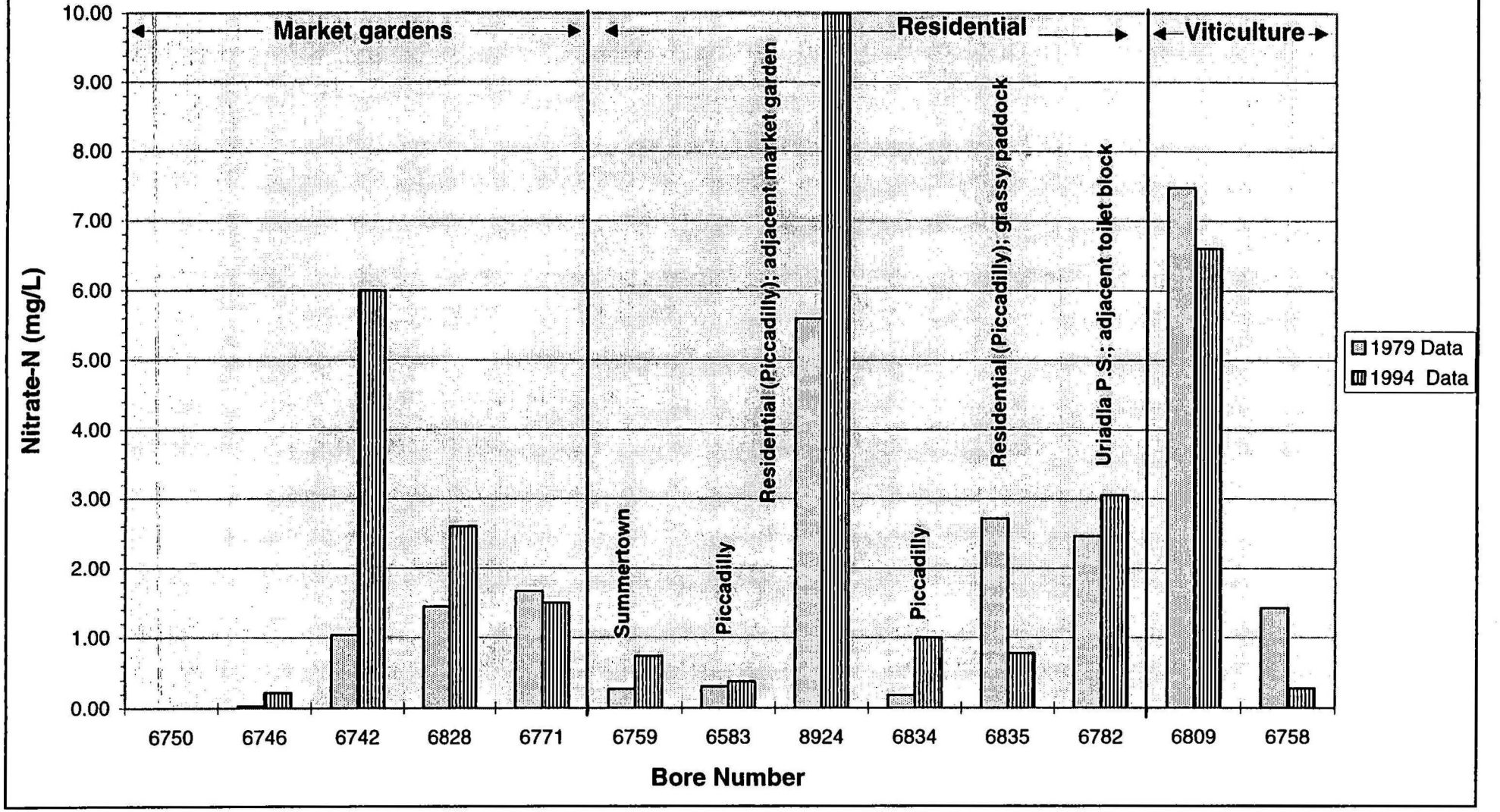


Fig 7.14 Piccadilly Valley: April-May 1994 Groundwater Total Oxidised Nitrogen-N Concentrations

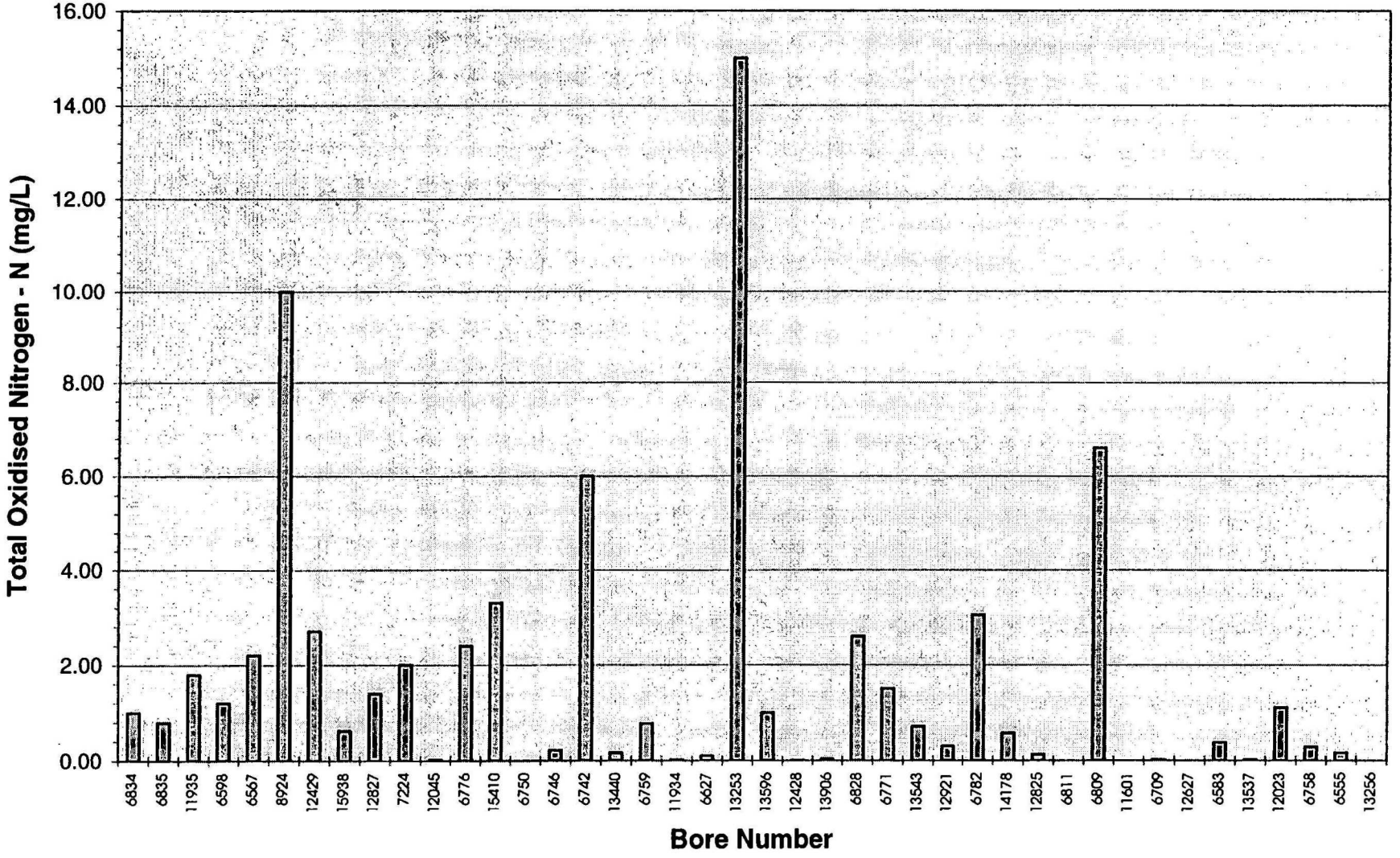


Fig 7.15 Piccadilly Valley: April-May 1994 Groundwater Total Nitrogen-N Concentrations

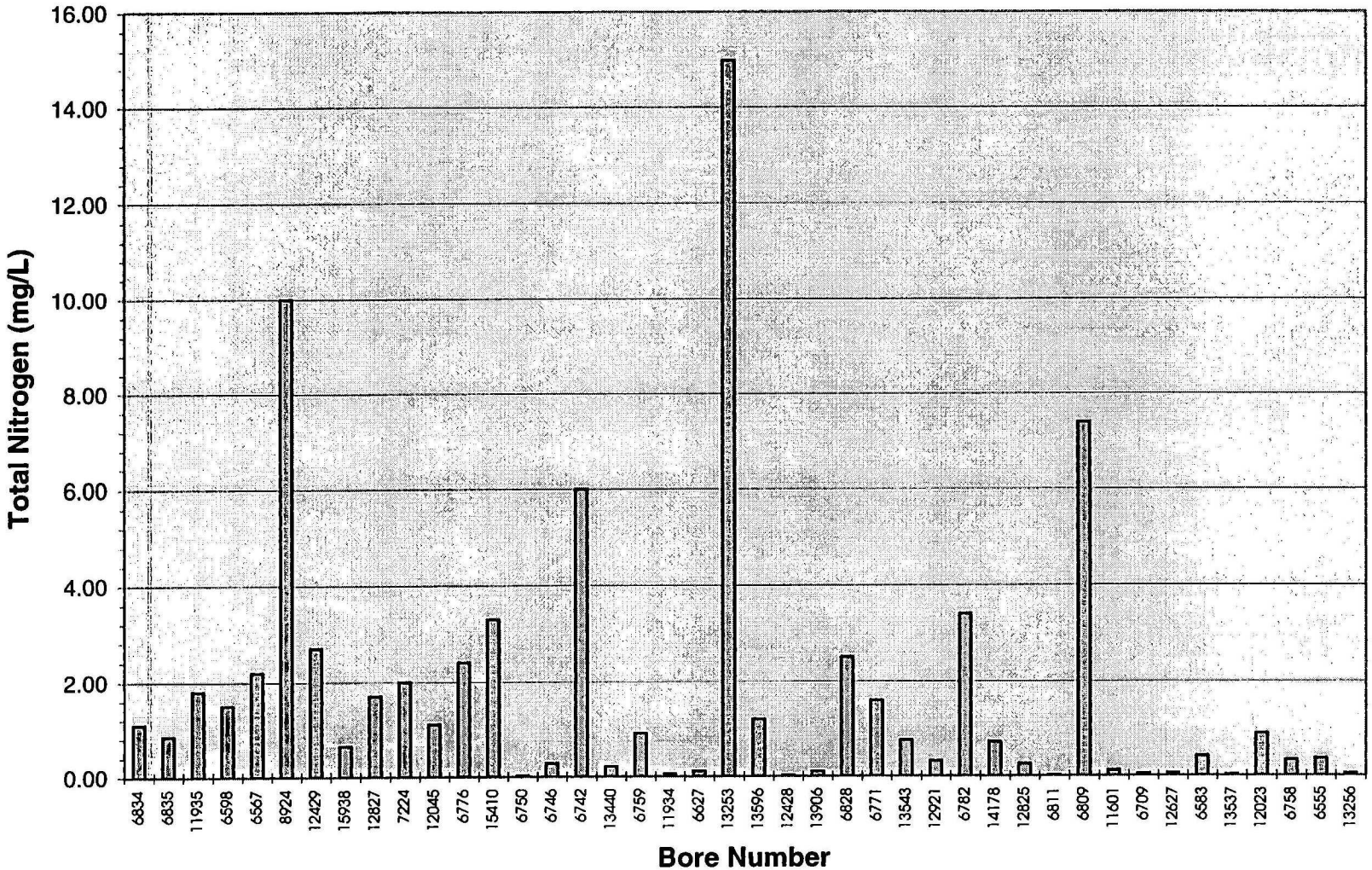


Fig 7.16 Piccadilly Valley: April-May 1994 Groundwater Total Dissolved Phosphate-P Concentrations

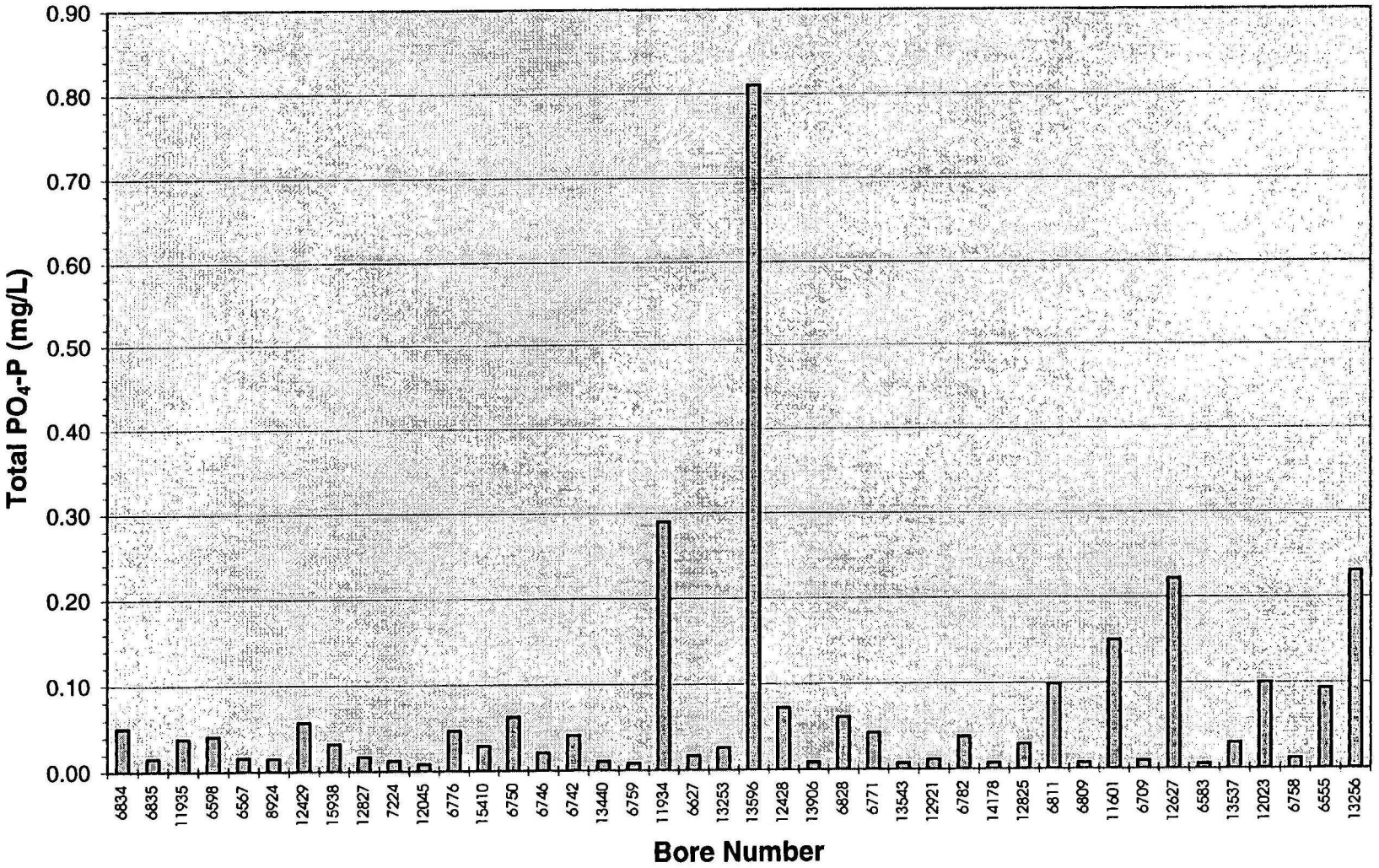


Fig 7.17 Piccadilly Valley: April-May 1994 Groundwater Dissolved Acid Hydrolysable Phosphate-P Concentrations

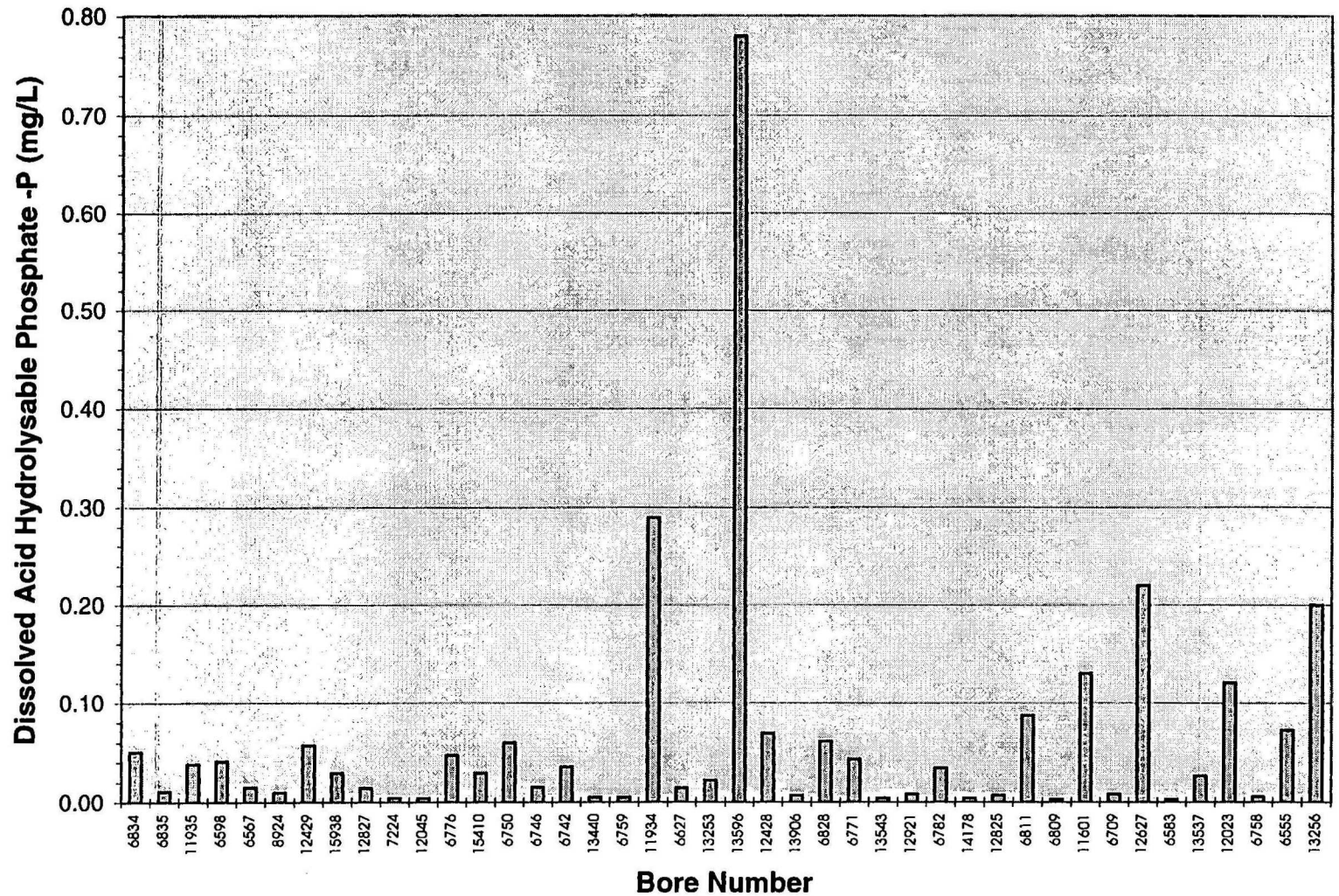
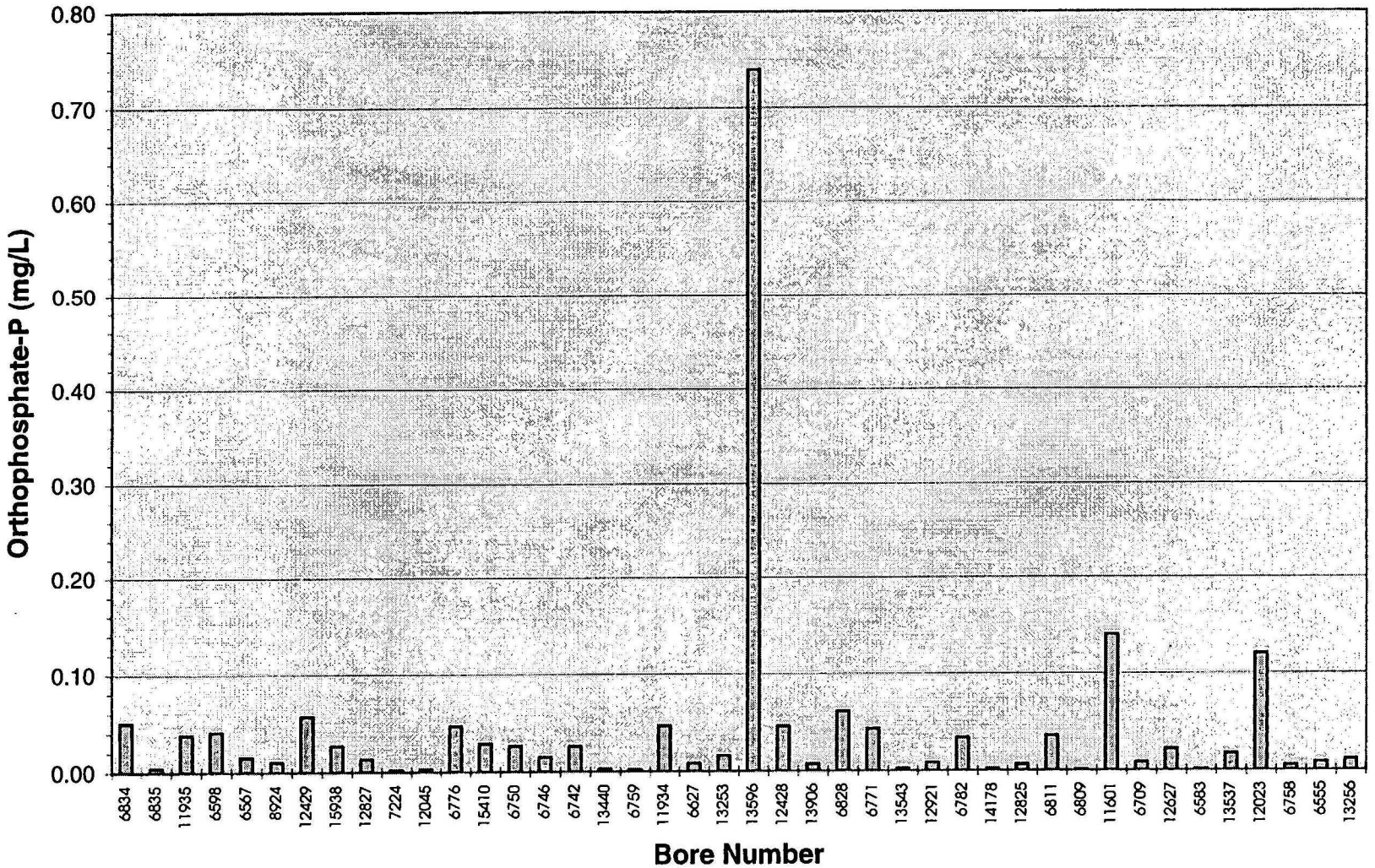


Fig 7.18 Piccadilly Valley: April-May 1994 Groundwater Dissolved Orthophosphate-P Concentrations



8.0 MICROBIOLOGY

Like natural habitats everywhere, the subsurface environment, including groundwater, has been found to contain a broad spectrum of microbial types similar to those found in surface soils and waters; microbial groups present encompass bacteria, fungi and protozoa, and are representative of most physiological types. On occasion pathogenic viruses, bacteria and protozoans of gastrointestinal origin from domestic, agricultural and other anthropogenic activities, may infiltrate through soils, sediments and rocks to the underlying groundwaters. There they may survive for sufficient time to be ingested by humans and livestock drinking extracted groundwater. Representatives of both indigenous and contaminant microbes were recovered and enumerated from Piccadilly Valley Groundwaters.

8.1 FAECAL INDICATOR BACTERIA - BACKGROUND

Faecal Indicator Bacteria (FIB) are used as surrogates for pathogenic microbes of gastrointestinal origin (including bacteria, viruses and protozoa) since the difficulty and cost of routinely enumerating the latter remains significant. Their presence in a water sample indicates that the water has received faecal contamination from humans and/or other warm-blooded animals. FIB are generally present in the gastrointestinal tract (GIT) in large numbers and their public health utility is based on the assumption that they survive in aquatic environments at least as long as GIT-borne pathogens. Many pathogens found in the GIT of warm-blooded animals, such as *Salmonella*, *Leptospira*, *Campylobacter*, *Giardia*, and *Cryptosporidium* will also infect humans ingesting contaminated water.

Three classes of FIB were target indicators for our groundwater quality assessment of the Piccadilly Valley - faecal (thermotolerant) coliforms (FC), faecal streptococci (FS), and spores of *Clostridium perfringens* (Cp). FC and FS are "normal" bacterial cells whose survival outside the GIT is commonly reported to range from hours-to-days while Cp spores are dormant cells which survive indefinitely under a wide range of environmental conditions. The latter thus provide a long-lived indicator of faecal contamination.

Most public health and/or regulatory agencies set standards/guidelines using FC (i.e., FC should not be detectable in any sample; minimum volume 100mL). FS provide an additional, and possibly more sensitive, indicator because they may be present in some faecal material in considerably higher numbers than FC, appear to be more persistent in aquatic environments than FC and, as a consequence of their wall structure, should be more resistant to drying (thereby better surviving episodic transport through the vadose zone). Cp, as a consequence of their longevity (of the order of years), may accumulate and be detected long after and far away from contamination event(s) and

thus indicate intermittent and/or remote contaminant sources not evident from FC or FS data.

8.2 A NOTE ON THE INTERPRETATION OF FIB DATA

The presence of FIB at any subsurface location is contingent upon processes such as transport and/or retention of FIB, their survival as entities capable of growth (and hence detection) after reaching groundwater, and the magnitude and frequency of contamination events.

Bacteria are usually of colloidal dimensions (ie of diameter <10μm, commonly as small as 1-2μm) which enable them to be transported with other particles from the soil surface into the subsurface by recharge events. Considerable vertical and lateral distances may be traversed in the subsurface before FIB succumb to the relatively hostile world outside the GIT. Depending on the surface properties of both bacteria and sediment particles and the surrounding aqueous medium, bacterial cells may adsorb reversibly or irreversibly to solid phase material in the subsurface environment.

Survival times (as assessed by eg half-life, $t_{1/2}$) for both FC and FS are dependent on environmental constraints and are variously reported in the range hours to days depending on environmental conditions; they are sufficiently variable as to be no more than a general guide. Cp spores are stable over long periods as a consequence of their resistant structure and metabolic dormancy, and thus provide a long-lived signal of faecal contamination.

Survival of gastrointestinal bacteria and viruses in the (subsurface) environment appears to be promoted by low temperature, saturated conditions, and sufficient amounts of organic matter (but compromised by sunlight [UV], low pH, and indigenous microbes which are antagonistic or predatory).

Most investigations of FIB survival have been carried out in temperate zone climates. These studies suggest that survival time is increased markedly at lower temperatures and at temperatures below 4°C survival for months or years has been reported. At higher temperatures (*ca* 5-30°C) the die-off rate approximately doubles for each 10°C temperature increase. Survival would be enhanced during and/or immediately following cooler months when shallow unconfined water tables would decrease in temperature.

8.3 FIB CONTAMINATION AND LAND USE

One or more classes of FIB were detected in 8 of the 42 bores sampled (19%; Table 8.1). While the Australian Drinking Water Guidelines (NH&MRC/ ARMCANZ, 1996) use FC to determine microbiological water quality (FC should be undetectable in 100 mL of sample), only 4 samples (10%) contained FC (range 1-196

Table 8.1: Piccadilly Valley Groundwater Microbiology

PICCADILLY VALLEY - MARCH-APRIL 1994; FIB and Indigenous Microbes						
WQ No.	Bore Number	Faecal Indicator Bacteria			R2A-H	HDNB
		FC	FS	Cp		
		CFU/100m	CFU/100mL	CFU/L	CFU/mL	MPN/mL*
94/58	6834	<1	<1	<1	60	50
94/59	6835	<1	<1	<1	54	90
94/60	11935	<1	<1	<1	7	17
94/61	6598	<1	<1	<1	10	30
94/62-3**	6567	0.5	<1	<1	22	9
94/65	8924	<1	<1	<1	7	1
94/66	12429	<1	1	<1	10	23
94/67	15938	<1	<1	<1	207	80
94/68	12827	<1	<1	<1	194	300
94/69	7224	<1	<1	<1	91	500
94/70	12045	<1	<1	<1	10	500
94/71	6776	26	120	<1	1973	50
94/72	15410	<1	<1	<1	205	130
94/73-74**	6750	<1	<1	<1	0.6	<1
94/76	6746	<1	<1	<1	70	1300
94/77	6742	5	8	>1***	1827	110
94/78	13440	<1	<1	<1	145	280
94/79	6759	<1	<1	<1	336	1400
94/80	11934	<1	<1	<1	382	220
94/81	6627	<1	22	<1	10	110
94/82	13253	<1	<1	<1	100	70
94/83	13596	<1	<1	<1	95	17
94/84	12428	<1	<1	<1	8	2
94/85	13906	<1	<1	<1	691	2800
94/86	6828	<1	<1	<1	618	140
94/87	6771	<1	<1	<1	5	2
94/88	13543	<1	<1	<1	6	30
94/89	12921	<1	<1	<1	8	3
94/90-1**	6782	<1	8	<1	86	2
94/93	14178	<1	<1	<1	85	17
94/94	12825	<1	<1	<1	3200	5000
94/95	6811	<1	<1	<1	NR****	<1
94/96	6809	<1	<1	<1	109	700
94/97	11601	<1	<1	<1	31	17
94/98	6709	<1	<1	<1	68	27
94/99	12627	<1	<1	<1	81	9
94/100	6583	<1	1	<1	418	170
94/101	13537	<1	<1	<1	5	1
94/102	12023	<1	<1	<1	8	1
94/103-4**	6758	<1	<1	<1	487	2050
94/106	6555	196	41	<1	7182	13
94/107	13256	<1	<1	<1	409	27
Validated JB 23 May 1997						
*; MPN/mL < 5 rounded to nearest integer. **; values are mean of duplicate samples						
***; Cp spores confirmed but could not be enumerated						
**** NR; No Result - contamination						
FC = Faecal Coliforms; FS = Faecal Streptococci						
Cp = Clostridium perfringens spores HDNB = heterotrophic denitrifying bacteria						
R2A-H = heterotrophic bacteria enumerated on R2A medium						

CFU/100mL). The difference in faecal contaminant frequency was due to the presence of faecal streptococci in the absence of FC. These findings are consistent with those of other study areas across the country for both fractured rock and unconsolidated sedimentary aquifers, where the frequency of groundwater faecal contamination as indicated by FS is usually 2-3 times that determined by FC (Bauld & Plazinska, unpublished). They are also consistent with the experimental findings of (McFeters et al., 1974) who showed that FS survived longer than FC in Montana groundwater, irrespective of whether the microbes tested were from laboratory cultures, animal droppings or raw domestic sewage. Confirmed Cp spores were recovered from only one bore (6742) in the presence of low numbers of both FC and FS (Table 8.1).

Attempts to relate the incidence of FIB contamination to surrounding land use proved equivocal, though circumstantial evidence would tend to implicate principally residential sources. All but two contaminated sites were associated with (rural) residential land use, or other similar uses, which would employ septic tanks - the latter include the Uraidla School (6782) and the Botanic Gardens (6567). Despite its location in an orchard, Bore 6555 was the most heavily contaminated (Table 8.1) - the most likely sources would be nearby septic tanks lying upgradient on the edge of Piccadilly township and/or on the property itself. Because fractures have the capacity to transport water and contaminants rapidly over large distances, neither adjacent livestock grazing nor more remote sources can be precluded. *Enterococcus gallinarum* strains were frequently recovered from the area, including the market garden sites, and it may be that the application of fresh poultry manure could provide a source of contamination.

8.4 FIB CONTAMINATION: RELATIONSHIP TO OTHER PARAMETERS

Substantially elevated nitrate-N concentrations (2.2-6.0 mg /L) were found in five of the FIB-positive bores (Table 8.2). Two of the remaining three FIB-positive bores contained nitrate-N concentrations (0.2 and 0.4 mg N/L) which were close to apparent background (0.25 mg N/L, see section 7.2.3). $\delta^{15}N$ values (see also section 7.2.3.4) were determined for samples containing sufficient concentrations (> 0.5-1.0 mg) of nitrate-N (ie. 5 of the FIB-positive samples). Four of these samples had relatively high $\delta^{15}N$ values (9.57-12.56 per mil; Table 8.2) consistent with nitrate-N arising from organic-N of human or animal origin, and thus with leaking septic tanks as the most probable source of contamination. Nitrate-N in the remaining sample (6742) had a $\delta^{15}N$ value of 6.97 per mil, suggesting possible derivation from natural soil organic-N, or a mixture of human/animal N (ie faecal material and/or organic-N fertilizer) and inorganic fertilizer nitrogen. The confirmed presence of *Clostridium perfringens* spores suggests that the latter is the more probable source.

In contrast to samples contaminated by pesticides and nitrate-N, which contain modern water (ie < *ca* 25 years; equivalent to $^{3}H > 1.4TU$), less than half (3/7) of FIB-positive samples contained measurable quantities of modern recharge water (Table

Table 8.2: Piccadilly Valley - Faecal Indicator Bacteria and Related Parameters

WQ #	Bore #	FC[1] CFU/100mL	FS[2] CFU/100mL	Cp[3] CFU/L	R2A[4] CFU/mL	NO_3-N mg/L	$\delta^{15}NO_3$ per mil	^3H TU
94/62&63	6567	0.5[5]	< 1	< 1	22	2.2	9.57	1.3
94/66	12429	< 1	1	< 1	10	2.7	9.92	0.9
94/71	6776	26	120	< 1	1973	2.4	11.09	1.5
94/77	6742	5	8[5]	+[6]	1827	6.0	6.97	1.9
94/81	6627	< 1	22	< 1	10	0.1	n.d.[7]	0.9
94/90&91	6782	< 1	8	< 1	86	3.1	12.56	0.8
94/100	6583	< 1	1	< 1	418	0.4	n.d.[7]	n.d.[8]
94/106	6555	196	41	< 1	7182	0.2	n.d.[7]	1.9

[1] FC = Faecal Coliforms; [2] FS = Faecal Streptococci; [3] Cp = *Clostridium perfringens* spores; [4] R2A = heterotrophic bacteria; [5] mean of duplicate samples; [6] could not enumerate presumptive colonies; [7] n.d. = not done, insufficient nitrate-N in sample; [8] n.d. = not done, sample lost

8.2; see also section 4.1.3). This finding is in apparent conflict with the environmental survival times for FC and FS (i.e., $t_{1/2}$ of the order of days to weeks, only possibly months). Possible explanations include the mixing of modern reticulated water from leaking septic tanks with older groundwaters and/or the use of groundwaters of varying ages for domestic purposes, which then carry septic tank leakage to sampling points.

The distribution of FIB-positive sites in the study area are aligned in a NE-SW orientation, roughly parallel to, and NW of, the Crafers Fault and associated with the NE-SW trending axis of the anticline (Fig 8.1). Five of the FIB-positive sites are within the Aldgate Sandstone, two within the nearby Woolshed Flat Shale and the last within the Stonyfell Quartzite. It may be that fractures are more frequent and/or more conductive in the rocks overlying the downthrust block of the Crafers Fault and along the axis of the anticline. It must be conceded, however, that the observed distribution could be merely coincidence related to the particular sampling period. Repeated sampling may clarify this speculative interpretation.

8.5 NATURALLY OCCURRING MICROBIAL POPULATIONS

Bacteria are the major biogeochemical agents within aquifer environments; other microbial groups, such as viruses, fungi and protozoa, are normally present at very low population densities relative to bacteria. Most bacteria are heterotrophs i.e., they use organic compounds such as carbohydrates and proteins (or their subunits e.g., glucose) as sources of both the carbon and energy required for growth; thus their activities contribute to the degradation of naturally occurring and contaminant organic matter. Since groundwaters generally contain low concentrations of organic matter (Thurman, 1985) the most appropriate media for the recovery and enumeration of microbes will contain similarly low concentrations. Medium R2A (Reasoner & Geldreich, 1985) was therefore chosen for the enumeration of aerobic and facultatively anaerobic heterotrophs in Piccadilly groundwater samples.

Heterotrophic bacteria enumerated on medium R2A ranged in population density from < 1 CFU/mL to 7182 CFU/mL (Table 8.2). Four groundwater samples (6555, 6742, 6776, & 12825) contained heterotrophic populations substantially higher than the remainder. Two of these (6555, 6742) were visibly turbid with suspended solids (clay?) while the other two were apparently clear. The field team noted, however, that sample 12825 was difficult to filter, suggesting the presence of colloidal particles. The presence of clay/colloidal particles could contribute to the higher numbers given the propensity for bacteria to adhere to surfaces under low nutrient conditions.

Three of the four groundwaters containing notably higher populations of heterotrophic bacteria were contaminated with FIB (6555, 6742, 6776; Table 8.2). The increased levels of energy and organic carbon levels associated with faecal contamination has presumably stimulated heterotrophic populations in the vicinity of these bores. Only one other sample contained such high populations (12825; FIB-negative, low nitrate-N) suggesting that faecal contamination or some other source of readily utilizable organic matter had previously found its way to this site.

Denitrification is the process whereby nitrate and nitrite are reduced to the dinitrogen gases N_2O and N_2. While abiotic denitrification is known to occur, the microbiological process is generally regarded as the most important quantitatively. The bacteria able to denitrify preferentially utilize oxygen as their terminal electron acceptor for respiration; however, when DO concentrations in the immediate vicinity of the bacterial cell fall to *ca.* 0.2-0.5 mg/L, they are able to switch to nitrate as an alternative electron acceptor. Thus, in the presence of sufficient utilizable organic carbon and the absence of DO, denitrifying bacteria will remove nitrate from groundwater.

High population densities of denitrifying bacteria (HDNB) were recovered from 5 groundwater samples. Only one of these (12825) also contained high populations of R2A heterotrophs while another (6759) contained the highest NH_4-N concentration (0.11 mg/L) of any sample. There was no association of high HDNB populations with other process-related parameters such as high DOC, or high nitrate-N concentrations. Two of the samples, however, did have low bulk DO concentrations, which would sustain denitrification (13906, 0.11mg DO/L; 6758, 0.60mg DO/L).

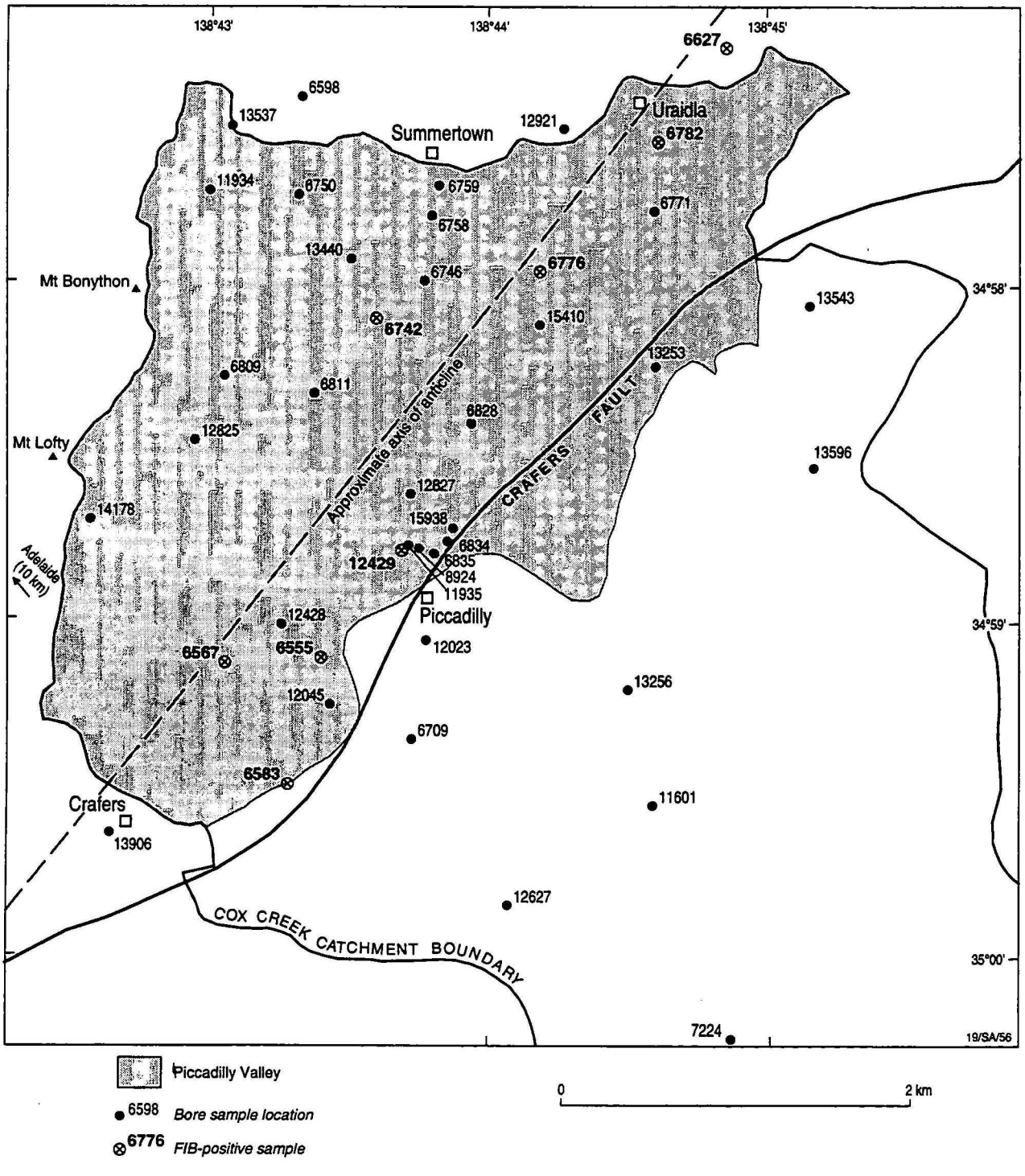


Figure 8.1 Distribution of FIB-positive sites in Piccadilly Valley Groundwaters

9.0 PESTICIDES

9.1 BACKGROUND

Pesticide contamination of groundwater resources is becoming an increasingly important global issue. Little is known of contaminant levels in rural areas of Australia. In an agriculturally diverse region such as the Piccadilly Valley it is important to benchmark the existing levels of pollution, particularly as it lies within the Adelaide metropolitan water supply catchment. As land uses of the region change over time, and in some instances increase in intensity, it is vital to characterise the influence of different agricultural practises on groundwater quality.

The NHMRC/ARMCANZ Australian Drinking Water Guidelines (1996) state that pesticides should not be detected in drinking water. The detection of pesticides in groundwater is of health significance as many exhibit toxic properties. Some insecticides, such as the organochlorine group, are persistent and relatively immobile in the vadose zone. They tend to bioaccumulate through the food chain, concentrating in body fat. In recent years organochlorines have been linked with cancer, reproductive and fertility disorders, hence their deregistration for most agricultural applications in the 1980's. Despite application restrictions, organochlorines remain a common contaminant of soils due to their widespread historical use and persistent nature (Bouwer, 1978). Organophosphorous insecticides are acutely toxic, but break down in the environment more rapidly than organochlorines. Triazine herbicides are relatively mobile and have often been found in Australian groundwater from rural regions (Bauld, 1994).

In this study, forty-two groundwater samples were extracted and analysed for pesticides from Schedule A (see Appendix E). Four replicate samples, four field-spiked samples and six field equipment blanks were extracted and analysed in conjunction with the bore samples. Twenty-seven bore samples were extracted and analysed for pesticides from Schedule B (see Appendix E), along with four field-spiked samples and four blanks. Forty-two samples were extracted and analysed for Schedule C analytes (see Appendix E) along with four duplicate samples and four field-spiked samples.

9.2 PREVIOUS WORK

Although pesticide contamination of surface water in the Piccadilly Valley has been well documented, little data is available on the quality of the groundwater.

The South Australian Health Commission conducted groundwater analyses in the region in 1990 (Nick Rose, pers. comm.). Analyses for hydrocarbons, organochlorine,

organophosphate and carbamate insecticides were performed on two of those samples. None of the investigated compounds were detected. The analyses were restricted to insecticide groups and certain herbicides, but did not include triazine herbicides and fungicides.

In contrast, pesticides were detected in 83.5% of surface waters sampled (Thoma, 1988). Either dacthal, DDT and/or DDT metabolites were detected in 100% of creek and river sediments sampled. Water samples were screened for four organochlorine and three organophosphate insecticides, two herbicides and two fungicides. Triazine herbicides were not included in the analytical schedule.

9.3 RESULTS AND DISCUSSION

Pesticides were detected in only two of the forty-two bores sampled (5%). Bore 8924 was found to contain the herbicide atrazine (0.02µg/L) and its degradation product desethylatrazine (0.03µg/L). A fungicide, vinclozolin, was identified in bore 11601 (0.02µg/L).

Recoveries of surrogate compounds for these two extractions were acceptable. Therefore, there is no reason to suspect that there were extraordinary inaccuracies associated with the extraction or analysis of pesticides from these two samples.

Acid herbicides (from Schedule B) were not detected in any of the samples. Similarly, analytes from Schedule C were not detected in any of the samples. Schedule C analytes (paraquat, diquat and glyphosate) have a high affinity for soil organic matter and clay minerals (Bewick, 1994). In addition their stability is known to be matrix-dependent. Despite their frequency of use they are, therefore, rarely found in groundwater.

Atrazine is used in agriculture on maize, asparagus, sorghum, sugarcane, and pineapple, none of which are currently produced in the study area. Atrazine has been widely applied in irrigation channels, forestry, grasslands and non-selectively on non-crop areas. It has a low soil reactivity (K_{oc} =100) and water solubility (33mg/L; Webber and Keller, 1994). K_{oc} values measure the capacity of a chemical to bind to organic carbon. Low K_{oc}'s indicate a low capacity to bind to organic carbon and, therefore, high mobility; high K_{oc}'s indicate the compound is more likely to bind to soil, hence low mobility. Atrazine has been described as a "leacher" (Beitz et al., 1994). It and/or its degradation products have been frequently found in groundwater, with emphasis on corn-growing areas (Ritter et al., 1994; Barrett and Williams, 1989).

The detection of the *s*-triazine herbicide atrazine and its phytotoxic degradation product, desethylatrazine, in groundwater from bore 8924 suggests that transport of triazine contaminants to the aquifer has been slow, allowing atrazine degradation and desethylatrazine accumulation. As desethylatrazine is more water soluble and mobile through soil than atrazine, the desethylatrazine:atrazine ratio (DAR) has been used to identify sources of contamination (Adams and Thurman, 1991). The presence of DEA

in groundwater of this study area suggests slow transport of the parent compound to the aquifer (Pereira and Hostettler, 1993).

The source of contamination in this case can not be unequivocally identified. Bore 8924 was located adjacent to market gardens, however atrazine application would have a deleterious effect on these particular crops. The DO in this sample was moderately high (4.49mg/L), as was the NO_3-N level (10mg/L), consistent with rapid recharge and transport of contaminants to the groundwater. This bore was deep (91.2m) with a depth to water table of 14m and the geology was Aldgate Sandstone. The tritium level of this groundwater (2.3±0.2 TU) was also consistent with modern recharge which may facilitate the transport of contaminants.

Groundwater from this bore is used for garden irrigation and drinking purposes. The Australian Drinking Water Guidelines (1996) state that pesticides should not be detected in drinking water. The level of atrazine found in bore 8924 is well below that considered to be of health concern (20µg/L), but should be regularly monitored and the source of contamination identified as prolonged exposure could present a health risk. Atrazine is not considered to be very toxic. The acute oral LD_{50} for rats is 1.87-3.08g TC/kg (Worthing and Hance, 1991; TC denotes Technical Grade). The presence of atrazine in the irrigation water may have a deleterious effect on the residential garden.

Vinclozolin is classed as a 3',5'-dichloroanilide contact fungicide. It is used selectively on grapes, oilseed rape, sunflowers, hops, strawberries, stone and pome fruits (apples, pears, peaches, apricots, plums, cherries, nectarines), vegetables and ornamentals and turf against *Botrytis cinerea*, *Sclerotinia* spp. and *Monilia* spp. The presence of vinclozolin in water from bore 11601 (golf course) suggests a possible source was application on turf for control of dollar spot (*Sclerotinia homeocarpa*).

The nitrate-N concentration of groundwater from bore 11601 was at background level, but phosphate levels were slightly elevated. One might expect elevated levels of nitrogen and phosphate at this site, due to the application of high levels of fertilizers on golf courses. As this was not the case it is possible that the source of vinclozolin contamination was not from the golf course itself. However, dissolved oxygen was sufficiently low (0.71mg/L) to permit denitrification i.e., nitrate removal, suggesting that the golf course can not yet be precluded as a source. Although the immediate surrounding area is bushland, viticulture upstream may be using vinclozolin.

Vinclozolin contamination of the groundwater may be due to recharge from contaminated surface water, Cox Creek for example, possibly following application to market gardens or viticulture. Surface water from Cox Creek in the immediate vicinity of this golf course was sampled between 1985 and 1987 (Thoma, 1988). Vinclozolin was identified in 40% of the samples, along with chlorpyrifos (23%), DDT and its metabolites (14%), lindane (27%), dacthal (91%) and propyzamide (52%). Tritium levels of this bore are 1.7±0.2 TU, indicating modern groundwater. The presence of vinclozolin in this groundwater is consistent with rapid contaminant transport as this compound has a short half-life (20 days; Weber and Keller, 1994). Bore 11601 is located close to a dam, which may be facilitating groundwater contamination following surface runoff and leakage.

Vinclozolin has been detected in groundwater in Europe (Beitz et al., 1994). It degrades rapidly to 3,5-dichloroaniline which, based on the properties of other chlorinated aromatic amines, is potentially more toxic to humans than the parent compound (Polettini et al., 1993). Vinclozolin is more mobile than its main degradation product which was not included in the present analyte schedules. Reanalysis of the mass spectral data, however, found no evidence of the breakdown product in this particular sample, though recovery information is lacking to prove the extraction procedure was suitable for this compound.

Repeated application of vinclozolin enhances biodegradation in the vadose zone (Walker and Welch, 1990), which seems to be pH-dependent. Vinclozolin has a very low water solubility (2.6mg/L), low volatility (2.6mm Hg x 10^{-6}) and a high soil reactivity (K_{oc} =10^4; Weber and Keller, 1994). These properties indicate that vinclozolin is unlikely to enter groundwater but more likely to bind to organic material in the vadose zone. Much of the golf course greens would contain sandy top soil, so vinclozolin would be more mobile under these conditions than in organic-rich soils.

There are no specific health guideline values for the fungicide vinclozolin. Groundwater from bore 11601 is also used for irrigation and occasionally as drinking water. Vinclozolin has a low toxicity to humans. The acute oral LD_{50} for rats is 10g TC/kg and the estimated Acceptable Daily Intake (ADI) for humans is 0.07mg/kg body weight (Worthing and Hance, 1991). In recent experiments with rats it has been determined to be an hormone-disruptor, binding and blocking androgen receptors (Colborn et al., 1996).

Bore 11601 was deep (152m), with a depth to water table (SWL) of ~16.3m. A high level of manganese (1030µg/L) was also detected in this bore. The high manganese level may be linked with application of manganese-containing dithiocarbamate pesticides such as mancozeb or maneb, both of which were excluded from this study due to their requirement for different analytical methodology. These dithiocarbamate fungicides have similar applications to vinclozolin (Worthing and Hance, 1991), being applied on turf, fruit and vegetable crops.

9.4 CONCLUSIONS

In this current study eighteen of the twenty-five compounds which were identified as being used in the region by Thoma (1988) were included in the analytical schedules, a more comprehensive screen than in earlier surface and ground water investigations of the region. Unfortunately previous studies of surface and ground water contamination, as described earlier, did not analyse triazine herbicides although atrazine was identified as one of the twenty-five compounds used by local growers when surveyed. Additional compounds were included in the present survey.

As the contaminated groundwater is used for drinking purposes it would be useful to trace the source of contamination. This would require a more intensive study of surface and groundwater of the Golf Course and Cox Creek region.

The identification of pesticides in the aquifers of this catchment shows that contamination can occur through fractured rock. Fractured rock may provide a rapid flow path for contaminants to reach aquifers.

Overall, this study identified a low number of pesticide-contaminated bores (5%). The land usage of viticulture and market gardening does not seem to have resulted in extensive groundwater contamination, despite the intensive use of pesticides in the latter as highlighted by the widespread surface water contamination of the region.

10.0 SUMMARY

10.1 MAJOR AND MINOR ION CHEMISTRY

- Piccadilly Valley Groundwaters evolve from a Na-Cl dominated meteoric recharge water to either a Na-Mg-Cl-HCO_3 type of water, or when influenced by the dissolution of dolomite, a Mg-Na-Ca-HCO_3-Cl water. Mixing is occurring between meteoric water and these two end members. The more elevated TDS values were associated with end-member water types and were not correlated with anthropogenic contamination.

- Table 10.1 summarises the minimum, maximum and median values found in the Piccadilly Valley Groundwaters for some of the physical parameters and inorganic chemical constituents measured. The bores which exceeded the 1996 NH&MRC/ARMCANZ guideline values are identified.

Table 10.1 Summary of April-May 1994 Piccadilly Valley groundwater analyses relevant to human consumption

Constituent	Guideline Value	# of Bores exceeding guideline value	Min	Max	Median	Bores exceeding health drinking water guideline value
TDS (mg/L)	500*	6	86	718	359	
pH	6.5-8.5*	15	4.74	7.77	6.77	
Aluminium (mg/L)	**0.2**	**1**	**<0.005**	**0.236**	**<0.005**	**6583**
Arsenic (µg/L)	7	0	<0.2	4.2	0.2	
Boron (mg/L)	0.3	0	0.018	0.141	0.037	
Cadmium (µg/L)	2	0	<1	<1	<1	
Chloride (mg/L)	250*	0	37.3	246	59.35	
Copper (mg/L)	2	0	<0.005	0.116	<0.005	
Fluoride (mg/L)	1.5	0	<0.05	0.94	0.37	
Iodide (mg/L)	**0.1**	**1**	**<0.05**	**0.16**	**0.03**	**6758**
Iron (mg/L)	0.3*	25	0.01	14.46	0.51	
Lead (µg/L)	10	0	<1	6	<1	
Manganese (mg/L)	**0.5**	**3**	**<0.005**	**1.034**	**0.05**	**11601, 6709, 13256**
Mercury (µg/L)	1	0	<0.1	<0.1	<0.1	
Nickel (µg/L)	**20**	**1**	**<0.1**	**23**	**<0.1**	**13253**
Nitrate-N (mg/L)	**11.3**	**1**	**<0.001**	**15.0**	**0.665**	**13253**
Total Phosphate-P	n/a		<0.002	0.81	0.03	
Selenium (µg/L)	10	0	<0.1	7	0.5	
Sodium (mg/L)	180*	0	24.2	153	45.65	
Sulphate (mg/L)	500	0	4.57	194	13.4	
Uranium (µg/L)	20	0	<0.1	1.4	0.1	
Zinc (mg/L)	3*	0	<0.005	0.924	0.05	

*Aesthetic rather than health guideline value
n/a Not applicable

- Metals were generally present at low concentrations and rarely exceeded drinking water standards, with the exception of iron, for which 60% of the bores exceeded the aesthetic guideline value of 0.3 mg/L. Many of the landholders in the Piccadilly Valley indicated problems with iron precipitate clogging irrigation systems and with borehole corrosion/encrustation. The elevated iron concentrations found in Piccadilly Valley Groundwaters are presumably naturally occurring and have as their source the igneous and metamorphic rocks found within the area.

10.2 ANTHROPOGENIC CONTAMINATION

Nutrients

- The principle form of nitrogen was nitrate. Nitrate-N concentrations ranged from <0.001 to 15 mg/L with a median value of 0.67 mg/L. Twenty-seven samples (64%) exceeded the reported background concentration of 0.25 mg/L.

- One sample exceeded the Australian drinking water guideline value of 11.3 mg/L.

- Most of the samples (77%) had nitrogen-15 isotope values above +9 per mil, suggesting that human and/or animal wastes are the predominant source of nitrate. Organic fertilisers and leaking septic tanks are the most likely sources of nitrate.

- When comparing the nitrate results from this study to those of Harvey (1979), there appears to have been little increase in nitrate concentrations over the past 15 years.

- Total phosphate concentrations ranged from <0.002 to 0.81 mg/L with a median value of 0.03 mg/L. Four samples contained concentrations greater than 0.02 mg/L.

Microbiology

- Faecal indicator bacteria (FIB) were found in 8/42 (19%) of the samples.

- Four samples contained faecal coliforms [FC] (range 1-196 CFU/100 mL). Of these four samples, three also contained faecal streptococci [FS] (range 1-120 CFU/100mL).

- Three samples contained FS but no FC. While the 1996 NH&MRC Australian Drinking Water Guidelines refer to FC to determine microbiological water quality (FC should be undetectable in 100 mL of sample), the presence of FS is also evidence of faecal contamination.

- One sample which contained both FC and FS, also contained *Clostridium perfringens* spores, consistent with the possibility that faecal contamination might have been occurring for some time.

- The principle source for FIB are most likely leaking septic tanks, although livestock cannot be precluded.

- The presence of FIB in Piccadilly Valley Groundwaters indicates the potential for the transmission of gastrointestinal-borne pathogens when untreated groundwater is used as a drinking source.

Pesticides

- Two bores were found to be contaminated with pesticides. One was found to contain the triazine herbicide atrazine (0.02 µg/L) and one of its degradation products desethylatrazine (0.03 µg/L). The other sample contained the fungicide vinclozolin, at 0.02 µg/L.

- The 1996 NH&MRC Australian Drinking Water Guidelines state that pesticides should not be detected in drinking water. The level of atrazine found is well below that at which atrazine is considered to be of a health concern (20 µg/L). There are no specific health guideline values for the fungicide vinclozolin.

10.3 ENVIRONMENTAL ISOTOPES

Tritium

- Tritium concentrations for Piccadilly Valley groundwater samples ranged from <0.5 to 3.8TU with a median value of 0.9TU. One third of the samples contained tritium concentrations greater than 1.4TU, indicating that these samples contain detectable quantities of water recharged within the past 25 years. All but one sample contained tritium suggesting that the maximum residence time of groundwaters in the Piccadilly Valley Catchment is about 50 years; however, mixing between tritiated and non tritiated waters may give rise to an intermediate tritium concentration which does not reflect these semi-quantitative ages, and the possibility exists that some of the groundwaters may have been recharged more than 50 years ago.

- Tritium concentrations were generally greatest at the margins of the Piccadilly Valley (excepting the northern margin) and, in some instances, in the vicinity of the Cox Creek and its tributaries, indicating that these areas are receiving detectable quantities of recharge water.

- Tritium concentrations showed no correlation with bore depth, depth to aquifer (top of slotted casing depth) or depth to water table, and adjacent bores often had differing tritium concentrations. Tritium concentrations above 1.4TU were found in bores as deep as 200m. These data suggest that groundwater flow in the Piccadilly Valley primarily occurs via preferential flow paths within fracture planes.

- The bore samples containing elevated nitrate concentrations, pesticides and the highest faecal indicator bacteria numbers had tritium concentrations greater than 1.4TU. This confirms that the potential for groundwater contamination in the Piccadilly Valley is highest in areas where recharge to the aquifer is greatest. The presence of vinclozolin, with an estimated half-life of 1 to 32 days, and FIB, with half-lifes on the order of hours to days, suggests recent recharge prior to our sampling.

Deuterium and Oxygen-18

- The deuterium and oxygen-18 isotopes are depleted relative to both the Global Meteoric Water Line and the "local" (Chain of Ponds) meteoric water line. This suggests the possibility that the Chain of Ponds meteoric water line is not appropriate for the Piccadilly Valley and/or that the Piccadilly Valley groundwaters contain a percentage of "fossil" paleowaters (which have been recharged under a different climatic regime); however, as tritium was found in all but one sample, one would not expect the presence of paleowaters. Low temperature rock-water interactions may also potentially be responsible for the relative depletion in $\delta^{18}O$ and δD, but it is beyond the scope of this report to determine whether this has occurred.

Chlorine-36

- The chlorine-36 isotopes confirm that mixing is occurring between different ages of water.

- Older waters are flowing from the northwestern portion of the study area (where less recharge occurs) and suggests the possibility that the hydrogeological catchment boundary may continue to the north and may be distinct from the surface water catchment boundary.

11.0 CONCLUSIONS AND RECOMMENDATIONS

Despite the Piccadilly Valley's near 100 year history of horticultural activity, the quality of the region's groundwaters appear to be relatively good. It seems probable that the steep topography of the Piccadilly Valley has favoured surface water run off, rather than infiltration to the underlying groundwaters.

Groundwater nitrate concentrations were generally low and appear similar to those documented in 1979; median concentrations are comparable, having risen slightly from 0.38 to 0.67 mg/L of nitrate-N. On the other hand, about two-thirds of groundwater samples showed slight to substantial increases above apparent background concentrations, although only one sample (15 mg/L) exceeded the drinking water guideline value of 11.3 mg/L nitrate-N. The isotopic signatures of nitrate-N were consistent with derivation from human and/or animal wastes and with leaking septic tanks as the most probable sources.

Faecal indicator bacteria were detected in 19% of bores in the area. Again, leaking septic tanks are the most probable source of contamination, which suggests that there is some potential for pathogen transmission if untreated groundwater is used for drinking purposes.

Pesticides were detected in only 5% of bores. The compounds found (atrazine, a herbicide and vinclozolin, a fungicide) were present at low concentrations and are regarded as having low toxicity. Potential sources of these compounds include their use in weed control, market gardening, orcharding, viticulture and turf maintenance.

Some naturally occurring elements were elevated above drinking water guideline values on aesthetic or health criteria. Health drinking water guideline values were exceeded for 4 elements: aluminium, iodide and nickel in one sample each; manganese in a further three samples. Approximately two-thirds of samples contained iron concentrations which exceeded the aesthetic guideline value.

Hydrochemical and environmental isotopic data acquired at the same time enable the contamination documented to be understood in the context of the hydrological processes taking place in the Piccadilly Valley. Tritium data suggests that groundwater recharge and groundwater movement occurs primarily via preferential flow paths and that the maximum residence time for Piccadilly Valley Groundwaters is of the order of 50 years. Recharge appears to be generally greatest around the margins of the Piccadilly Valley, with the exception of the northern margin.

Anthropogenic contamination was directly correlated with tritium concentrations, and hence aquifer recharge. This study highlights the importance of identifying areas in the Piccadilly Valley where recharge to the aquifer is greatest in order to better protect the groundwater resources from anthropogenic contamination.

Recommendations for Future Work

The recommendations arising from this investigation emphasise the need not only to benchmark and monitor groundwater quality but also the concomitant need to understand the influences of natural hydrogeolgical and geochemical processes, especially recharge, in order to protect groundwater resources from anthropogenic contamination arising from various land use and management regimes. The recommendations are as follow:

- Integrate the results from this study with the currently ongoing revision of the geology of the Piccadilly Valley, with an emphasis on the association between fracture geometry, groundwater recharge and groundwater contamination.

- Integrate the results of this study with soils mapping in order to determine the association between soil types, rates of groundwater recharge and groundwater contamination in the Piccadilly Valley.

- Obtain fertiliser and pesticide application rates and calculate a contaminant budget for the Piccadilly Valley Catchment..

- Review land management practices in vulnerable areas where recharge to the aquifer is greatest in order to better protect the groundwater resources.

- Re-sample bores during or immediately following high natural recharge events i.e., winter rains (our data were acquired in autumn). A repeat sampling would give a clearer indication of the processes affecting groundwater quality, temporal changes in contaminant concentration, and the range of medium to long-term natural fluctuations in groundwater chemistry.

- Monitor bores that were positive for faecal indicator bacteria, pesticides and those which had elevated nitrate concentrations.

- Monitor bores used for drinking water purposes for the range of contaminants found in this study and advise land holders when bore samples exceed drinking water guideline values.

- More accurately determine the ages of the groundwaters by sampling discrete fracture systems that have been isolated with down hole packers and by analysing those samples for a range of isotopes, eg., tritium, deuterium, oxygen-18 and carbon-14.

- Sample bores to the north of the Piccadilly Valley in order to determine whether the hydrogeological catchment is distinct from, and continues to the north of the Piccadilly Valley surface water catchment.

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13.0 APPENDICES

13.1 APPENDIX A: ®EXCEL FILES ON DISK

The data collected for this study has been placed into two EXCEL® spreadsheets (diskette in back pocket).

Pvraw.xls - This spreadsheet includes raw data for the 1994 AGSO Groundwater Quality Assessment Project of the Piccadilly Valley. This spreadsheet includes QA/QC data for spikes and duplicates. GPS location data in map datum AGD66.

Pvavg.xls - In this spreadsheet the spiked data has been deleted and the duplicate samples have been averaged. For data below the limit of detection, a value of half the detection limit has been substituted. Data tables from the main body of this report are contained in this spreadsheet. GPS location data in map datum AGD66.

13.2 APPENDIX B: SUMMARY OF DEPARTMENT OF MINES AND ENERGY, SA BORE RECORD DATA

Appendix B: Summary of Department of Mines and Energy, SA - Bore Record Data for the Piccadilly Valley

Bore Number	Saturated Thickness (m)	Altitiude (m)	Drill Method	Year first drilled	Bore Depth from surface (m)	Year Deepened	Casing Diameter (m)	Total Depth from surface (m)	Casing Depth from surface (m)
6555	-3.40	490		1978			0.110	61.0	
6567	20.90	505	Rotary	1977			0.152	47.5	47.5
6583	3.85	560	Cable Tool	1950			0.153	29.0	29.0
6598	7.94	564		1962			0.152	115.8	44.5
6627	44.90	527	Rotary Hammer/Air	1977	151.00	1984	0.152	181.8	13.5
6709	65.50	474	Cable Tool	1960?	121.80	1990	0.153 and 1x1 old timber	199.6	184.4
6742	13.71	496	Cable Tool	1930			0.153 and 1x2m old timber casing	39.3	14.6
6746	11.20	482	Air Hammer	1978			0.153	142.0	109.4
6750	43.50	502	Air Hammer	1977			0.150	101.0	87.3
6758	49.00	523	Air Hammer	1977			0.153	105.0	84.0
6759	14.00	526	Rotary Air	1976			0.153	130.0	56.0
6771	0.00	477	Cable Tool	1952			0.203	117.6	112.7
6776	-6.50	473		1940			0.203 and 1x2m old timber casing	30.5	18.6
6782	-19.70	492		1962				67.1	
6809	0.00	544		1973?			0.153	48.7	48.7
6811	0.00	498	Cable Tool	1954?			0.153	100.5	42.6
6828	0.00	465	Cable Tool	1958			0.203	120.0	
6834	10.00	476	Cable Tool	1959	24.40	1982	0.153	49.4	49.4
6835	45.76	472	Rotary	1972			0.153	54.8	54.8
7224	23.00	450	Rotary Air/Hammer	1984			0.152	94.0	94.0
8924	24.00	475	Rotary Air	1978				91.2	42.6
11601	27.20	415	Rotary Air	1979			0.200	152.4	6.0
11934	8.00	557	Air Hammer	1981			0.150	120.0	63.0
11935	11.00	471	Hammer	1981			0.150	35.6	30.5
12023	19.00	457	Rotary Hammer	1987			0.155	136.0	65.6
12045	36.00	520	Rotary Air	1982			0.152	56.2	56.2
12428	6.90	484	Rotary Hammer	1982			0.152	28.0	28.0
12429	10.58	468	Rotary Hammer	1982				96.0	24.0
12627	-32.30	475	Air Hammer	1983			0.153	108.8	6.1

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Bore Number	Saturated Thickness (m)	Altitiude (m)	Drill Method	Year first drilled	Bore Depth from surface (m)	Year Deepened	Casing Diameter (m)	Total Depth from surface (m)	Casing Depth from surface (m)
12825	40.00	570	Rotary Hammer	1984			0.153	153.0	132.6
12827	-2.00	464		1992				63.0	56.0
12921	57.10	503	Rotary Air	1984			0.150	304.0	152.0
13253	41.00	512	Rotary Hammer/Air	1985			0.158	190.0	92.0
13256	16.00	445	Rotary Air	1985			0.150	53.2	27.0
13440	26.00	499	Rotary Air	1985			0.150	120.0	91.0
13537	8.20	575	Rotary Hammer	1985			0.153	183.0	173.7
13543	35.00	524	Rotary Air	1985			0.150	152.0	104.0
13596	20.00	507	Rotary Air	1985			0.150	68.9	21.0
13906	9.80	600	Rotary Hammer	1987			0.152	131.6	6.0
14178	8.00	680	Rotary Air	1988			0.157	110.0	110.0
15410	28.00	469	Rotary Hammer	1990			0.155	99.0	84.4
15938	32.00	465	Rotary Air	1992				191.0	113.0
Blank cells indicate no data available									

Appendix B: Summary of Department of Mines and Energy, SA - Bore Record Data for the Piccadilly Valley

Bore Number	Slotted Casing Interval Depth from surface (m)	Final Standing Water Level from surface (SWL) (m)	SWL Date Measured	Water Level (AHD)	Final Yield m^3/day	Depth to first water cut from surface (m)	Approximate Soil Thickness (m)	TDS (mg/L)	NO_3 (mg/L)	NO_3-N (mg/L)	TDS/NO_3 Analysis Date
6555		3.40	19/4/78	486.60	550.0			207.00			19/4/78
6567	35-47.5	17.10		487.90	1540.0	38.00	2.00	270.00			25/2/77
6583		15.65	18/04/78	544.35	110.0	19.50	1.80	110.00	1.37	0.31	4/4/79
6598		74.36		489.64	283.7	82.30	0.46	286.00			18/3/78
6627		41.10		485.90	120.0	86.00		587.00	0.02		13/4/84
6709	120-184.4	4.50	16/5/90	469.50	648.0	70.00	3.00	356.00			14/5/90
6742	13.7-14.6			496.00	110.0	13.71	7.60	210.00	4.60	1.04	30/3/79
6746	0.4-109.4	21.80		460.20	1944.0	33.00	12.00	270.00	0.13	0.03	30/3/79
6750	0.5-87.3	11.50		490.50	1296.0	55.00	8.00	465.00	0.02	0.00	7/4/77
6758		36.00	11/1/78	487.00	95.0	85.00	2.00	130.00	6.30	1.42	14/3/79
6759		44.00		482.00	66.0	58.00	1.00	170.00	1.20	0.27	14/3/79
6771		0.00		477.00				320.00	7.40	1.67	12/3/79
6776		6.50		466.50	648.0			415.00			22/1/74
6782		19.70	24/8/62	472.30	490.9		2.40		10.90	2.46	
6809	42.23-48.7			544.00				150.00	33.10	7.47	2/4/79
6811				498.00				327.00			1/3/78
6828				465.00	660.0			312.00	6.40	1.44	5/4/78
6834	33-49	18.00		458.00	272.2	28.00	3.00	290.00	0.80	0.18	2/4/79
6835	42.6-54.8	9.14		462.86	833.8	54.90	3.00	145.00	12.00	2.71	15/1/74
7224	42.5-55 68.5-94	7.00		443.00	259.2	30.00					
8924	32-39	14.00		461.00	165.0	38.00	3.00	320.00	24.80	5.60	2/4/79
11601		16.30	15/3/79	398.70		43.50	3.00	249.00			2/3/79
11934		42.00		515.00		50.00	8.00	286.00			30/11/81
11935	23-30	12.00		459.00	648.0	23.00	5.80	348.00			2/12/81
12023	30-65	18.00	2/7/82	439.00	414.7	37.00	1.00	109.00			29/6/82
12045	45-55	11.00		509.00	392.8	47.00	0.60	124.00			29/9/82
12428		0.10		483.90	388.8	7.00	7.00	333.00			9/8/82
12429	20.4-23.4	7.62		460.38	972.0	18.20	9.10	384.00			6/8/82
12627		78.00	13/12/83	397.00	194.4	45.70	4.50	477.00			14/12/83

Appendix B: Summary of Department of Mines and Energy, SA - Bore Record Data for the Piccadilly Valley

Bore Number	Slotted Casing Interval Depth from surface (m)	Final Standing Water Level from surface (SWL) (m)	SWL Date Measured	Water Level (AHD)	Final Yield m^3/day	Depth to first water cut from surface (m)	Approximate Soil Thickness (m)	TDS (mg/L)	NO_3 (mg/L)	NO_3-N (mg/L)	TDS/NO_3 Analysis Date
12825	121.5-132.6	58.00	18/2/84	512.00	485.6	98.00	2.00	210.00			26/3/84
12827	30-56	2.00		462.00	1036.8			160.00			20/1/84
12921	116-123	45.50	29/2/84	457.50	205.6	102.60	0.50	680.00			29/2/84
13253	48-92			512.00	324.0	41.00	3.50	388.00			28/2/85
13256	21-27	5.00	15/2/85	440.00	194.4	21.00	3.00	321.00			15/2/85
13440	40.5-91	9.00		490.00	388.8	35.00	16.00	246.00			4/9/85
13537		74.00	24/10/85	501.00	485.6	82.20	1.60	433.00			24/10/85
13543	36.6-40 58-80	1.00		523.00	108.0	36.00	2.00	139.00			30/11/85
13596		19.50		487.50	108.0	39.50	14.00				
13906		39.60		560.40	756.0	49.40	4.60	136.00			4/3/87
14178	74-110	52.00	25/2/88	628.00	475.2	60.00	1.00	109.00			24/2/88
15410	0.3-84.4	3.00		466.00	1080.0	31.00	7.00	236.00			21/11/90
15938	80-113	13.00		452.00	950.4	45.00	3.00	343.00			7/2/92
Blank cells indicate no data available											

Appendix B: Summary of Department of Mines and Energy, SA - Bore Record Data for the Piccadilly Valley

Bore Number	Surface Expression of Geology	Log Available ?
6555	Woolshed Flat Shale	N
6567	Woolshed Flat Shale	Y
6583	Stonyfell Quartzite	Y
6598	Aldgate Sandstone	Y
6627	Aldgate Sandstone	Y
6709	Barossa Complex	Y
6742	Aldgate Sandstone	N
6746	Aldgate Sandstone	Y
6750	Aldgate Sandstone	Y
6758	Aldgate Sandstone	Y
6759	Aldgate Sandstone	Y
6771	Aldgate Sandstone	N
6776	Aldgate Sandstone	N
6782	Aldgate Sandstone	N
6809	Woolshed Flat Shale	N
6811	Aldgate Sandstone	N
6828	Aldgate Sandstone	N
6834	Aldgate Sandstone/Woolshed Flat Shale/Barossa Complex junction	Y
6835	Woolshed Flat Shale	Y
7224	Barossa Complex	Y
8924	Aldgate Sandstone/Woolshed Flat Shale junction	Y
11601	Barossa Complex	Y
11934	Woolshed Flat Shale	Y
11935	Aldgate Sandstone	Y
12023	Barossa Complex	Y
12045	Woolshed Flat Shale	Y
12428	Woolshed Flat Shale	Y
12429	Aldgate Sandstone	Y
12627	Barossa Complex	Y

Appendix B: Summary of Department of Mines and Energy, SA - Bore Record Data for the Piccadilly Valley

Bore Number	Surface Expression of Geology	Log Available ?
12825	Woolshed Flat Shale	Y
12827	Aldgate Sandstone	N
12921	Aldgate Sandstone	Y
13253	Barossa Complex	Y
13256	Barossa Complex	Y
13440	Aldgate Sandstone	Y
13537	Aldgate Sandstone	Y
13543	Barossa Complex	Y
13596	Aldgate Sandstone	Y
13906	Stonyfell Quartzite	Y
14178	Stonyfell Quartzite	Y
15410	Aldgate Sandstone	Y
15938	Aldgate Sandstone	Y
Blank cells indicate no data available		

13.3 APPENDIX C: INORGANIC AND NUTRIENT CHEMISTRY: QUALITY ASSURANCE AND QUALITY CONTROL ASSESSMENT

In this section an attempt has been made to assess the quality of the analytical results both in terms of precision and accuracy (Vitale et al., 1991). In this case precision is defined as the degree of mutual agreement among individual measurements and has been determined by assessing the degree of agreement between duplicate samples.

The relative percentage difference (RPD) is defined as:
RPD = (Sample A - Sample B)/(Average Sample A+B) * 100

The accuracy is defined as the difference between the average value and the true value, when the true value is known, and has been determined by assessing the percentage recovery of the spiked samples.

The percentage recovery is defined as:
% Recovery = (Spike Result - Unspiked Result)/Concentration Added *100

C.1 SUMMARY OF MAJOR INORGANIC CHEMISTRY

(AGSO Lab Data - refer to table C1)

Iron: The relative percentage difference for duplicate samples ranged from 0.7 to 66.7 %. The larger percentage difference was for bore number 6567, which contained low concentrations of iron. The precision of the analytical results is considered to be good. No samples were spiked with iron.

Manganese: The relative percentage difference for duplicated samples ranged from 0.3 to 25 %, with the larger percentage difference obtained in a sample with extremely low concentrations of manganese. The precision of the analytical results is considered to be good. No samples were spiked with manganese.

Calcium, magnesium, sodium, potassium, sulphur, bicarbonate, chloride and sulphate: The relative percentage differences for duplicate samples were less than 10 % and the recoveries of spiked samples ranged from 85 to 112 %. The precision and accuracy of the analytical results are considered to be good.

Silicon: The relative percentage difference for duplicate samples was less than 0.6 %. The precision of the analytical results is considered to be good. No samples were spiked with silicon.

C.2 SUMMARY OF FLUORIDE AND IODIDE

(ACTEW Lab Data - refer to Table C2)

Fluoride: The relative percentage difference for duplicate samples ranged from 1.6 to 5.1 % and the recovery of spiked samples ranged from 84 to 89%. The precision and accuracy of the analytical results are considered to be good.

Iodide: The relative percentage difference for duplicate samples ranged from 0 to 41.8 % and the recovery of spiked samples ranged from 74 to 75 %. The precision and accuracy of the analytical results are considered to be good.

C.3 SUMMARY OF NUTRIENTS

(ACTEW Lab Data - refer to Table C3)

Total Organic Carbon: The relative percentage difference for duplicate samples was 0 % and the recovery of spiked samples ranged from 110 to 120 %. The precision and accuracy of the analytical results are considered to be good.

Ammonium: The relative percentage difference for duplicate samples ranged from 0 to 133.3 % and the recovery of spiked samples ranged from 186 to 199 %. As the spiked recoveries were consistently about 200 %, it is likely that an error was made in creation of the spiking solution. The precision and accuracy of the analytical results are considered to be good.

Nitrite: The relative percentage difference for duplicate samples was 0 %. No samples were spiked with nitrite. The precision is considered to be good.

Nitrate: The relative percentage difference for duplicate samples ranged from 0 to 50%. The difference of 50 % has been exaggerated by the very low concentrations of nitrate. The precision is thus considered to be good. The recovery of spiked samples ranged from 83 to 734.4 %. It is believed that a dilution or spiking error has been made for the sample (WQ94/105) recovering 734.4 %. This error casts some doubt on the accuracy of the results. However, the Total Nitrogen can be used to validate the nitrate values due to nitrate being the predominant form of nitrogen in these waters.

Total Oxidised Nitrogen: The relative percentage difference for duplicate samples ranged from 0 to 50 %. The difference of 50 % was obtained for a sample at trace concentrations of nitrogen and exaggerates the difference. The precision is thus considered to be good. The recovery of spiked samples ranged from 83 to 102 % with one sample (WQ94/105) having a recovery of 734.4 %. It is believed that a dilution or spiking error has been made for this sample. This error casts some doubt on the accuracy of the results; nonetheless, the accuracy is generally considered to be good.

Total Nitrogen: The relative percentage difference for duplicate samples ranged from 0 to 60.6 %. The larger percentage differences were obtained for those samples

containing smaller concentrations of nitrogen. The precision is thus considered to be good. The recovery of spiked samples ranged from 109.09 to 117.91 % with one sample (WQ94/105) having a recovery of 436.06 %. It is believed that a dilution error has been made for this sample. This error casts some doubt on the accuracy of the results; nonetheless, the accuracy is generally considered to be good.

Ortho-Phosphate: The relative percentage difference for duplicate samples ranged from 0 to 40 %. The sample with a difference of 40 % contained trace levels of ortho-phosphate and the difference is therefore exaggerated. The recovery of spiked samples ranged from 78.5 to 98.5 %. The precision and accuracy of the samples are considered to be good.

Acid Hydrolysed Phosphate: The relative percentage difference for duplicate samples ranged from 0 to 16.6 %. The precision is considered to be good. No samples were spiked.

Total Phosphate: The relative percentage difference for duplicate samples ranged from 0 to 8.3 %. The precision is considered to be good. No samples were spiked.

C.4 SUMMARY OF TRACE ELEMENT CHEMISTRY (AGSO LAB)

(refer to Table C4)

Aluminium: The relative percentage difference for duplicate samples ranged from 0 to 122.6 %. The sample with a percentage difference of 122.6 % was for a concentration difference of about 0.004 mg/L and is exaggerated due to the small concentrations involved. The precision is considered to be good.

Copper: The relative percentage difference for duplicate samples ranged from 0 to 82.4 %. The sample with a percentage difference of 82.4 % is exaggerated due to the small concentrations involved. The precision is considered to be good.

Zinc: The relative percentage difference for duplicate samples ranged from 0 to 32 %. The sample with a percentage difference of 32 % was for a concentration difference of 0.008 mg/L and is exaggerated due to the small concentrations involved. The precision is considered to be good.

Strontium: The relative percentage difference for duplicate samples ranged from 0 to 2.7 %. The precision is considered to be good.

Lithium: The relative percentage difference for duplicate samples ranged from 6.9 to 28.6 %. The sample with a percentage difference of 82.4 % was for a concentration difference of 0.003 mg/L and is exaggerated due to the small concentrations involved. The precision is considered to be good.

Boron: The relative percentage difference for duplicate samples ranged from 5.4 to 46.7 %. In one case (WQ94/73-74) the difference was 161.7% and this error is

believed to be due to a typographical error in the laboratory printout (e.g., 0.255 mg/L instead of 0.025 mg/L). The precision is considered to be good.

Barium: The relative percentage difference for duplicate samples ranged from 1.2 to 5.2 %. The precision is considered to be good.

C.5 SUMMARY OF TRACE ELEMENT CHEMISTRY (AMDEL LAB)

(refer to Table C5)

Copper: The relative percentage difference for duplicate samples ranged from 0 to 120 %. The sample with a percentage difference of 120 % was for a concentration difference of 3 µg/L and is exaggerated due to the small concentrations involved. The precision is considered to be good. The recovery of spiked samples ranged from 94.8 to 99.8 % and the accuracy is considered to be good.

Iron: The relative percentage difference for duplicate samples ranged from 6 to 116%. The recovery of spiked samples ranged from 67.8 to 119.25 %. The precision is considered to be fair and the accuracy good.

Manganese: The relative percentage difference for duplicate samples ranged from 0 to 7 %. The recovery of spiked samples ranged from 78.5 to 112.5 %. The precision and accuracy are considered to be good.

Antimony: The relative percentage difference for duplicate samples ranged from 0 to 28.6 %. The sample with a percentage difference of 28.6 % was for a concentration at the limit of detection and is exaggerated due to the small concentrations involved. The precision is considered to be good. No samples were spiked.

Zinc: The relative percentage difference for duplicate samples ranged from 7 to 53%. The sample with a percentage difference of 53 % was for a concentration difference of 40 µg/L and is exaggerated due to the small concentrations involved. The precision is considered to be good. The recovery of spiked samples ranged from 47.5 to 90.3 and is considered to be fair, with a tendency towards underestimation.

Aluminium: The relative percentage difference for duplicate samples ranged from 75 to 189 %. The sample with a percentage difference of 189 % was for a concentration difference of 105 µg/L. The precision is considered to be poor. The recovery of spiked samples ranged from 77.3 to 108 % and the accuracy is considered to be good.

Selenium: The relative percentage difference for duplicate samples ranged from 0 to 152.2 %. The sample with a percentage difference of 152.2 % was for a concentration difference of about 4 µg/L and is exaggerated due to the small concentrations involved. The precision is considered to be good. No samples were spiked.

Arsenic: The relative percentage differences for duplicates were 0 %. The precision is considered to be excellent. The recovery of spiked samples ranged from 72 to 84 % and the accuracy is considered to be fair.

Uranium: The relative percentage differences for duplicates were 0 %. The precision is considered to be good. The recovery of spiked samples ranged from 0 (in WQ94/105) to 101 %. It has been assumed that the solution was not spiked for sample WQ94/105. The accuracy is considered to be good.

Mercury: The relative percentage differences for duplicates were 0 %. No spikes were performed. The precision is considered to be good, although it is difficult to interpret with samples below the detection limit.

Chromium: The relative percentage differences for duplicates were 0 %. No spikes were performed. The precision is considered to be good, although it is difficult to interpret with samples below the detection limit.

Nickel: The relative percentage differences for duplicates were 0 %. No spikes were performed. The precision is considered to be good, although it is difficult to interpret with samples below the detection limit.

Gold: The relative percentage differences for duplicates were 0 %. No spikes were performed. The precision is considered to be good, although it is difficult to interpret with samples below the detection limit.

Silver: The relative percentage differences for duplicates were 0 %. No spikes were performed. The precision is considered to be good, although it is difficult to interpret with samples below the detection limit.

Cadmium: The relative percentage differences for duplicates were 0 %. No spikes were performed. The precision is considered to be good, although it is difficult to interpret with samples below the detection limit.

Cobalt: The relative percentage difference for duplicates ranged from 0 to 138.9 %. The difference in duplicate samples of 138.9 % was for analytical results varying by about 2 µg/L and is an exaggerated figure. The precision is considered to be good, although it is difficult to interpret with samples below or close to the detection limit. No spikes were performed.

Molybdenum: The relative percentage difference for duplicates ranged from 0 to 190.6 %. The sample with the difference of 190.6 % was for duplicates varying by about 81 µg/L and is an exaggerated figure. The precision is considered to be fair, although it is difficult to interpret with samples below or close to the detection limit. No spikes were performed.

Vanadium: The relative percentage difference for duplicate samples ranged from 0 to 66.6 %. The sample with a percentage difference of 66.6 % was for a concentration difference of 1 µg/L. The precision is considered to be good, although it is difficult to interpret with samples below or close to the detection limit. The recovery of spiked samples ranged from 110 to 120 % and the accuracy is considered to be good.

Lead: The relative percentage difference for duplicate samples was 0 %. The precision is considered to be good, although it is difficult to interpret with samples below or close to the detection limit. The recovery of spiked samples ranged from 47.5 to 135 % and the accuracy is considered to be fair.

Tin: The relative percentage difference for duplicate samples ranged from 0 to 195.95 %. The sample with a percentage difference of 195.95 % was for a concentration difference of about 165 µg/L. The precision is considered to be poor. The recovery of spiked samples ranged from 1.65 to 31 % and the accuracy is considered to be poor.

Table C1: *Piccadilly Valley Major Inorganic Chemistry QA/QC Duplicates and Spikes*

BoreId	WQ Number	Lab Ref No.	Lab	Analysis Date		Fe (mg/L)	Mn (mg/L)	Ca (mg/L)	Mg (mg/L)	Na (mg/L)	K (mg/L)	Si (mg/L)	S (mg/L)	HCO3 (mg/L)	Cl (mg/L)	S04 (mg/L)
6567	94/62	940407	AGSO	06.07.94	Sample	0.066	0.061	29.30	31.0	38.3	3.54	12.8	4.21	175.00	50.0	10.9
6567	94/63	940408	AGSO	06.07.94	Duplicate	0.033	0.057	29.50	31.2	38.4	3.56	12.8	4.23	175.00	49.7	10.9
					Relative Percentage Difference	**66.667**	**6.780**	**-0.68**	**-0.6**	**-0.3**	**-0.56**	**0.0**	**-0.47**	**0.00**	**0.6**	**0.0**
					Mean Value	0.050	0.059	29.40	31.1	38.4	3.55	12.8	4.22	175.00	49.9	10.9
6567	94/64	940409	AGSO	28.07.94	Spike			8.83	28.3	229.0	8.36		19.10		371.0	48.2
					Spike Concentration (*added to distilled water*)			8.44	26.6	221.6	8.04		18.06		398.6	55.8
					Percent Recovery	**ND**	**ND**	**104.62**	**106.4**	**103.3**	**103.98**	**ND**	**105.76**	**ND**	**93.1**	**86.4**
6750	94/73	940418	AGSO	06.07.94	Sample	0.489	0.266	57.70	43.1	71.2	4.88	18.4	6.09	300.50	96.9	15.5
6750	94/74	940419	AGSO	06.07.94	Duplicate	0.542	0.267	57.70	43.0	70.9	4.88	18.4	6.08	300.00	98.0	15.7
					Relative Percentage Difference	**-10.281**	**-0.375**	**0.00**	**0.2**	**0.4**	**0.00**	**0.0**	**0.16**	**0.17**	**-1.1**	**-1.3**
					Mean Value	0.516	0.267	57.70	43.1	71.1	4.88	18.4	6.09	300.25	97.5	15.6
6750	94/75	940420	AGSO	06.07.94	Spike			8.61	27.5	226.0	8.18		18.90		376.0	47.8
					Spike Concentration (*added to distilled water*)			8.44	26.6	221.6	8.04		18.06		398.6	55.8
					Percent Recovery	**ND**	**ND**	**102.01**	**103.4**	**102.0**	**101.74**	**ND**	**104.65**	**ND**	**94.3**	**85.7**
6782	94/90	940435	AGSO	06.07.94	Sample	0.119	0.009	25.40	28.6	42.5	3.07	17.7	7.13	137.50	68.4	21.3
6782	94/91	940436	AGSO	06.07.94	Duplicate	0.113	0.007	25.50	28.6	42.6	3.08	17.8	7.14	136.25	64.7	20.1
					Relative Percentage Difference	**5.172**	**25.000**	**-0.39**	**0.0**	**-0.2**	**-0.33**	**-0.6**	**-0.14**	**0.91**	**5.6**	**5.8**
					Mean Value	0.116	0.008	25.45	28.6	42.6	3.08	17.8	7.14	136.88	66.6	20.7
6782	94/92	940437	AGSO	06.07.94	Spike			9.46	28.1	230.0	8.42		19.70		422.0	54.7
					Spike Concentration (*added to distilled water*)			8.44	26.6	221.6	8.04		18.06		398.6	55.8
					Percent Recovery	**ND**	**ND**	**112.09**	**105.6**	**103.8**	**104.73**	**ND**	**109.08**	**ND**	**105.9**	**98.0**
6758	94/103	940448	AGSO	10.08.94	Sample	1.271	0.323	8.14	12.7	82.9	6.13	21.7	4.38	87.50	100.0	11.8
6758	94/104	940449	AGSO	10.08.94	Duplicate	1.280	0.324	8.07	12.6	82.1	6.13	21.6	4.33	87.50	99.4	11.9
					Relative Percentage Difference	**-0.706**	**-0.309**	**0.86**	**0.8**	**1.0**	**0.00**	**0.5**	**1.15**	**0.00**	**0.6**	**-0.8**
					Mean Value	1.276	0.324	8.11	12.7	82.5	6.13	21.7	4.36	87.50	99.7	11.9
6758	94/105	940450	AGSO	10.08.94	Spike			8.68	28.3	229.0			19.40		405.0	52.5
					Spike Concentration (*added to distilled water*)			8.44	26.6	221.6	8.04		18.06		398.6	55.8
					Percent Recovery	**ND**	**ND**	**102.84**	**106.4**	**103.3**	**0.00**	**ND**	**107.42**	**ND**	**101.6**	**94.1**

ND= Not determined

Table C2: *Piccadilly Valley Fluoride and Iodide (ACTEW Lab) QA/QC Duplicates and Spikes*

Boreid	WQ Number	Lab Ref No.	Lab	Analysis Date		Fluoride (mg/L)	Iodide (mg/L)
6567	94/62	18219	ACTEW	01.07.94	Sample	0.40	<0.05
6567	94/63	18220	ACTEW	01.07.94	Duplicate	0.38	<0.05
					Relative Percentage Difference	**5.13**	**0.00**
					Mean Value	0.39	<0.05
6567	94/64	18221	ACTEW	01.07.94	Spike Result	0.81	0.40
					Spike Concentration (*added to sample*)	0.50	0.50
					Percent Recovery	**84.00**	**74.00**
6750	94/73	18230	ACTEW	01.07.94	Sample	0.37	<0.05
6750	94/74	18231	ACTEW	01.07.94	Duplicate	0.38	<0.05
					Relative Percentage Difference	**-2.67**	**0.00**
					Mean Value	0.38	<0.05
6750	94/75	18232	ACTEW	01.07.94	Spike Result	2.60	1.90
					Spike Concentration (*added to sample*)	2.50	2.50
					Percent Recovery	**89.00**	**75.00**
6782	94/90	18249	ACTEW	01.07.94	Sample	0.35	<0.05
6782	94/91	18250	ACTEW	01.07.94	Duplicate	0.39	<0.05
					Relative Percentage Difference	**-2.70**	**0.00**
					Mean Value	0.37	<0.05
6782	94/92	18251	ACTEW	01.07.94	Spike Result	2.60	1.90
					Spike Concentration (*added to sample*)	2.50	2.50
					Percent Recovery	**89.20**	**75.00**
6758	94/103	18264	ACTEW	01.07.94	Sample	0.48	<0.05
6758	94/104	18265	ACTEW	01.07.94	Duplicate	0.45	0.28
					Relative Percentage Difference	**1.61**	**-41.80**
					Mean Value	0.47	0.16
6758	94/105	18266	ACTEW	01.07.94	Spike Result	Broken	Broken
					Unknown recovery due to broken bottle		

Table C3: *Piccadilly Valley Nutrient QA/QC Duplicates and Spikes*

BoreId	WQ Number	Lab Ref No.	Lab	Analysis Date		DOC (mg/L)	NH4-N (mg/L)	N02-N (mg/L)	N03-N (mg/L)	Total Oxidised Nitrogen-N (mg/L)	Total Nitrogen-N (mg/L)	Ortho P04-P (mg/L)	Acid Hydrolysed P04 - P (mg/L)	Total-P (mg/L)
6567	94/62	18219	ACTEW	01.07.94	Sample	<1.0	0.02	<0.01	2.200	2.200	2.20	0.015	0.015	0.016
6567	94/63	18220	ACTEW	01.07.93	Duplicate	<1.0	0.02	<0.01	2.200	2.200	2.20	0.015	0.015	0.016
					Relative Percentage Difference	**0**	**0.00**	**0**	**0.000**	**0.000**	**0.00**	**0.000**	**0.000**	**0.000**
					Mean	<1.0	0.02	<0.01	2.200	2.200	2.00	0.015	0.015	0.016
6567	94/64	18221	ACTEW	01.07.94	Spike Result	6.4	2.00	<0.01	7.200	7.200	14.00	1.000		
					Spike Concentration (*added to sample*)	5.0	1.00	ND	5.000	5.000	11.00	1.000		
					Percent Recovery	**118.0**	**198.00**	**ND**	**100.000**	**100.000**	**109.09**	**98.500**	**ND**	**ND**
6750	94/73	18230	ACTEW	01.07.94	Sample	<1.0	0.05	<0.01	0.001	0.001	0.03	0.027	0.059	0.061
6750	94/74	18231	ACTEW	01.07.94	Duplicate	<1.0	0.01	<0.01	<0.001	<0.001	0.02	0.026	0.060	0.064
					Relative Percentage Difference	**0.0**	**133.33**	**0.00**	**50.000**	**50.000**	**33.33**	**3.704**	**-1.667**	**-4.762**
					Mean	0.5	0.03	<0.01	0.001	0.001	0.03	0.027	0.060	0.063
6750	94/75	18232	ACTEW	01.07.95	Spike	6.0	2.00	<0.01	5.100	5.100	13.00	1.000		
					Spike Concentration (*added to sample*)	5.0	1.00	ND	5.000	5.000	11.00	1.000		
					Percent Recovery	**110.0**	**197.00**	**ND**	**101.980**	**101.980**	**117.91**	**97.300**	**ND**	**ND**
6782	94/90	18249	ACTEW	01.07.94	Sample	<1.0	0.06	<0.01	3.300	3.300	3.40	0.034	0.034	0.038
6782	94/91	18250	ACTEW	01.07.94	Duplicate	<1.0	0.02	<0.01	2.800	2.800	3.40	0.034	0.034	0.038
					Relative Percentage Difference	**0.0**	**100.00**	**0.00**	**16.393**	**16.393**	**0.00**	**0.000**	**0.000**	**0.000**
					Mean	<1.0	0.04	<0.01	3.050	3.050	3.40	0.034	0.034	0.038
6782	94/92	18251	ACTEW	01.07.95	Spike	6.5	1.90	<0.01	7.200	7.200	16.00	1.000		
					Spike Concentration (*added to sample*)	5.0	1.00	ND	5.000	5.000	11.00	1.000		
					Percent Recovery	**120.0**	**186.00**	**ND**	**83.000**	**83.000**	**114.55**	**96.600**	**ND**	**ND**
6758	94/103	18264	ACTEW	01.07.94	Sample	<1.0	<0.01	<0.01	0.280	0.280	0.32	0.004	0.005	0.011
6758	94/104	18265	ACTEW	01.07.94	Duplicate	<1.0	0.01	<0.01	0.280	0.280	0.34	0.006	0.006	0.012
					Relative Percentage Difference	**0.0**	**-50.00**	**0.00**	**0.000**	**0.000**	**-60.61**	**-40.000**	**-16.667**	**-8.333**
					Mean	<1.0	0.01	<0.01	0.280	0.280	0.03	0.005	0.006	0.012
6758	94/105	18266	ACTEW	01.07.95	Spike	6.30	2.00	<0.01	37.000	37.000	48.00	0.790		
					Spike Concentration (*added to sample*)	5.0	1.00	ND	5.000	5.000	11.00	1.000		
ND= Not determined					**Percent Recovery**	**116**	**199.00**	**ND**	**734.400**	**734.400**	**436.06**	**78.500**	**ND**	**ND**

Appendix C

Table C4: *Piccadilly Valley Trace Element Chemistry QA/QC Duplicates*

Boreid	WQ	Lab Ref	Lab	Analysis		Al (mg/L)	Cu (mg/L)	Zn (mg/L)	Sr (mg/L)	Li (mg/L)	B (mg/L)	Ba (mg/L)
6567	94/62	940407	AGSO	06.07.94	Sample	0.001	<0.005	0.031	0.072	0.012	0.023	0.084
6567	94/63	940408	AGSO	06.07.94	Duplicate	<0.005	<0.005	0.031	0.074	0.009	0.037	0.081
					Relative Percentage Difference	**-122.581**	**0.000**	**0.000**	**-2.740**	**28.571**	**-46.667**	**3.636**
					Mean Value	0.002	<0.005	0.031	0.073	0.011	0.030	0.083
6750	94/73	940418	AGSO	06.07.94	Sample	<0.005	<0.005	0.047	0.177	0.013	0.027	0.126
6750	94/74	940419	AGSO	06.07.94	Duplicate	<0.005	<0.005	0.037	0.176	0.012	0.255	0.126
					Relative Percentage Difference	**0.000**	**0.000**	**23.810**	**0.567**	**8.000**	**-161.702**	**0.000**
					Mean Value	<0.005	<0.005	0.042	0.177	0.013	0.141	0.126
6782	94/90	940435	AGSO	06.07.94	Sample	<0.005	<0.005	0.029	0.071	0.014	0.031	0.039
6782	94/91	940436	AGSO	06.07.94	Duplicate	<0.005	<0.005	0.021	0.072	0.012	0.043	0.037
					Relative Percentage Difference	**0.000**	**0.000**	**32.000**	**-1.399**	**15.385**	**-32.432**	**5.263**
					Mean Value	<0.005	<0.005	0.025	0.072	0.013	0.037	0.038
6758	94/103	940448	AGSO	10.08.94	Sample	<0.005	<0.005	0.924	0.014	0.014	0.038	0.079
6758	94/104	940449	AGSO	10.08.94	Duplicate	<0.005	0.006	0.923	0.014	0.015	0.036	0.080
					Relative Percentage Difference	**0.000**	**-82.353**	**0.108**	**0.000**	**-6.897**	**5.405**	**-1.258**
					Mean Value	<0.005	0.004	0.924	0.014	0.015	0.037	0.080

Table C5: *Piccadilly Valley Trace Element Chemistry QA/QC Duplicates and Spikes*

Boreid	WQ Number	Lab Ref No.	Lab	Analysis Date		Cu (µg/L)	Fe (µg/L)	Mn (µg/L)	Sb (µg/L)	Zn (µg/L)	Al (µg/L)	Se (µg/L)
6567	94/62	L4301/94	AMDEL	17.06.94	Sample	1	29	42	0.4	34	108	1.0
6567	94/63	L4301/94	AMDEL	17.06.94	Duplicate	4	14	44	0.3	25	3	0.5
					Relative Percentage Difference	**-120**	**70**	**-5**	**28.6**	**31**	**189**	**66.7**
					Mean	3	22	43	0.4	30	56	0.8
6567	94/64	L4301/95	AMDEL	17.06.95	Spike Result	200	260	200		210	210	
					Spike Concentration (*added to sample*)	200	200	200		200	200	
					Percent Recovery	**99**	**119**	**79**	**ND**	**90**	**77**	**ND**
6750	94/73	L4301/94	AMDEL	17.06.94	Sample	<1	580	260	<0.1	32	130	<1
6750	94/74	L4301/94	AMDEL	17.06.94	Duplicate	<1	650	270	<0.1	40	9	<1
					Relative Percentage Difference	**0**	**-11**	**-4**	**0.0**	**-22**	**174**	**0.0**
					Mean	<1	615	265	<0.1	36	70	<1
6750	94/75	L4301/95	AMDEL	17.06.95	Spike Result	190	770	490		190	260	
					Spike Concentration (*added to sample*)	200	200	200		200	200	
					Percent Recovery	**95**	**78**	**113**	**ND**	**77**	**95**	**ND**
6782	94/90	L4301/94	AMDEL	17.06.94	Sample	<1	181	15	0.1	56	7	4.0
6782	94/91	L4301/94	AMDEL	17.06.94	Duplicate	<1	48	15	<0.1	96	1	<1
					Relative Percentage Difference	**0**	**116**	**0**	**62.5**	**-53**	**150**	**152.2**
					Mean	<1	115	15	0.1	76	4	2.3
6782	94/92	L4301/95	AMDEL	17.06.95	Spike Result	200	250	200		210	220	
					Spike Concentration (*added to sample*)	200	200	200		200	200	
					Percent Recovery	**100**	**68**	**93**	**ND**	**67**	**108**	**ND**
6758	94/103	L4301/94	AMDEL	17.06.94	Sample	<1	1280	310	<0.1	1030	10	<1
6758	94/104	L4301/94	AMDEL	17.06.94	Duplicate	<1	1360	290	<0.1	960	22	<1
					Relative Percentage Difference	**0**	**-6**	**7**	**0.0**	**7**	**-75**	**0.0**
					Mean	<1	1320	300	<0.1	995	16	<1
6758	94/105	L4301/95	AMDEL	17.06.95	Spike Result	190	1500	480		1090	230	
					Spike Concentration (*added to sample*)	200	200	200		200	200	
					Percent Recovery	**95**	**90**	**90**	**ND**	**48**	**107**	**ND**
ND = Not determined												

Table C5: *Piccadilly Valley Trace Element Chemistry QA/QC Duplicates and Spikes*

WQ Number	Lab Ref No.	Lab	Analysis Date		As (µg/L)	U (µg/L)	Hg (µg/L)	Cr (µg/L)	Ni (µg/L)	Au (µg/L)	Ag (µg/L)	Cd (µg/L)	Co (µg/L)
94/62	L4301/94	AMDEL	17.06.94	Sample	0.2	0.1	<0.1	<1	<1	<0.1	<0.1	<0.5	<1
94/63	L4301/94	AMDEL	17.06.94	Duplicate	0.2	0.1	<0.1	<1	<1	<0.1	<0.1	<0.5	<1
				Relative Percentage Difference	**0.0**	**0.0**	**0**	**0**	**0**	**0.0**	**0.0**	**0.0**	**0**
				Mean	0.2	0.1	<0.1	<1	<1	<0.1	<0.1	<0.5	<1
94/64	L4301/95	AMDEL	17.06.95	Spike Result	144	202							
				Spike Concentration (*added to sample*)	200	200							
				Percent Recovery	**72**	**101**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**
94/73	L4301/94	AMDEL	17.06.94	Sample	3.6	0.1	<0.1	<1	<1	<0.1	<0.1	<0.5	<1
94/74	L4301/94	AMDEL	17.06.94	Duplicate	3.8	0.1	<0.1	<1	<1	<0.1	<0.1	<0.5	<1
				Relative Percentage Difference	**-5.4**	**0.0**	**0**	**0**	**0**	**0.0**	**0.0**	**0.0**	**0**
				Mean	3.7	0.1	<0.1	<1	<1	<0.1	<0.1	<0.5	<1
94/75	L4301/95	AMDEL	17.06.95	Spike Result	143	199							
				Spike Concentration (*added to sample*)	200	200							
				Percent Recovery	**72**	**100**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**
94/90	L4301/94	AMDEL	17.06.94	Sample	<0.2	<0.1	<0.1	<1	<1	<0.1	0.2	<0.5	3
94/91	L4301/94	AMDEL	17.06.94	Duplicate	<0.2	<0.1	<0.1	<1	<1	<0.1	0.2	<0.5	<1
				Relative Percentage Difference	**0.0**	**0.0**	**0**	**0**	**0**	**0.0**	**0.0**	**0.0**	**139**
				Mean	<0.2	<0.1	<0.1	<1	<1	<0.1	0.2	<0.5	2
94/92	L4301/95	AMDEL	17.06.95	Spike Result	147	191							
				Spike Concentration (*added to sample*)	200	200							
				Percent Recovery	**73**	**95**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**
94/103	L4301/94	AMDEL	17.06.94	Sample	<0.2	<0.1	<0.1	<1	<1	<0.1	<0.1	<0.5	<1
94/104	L4301/94	AMDEL	17.06.94	Duplicate	0.1	<0.1	<0.1	<1	<1	<0.1	<0.1	<0.5	<1
				Relative Percentage Difference	**0.0**	**0.0**	**0**	**0**	**0**	**0.0**	**0.0**	**0.0**	**0**
				Mean	0.1	<0.1	<0.1	<1	<1	<0.1	<0.1	<0.5	<1
94/105	L4301/95	AMDEL	17.06.95	Spike Result	167	<0.1							
				Spike Concentration (*added to sample*)	200	200.0							
				Percent Recovery	**83**	**0.0**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**	**ND**

Table C5: *Piccadilly Valley Trace Element Chemistry QA/QC Duplicates and Spikes*

WQ Number	Lab Ref No.	Lab	Analysis Date		Mo (µg/L)	V (µg/L)	Pb (µg/L)	Sn (µg/L)
94/62	L4301/94	AMDEL	17.06.94	Sample	83.0	<1	<1	0.1
94/63	L4301/94	AMDEL	17.06.94	Duplicate	2.0	<1	<1	0.1
				Relative Percentage Difference	**190.6**	**0**	**0**	**66.7**
				Mean	42.5	<1	<1	0.1
94/64	L4301/95	AMDEL	17.06.95	Spike Result		240	98	62.0
				Spike Concentration (*added to sample*)		200	200	200.0
				Percent Recovery	**ND**	**120**	**49**	**31.0**
94/73	L4301/94	AMDEL	17.06.94	Sample	<0.5	<1	<1	<0.1
94/74	L4301/94	AMDEL	17.06.94	Duplicate	<0.5	<1	<1	0.1
				Relative Percentage Difference	**0.0**	**0**	**0**	**62.5**
				Mean	<0.5	<1	<1	0.1
94/75	L4301/95	AMDEL	17.06.95	Spike Result		220	270	3.3
				Spike Concentration (*added to sample*)		200	200	200.0
				Percent Recovery	**ND**	**100**	**100**	**99.5**
94/90	L4301/94	AMDEL	17.06.94	Sample	0.5	<1	<1	166.0
94/91	L4301/94	AMDEL	17.06.94	Duplicate	<0.5	1	<1	1.7
				Relative Percentage Difference	**62.5**	**-67**	**0**	**195.9**
				Mean	0.4	1	<1	83.9
94/92	L4301/95	AMDEL	17.06.95	Spike Result		240	95	59.0
				Spike Concentration (*added to sample*)		200	200	200.0
				Percent Recovery	**ND**	**120**	**47**	**-12.4**
94/103	L4301/94	AMDEL	17.06.94	Sample	<0.5	<1	<1	<0.1
94/104	L4301/94	AMDEL	17.06.94	Duplicate	<0.5	<1	<1	<0.1
				Relative Percentage Difference	**0.0**	**0**	**0**	**0.0**
				Mean	<0.5	<1	<1	<0.1
94/105	L4301/95	AMDEL	17.06.95	Spike Result		230	270	4.6
				Spike Concentration (*added to sample*)		200	200	200.0
				Percent Recovery	**ND**	**115**	**135**	**2.3**

13.4 APPENDIX D: MICROBIAL POPULATIONS - SAMPLE TREATMENT & ENUMERATION

Samples were acquired under aseptic conditions and stored chilled in the dark prior to processing within 2-4h of collection. Field equipment blanks and duplicate samples were processed after ca every tenth sample. Enumeration of Faecal (thermotolerant) Coliforms and Faecal Streptococci followed standard protocols (APHA, 1989) for membrane filtration techniques using M-FC (Millipore) and KF Streptococcus (BBL) media respectively. Presumptive colonies were randomly selected for confirmation tests.

Enumeration of *Clostridium perfringens* spores employed supplemented Perfringens Agar medium (OPSP; Oxoid) and membrane filtration of 75°C-treated (10min) samples. Plates were incubated for 18-24h at 35°C under anaerobic conditions. Black or grey colonies (presumptive) were inoculated into freshly prepared Litmus Milk medium (Oxoid); colonies producing stormy clotting within 18-24h at 35°C were recorded as confirmed.

Enumeration of heterotrophic bacteria was also by membrane filtration, using R2A medium (Reasoner & Geldreich, 1985). Plates were incubated for 10d at 28°C. Heterotrophic denitrifying bacteria were enumerated using the MPN method of Focht & Joseph (1973). In addition to scoring for growth and gas production the presence of nitrate and nitrite was tested for using diphenylamine and sulphanilamide with N-(1-naphthyl)-ethylendiammoniumdichloride respectively.

13.5 APPENDIX E: PESTICIDES

E.1: ANALYTE SCHEDULE

Schedules A, B and C contain the analytes for which samples were screened. These lists contain compounds from various groups of herbicides, insecticides and fungicides (Worthing and Hance, 1991).

Herbicide groups comprised triazines (eg. atrazine, simazine and their degradation products desethylatrazine and desisopropylatrazine), carbamates (eg. chlorpropham), chloroacetanilides (eg. metolachlor, alachlor), uracils (eg. bromacil, terbacil), ureas (eg. linuron, diuron, methabenzthiazuron, metoxuron), phenoxyacids (eg. 2,4-D, 2,4,5-T, MCPA) and miscellaneous acids (triclopyr, picloram). Quaternary ammonium compounds (eg. paraquat, diquat) and glyphosate, a phosphonic acid herbicide, were included for analysis due to their widespread use.

Insecticide groups included organochlorines (eg. methoxychlor, dieldrin, endosulfan, DDT and its breakdown products), organophosphates (eg. diazinon, malathion, parathion, chlorpyrifos), carbamates (eg. carbofuran, carbaryl), pyrethroids (eg. permethrin).

Fungicide groups incorporated conazoles (eg. cyproconazole, penconazole, triadimenol, triadimefon), phthalimides (eg. captafol, captan) and various miscellaneous fungicides (anilazine, chlorothalonil, vinclozolin, chinomethionate, metalaxyl).

In recognition that some compounds degrade over time to products which may also be toxic or carcinogenic, many breakdown products were included in Schedule A (eg. DDE, DDD, carbofuran-3-hydroxy, carbofuran-3-keto, endosulfan sulfate, heptachlor epoxide, desethylatrazine, desisopropylatrazine).

It should be noted that the pesticides listed in Schedules A, B and C are not exhaustive. Compounds in Schedule A are, more or less, amenable to Gas Chromatography. Schedule B compounds chromatograph on a Gas Chromatograph (GC) only with derivatization. Schedule C compounds require specific extraction and analytic procedures for determination by High Performance Liquid Chromatography (HPLC). Varied extraction and/or analytical techniques could extend these lists even further, but the analytical cost involved makes this action prohibitive.

SCHEDULE A ANALYTES AND THEIR RESPECTIVE DETECTION LIMITS

ANALYTE	DETECTION LIMIT (µg/L)	ANALYTE	DETECTION LIMIT (µg/L)
Alachlor	0.01	Fluroxypyr	0.05
Aldrin	0.05	HCB	0.05
Ametryn	0.01	Heptachlor	0.05
Anilazine	0.01	Heptachlor epoxide	0.05
Atrazine	0.01	Hexazinone	0.05
Azinphos ethyl	0.05	Iodofenphos	0.05
Azinphos methyl	0.05	Iprodione	0.05
Aziprotyne	0.01	Isoproturon	0.05
Benfluralin	0.05	Lindane	0.05
BHC isomers	0.05	Linuron	0.1
Bromacil	0.05	Malathion	0.05
Captafol	0.05	Metalaxyl	0.05
Captan	0.05	Methabenzthiazuron	0.1
Carbaryl	0.05	Methidathion	0.05
Carbofenothion	0.05	Methoprotyne	0.01
Carbofuran	0.05	Methoxychlor	0.05
Carbofuran-3-keto	0.1	Metolachlor	0.01
Carbofuran-3-hydroxy	0.1	Metoxuron	0.1
Chinomethionate	0.05	Metribuzin	0.01
Chlordane	0.05	Monocrotophos	0.05
Chlorfenvinphos	0.05	Monolinuron	0.05
Chlorothalonil	0.05	Omethoate	0.05
Chloroxuron	0.3	Oxychlordane	0.05
Chlorpropham	0.02	Oxyfluorfen	0.05
Chlorpyrifos	0.05	Parathion	0.05
Chlorpyrifos methyl	0.05	Parathion methyl	0.05
Chlorthal dimethyl	0.05	Penconazole	0.05
Coumaphos	0.3	Pendimethalin	0.05
Cyanazine	0.01	Permethrins	0.05
Cyproconazole	0.05	Phorate	0.05
DDD	0.05	Phosmet	0.05
DDE	0.05	Prochloraz	0.05
DDT	0.05	Profenophos	0.05
Desethylatrazine	0.01	Prometon	0.01
Desisopropylatrazine	0.05	Prometryn	0.01
Demeton-S-methyl	0.05	Propachlor	0.05
Desmetryn	0.01	Propargite	0.05
Diazinon	0.05	Propazine	0.01
Dichlobenil	0.05	Propiconazole	0.05
Dichloran	0.05	Propoxur	0.05
Dichlorvos	0.05	Propyzamide	0.05
Dicofol	0.05	Quintozene	0.05
Dieldrin	0.05	Sebuthylazine	0.01
Dimethoate	0.05	Siduron	0.05
Disulfoton	0.05	Simazine	0.02
Diuron	0.2	Sulprofos	0.05
Endosulfan	0.05	Terbacil	0.05
Endosulfan sulfate	0.05	Terbumeton	0.01
Endrin	0.05	Terbuthylazine	0.01
Ethion	0.05	Terbutryne	0.01
Fenamiphos	0.05	Tetrachlorvinphos	0.05
Fenarimol	0.05	Triadimenol	0.05
Fenchlorphos	0.05	Triadimefon	0.05
Fenitrothion	0.05	Trietazine	0.01
Fenthion	0.05	Trifluralin	0.05
Fluometuron	0.1	Vinclozolin	0.02

SCHEDULE B ANALYTES AND THEIR RESPECTIVE DETECTION LIMITS

ANALYTE	DETECTION LIMIT (µg/L)	ANALYTE	DETECTION LIMIT (µg/L)
2,4-D	0.1	Dichlorprop/2,4-DP	0.1
2,4-DB	0.1	Mecoprop/MCPP	0.1
2,4,5-T	0.1	Dicamba	0.1
2,4,5-TP	0.1	Picloram	0.2
MCPA	0.1	Triclopyr	0.1

SCHEDULE C ANALYTES AND THEIR RESPECTIVE DETECTION LIMITS

ANALYTE	DETECTION LIMIT (µg/L)
Paraquat	2
Diquat	2
Glyphosate	5

E.2: ANALYTICAL STRATEGY

ANALYTICAL STRATEGY FOR INDIVIDUAL SAMPLES

BORE NUMBER	AGSO LAB. NUMBER	SITE IDENTIFICATION	SCHEDULE A	SCHEDULE B	SCHEDULE C
6834	WQ94/58	SCHOCROFT RD.	+	+	+
6835	WQ94/59	SCHOCROFT RD.	+	+	+
11935	WQ94/60	PICCADILLY RD.	+	+	+
6598	WQ94/61	GREENHILL RD.	+	+	+
6567	WQ94/62	MT. LOFTY BOTANIC GARDENS	+	+	+
8924	WQ94/65	PICCADILLY RD.	+	+	+
12429	WQ94/66	PICCADILLY RD.	+	+	+
15938	WQ94/67	SCHOCROFT RD.	+	+	+
12827	WQ94/68	SCHOCROFT RD.	+	+	+
7224	WQ94/69	ARBURY PARK OUTDOOR SCHOOL	+	+	+
12045	WQ94/70	PICCADILLY RD.	+	-	+
6776	WQ94/71	OFF BASIN RD.	+	+	+
15410	WQ94/72	OFF BASIN RD.	+	-	+
6750	WQ94/73	GREENHILL RD.	+	+	+
6746	WQ94/76	BONYTHON RD,	+	+	+
6742	WQ94/77	BONYTHON RD.	+	-	+
13440	WQ94/78	BONYTHON RD.	+	+	+
6759	WQ94/79	OFF GREENHILL RD.	+	-	+
11934	WQ94/80	PERCIVAL RD.	+	+	+
6627	WQ94/81	WILLSMORE PL.	+	-	+
13253	WQ94/82	OFF RICHARDSON RD.	+	+	+
13596	WQ94/83	OFF CAREY GULLY RD.	+	-	+
12428	WQ94/84	SPRIGG RD.	+	+	+
13906	WQ94/85	CAMPBELL RD.	+	-	+
6828	WQ94/86	BROOKS RD.	+	+	+
6771	WQ94/87	SWAMP RD.	+	-	+
13543	WQ94/88	OFF CAREY GULLY RD.	+	+	+
12921	WQ94/89	GREENHILL RD.	+	-	+
6782	WQ94/90	URAIDLA SCHOOL	+	+	+
14178	WQ94/93	SUMMIT RD.	+	+	+
12825	WQ94/94	OFF SPRIGG RD.	+	-	+
6811	WQ94/95	NURSERY, GORES RD.	+	+	+
6809	WQ94/96	GORES RD.	+	-	+
11601	WQ94/97	MT. LOFTY GOLF COURSE	+	+	+
6709	WQ94/98	OFF SCHOCROFT AVE., NEAR GOLF COURSE	+	-	+
12627	WQ94/99	OLD CAREY GULLY RD.	+	+	+
6583	WQ94/100	PICCADILLLY RD.	+	-	+
13537	WQ94/101	GREENHILL RD.	+	+	+
12023	WQ94/102	OFF SPRING GULLY RD.	+	-	+
6758	WQ94/103	OFF GREENHILL RD.	+	+	+
6555	WQ94/106	PICCADILLY RD.	+	+	+
13256	WQ94/107	OLD CAREY GULLY RD.	+	-	+

SAMPLES ANALYSED FOR SCHEDULE A PESTICIDES

BORE NO.	AGSO LAB NO.	DATE SAMPLED	SITE IDENTIFICATION	QA/QC INFORMATION
6834	WQ94/58	20/4/94	SCHOCROFT RD.	
-	WQ94/58A	20/4/94		BLANK
6835	WQ94/59	21/4/94	SCHOCROFT RD.	
11935	WQ94/60	21/4/94	PICCADILLY RD.	
6598	WQ94/61	22/4/94	GREENHILL RD.	
6567	WQ94/62	23/4/94	MT. LOFTY BOTANIC GARDENS	
6567	WQ94/63	23/4/94	MT. LOFTY BOTANIC GARDENS	DUPLICATE
6567	WQ94/64	23/4/94	MT. LOFTY BOTANIC GARDENS	SPIKE
8924	WQ94/65	24/4/94	PICCADILLY RD.	
12429	WQ94/66	24/4/94	PICCADILLY RD.	
15938	WQ94/67	25/4/94	SCHOCROFT RD.	
12827	WQ94/68	25/4/94	SCHOCROFT RD.	
7224	WQ94/69	26/4/94	ARBURY PARK OUTDOOR SCHOOL	
12045	WQ94/70	26/4/94	PICCADILLY RD.	
6776	WQ94/71	27/4/94	OFF BASIN RD.	
15410	WQ94/72	27/4/94	OFF BASIN RD.	
-	WQ94/72A	27/4/94		BLANK
6750	WQ94/73	28/4/94	GREENHILL RD.	
6750	WQ94/74	28/4/94	GREENHILL RD.	DUPLICATE
6750	WQ94/75	28/4/94	GREENHILL RD.	SPIKE
6746	WQ94/76	29/4/94	BONYTHON RD.	
6742	WQ94/77	29/4/94	BONYTHON RD.	
13440	WQ94/78	1/5/94	BONYTHON RD.	
6759	WQ94/79	1/5/94	OFF GREENHILL RD.	
11934	WQ94/80	2/5/94	PERCIVAL RD.	
6627	WQ94/81	2/5/94	WILLSMORE PL.	
13253	WQ94/82	3/5/94	OFF RICHARDSON RD.	
13596	WQ94/83	3/5/94	OFF CAREY GULLY RD.	
12428	WQ94/84	4/5/94	SPRIGG RD.	
13906	WQ94/85	4/5/94	CAMPBELL RD.	
6828	WQ94/86	5/5/94	BROOKS RD.	
-	WQ94/86A	5/5/94		BLANK
6771	WQ94/87	5/5/94	SWAMP RD.	
13543	WQ94/88	6/5/94	OFF CAREY GULLY RD.	
12921	WQ94/89	6/5/94	GREENHILL RD.	
6782	WQ94/90	7/5/94	URAIDLA SCHOOL	
6782	WQ94/91	7/5/94	URAIDLA SCHOOL	DUPLICATE
6782	WQ94/92	7/5/94	URAIDLA SCHOOL	SPIKE
14178	WQ94/93	9/5/94	SUMMIT RD.	
12825	WQ94/94	9/5/94	OFF SPRIGG RD.	
6811	WQ94/95	10/5/94	NURSERY, GORES RD.	
6809	WQ94/96	10/5/94	NURSERY, GORES RD.	
11601	WQ94/97	11/5/94	MT. LOFTY GOLF COURSE	
6709	WQ94/98	11/5/94	OFF SCHOCROFT AVE., NEAR GOLF COURSE	
6709	WQ94/98A	11/5/94		BLANK
12627	WQ94/99	12/5/94	OLD CAREY GULLY RD.	
6583	WQ94/100	12/5/94	PICCADILLLY RD.	
13537	WQ94/101	13/5/94	GREENHILL RD.	
12023	WQ94/102	13/5/94	OFF SPRING GULLY RD.	
6758	WQ94/103	14/5/94	OFF GREENHILL RD.	
6758	WQ94/104	14/5/94	OFF GREENHILL RD.	DUPLICATE
6758	WQ94/105	14/5/94	OFF GREENHILL RD.	SPIKE
-	WQ94/2002	14/5/94		BLANK
6555	WQ94/106	15/5/94	PICCADILLY RD.	
-	WQ94/106A	15/5/94		BLANK
13256	WQ94/107	15/5/94	OLD CAREY GULLY RD.	

SAMPLES ANALYSED FOR SCHEDULE B PESTICIDES

BORE NO.	AGSO LAB NO.	DATE SAMPLED	SITE IDENTIFICATION	QA/QC INFORMATION
6834	WQ94/58	20/4/94	SCHOCROFT RD.	
-	WQ94/58A	20/4/94		BLANK
6835	WQ94/59	21/4/94	SCHOCROFT RD.	
11935	WQ94/60	21/4/94	PICCADILLY RD.	
6598	WQ94/61	22/4/94	GREENHILL RD.	
6567	WQ94/62	23/4/94	MT. LOFTY BOTANIC GARDENS	
6567	WQ94/63	23/4/94	MT. LOFTY BOTANIC GARDENS	SPIKE
8924	WQ94/65	24/4/94	PICCADILLY RD.	
12429	WQ94/66	24/4/94	PICCADILLY RD.	
15938	WQ94/67	25/4/94	SCHOCROFT RD.	
12827	WQ94/68	25/4/94	SCHOCROFT RD.	
7224	WQ94/69	26/4/94	ARBURY PARK OUTDOOR SCHOOL	
6776	WQ94/71	27/4/94	OFF BASIN RD.	
6750	WQ94/73	28/4/94	GREENHILL RD.	
-	WQ94/73A	28/4/94		BLANK
6750	WQ94/75	28/4/94	GREENHILL RD.	SPIKE
6746	WQ94/76	29/4/94	BONYTHON RD.	
13440	WQ94/78	1/5/94	BONYTHON RD.	
11934	WQ94/80	2/5/94	PERCIVAL RD.	
13253	WQ94/82	3/5/94	OFF RICHARDSON RD.	
12428	WQ94/84	4/5/94	SPRIGG RD.	
-	WQ94/84A	4/5/94		BLANK
6828	WQ94/86	5/5/94	BROOKS RD.	
13543	WQ94/88	6/5/94	OFF CAREY GULLY RD.	
6782	WQ94/90	7/5/94	URAIDLA SCHOOL	
6782	WQ94/92	7/5/94	URAIDLA SCHOOL	SPIKE
14178	WQ94/93	9/5/94	SUMMIT RD.	
6811	WQ94/95	10/5/94	GORES RD.	
11601	WQ94/97	11/5/94	MT. LOFTY GOLF COURSE	
12627	WQ94/99	12/5/94	OLD CAREY GULLY RD.	
13537	WQ94/101	13/5/94	GREENHILL RD.	
6758	WQ94/103	14/5/94	OFF GREENHILL RD.	
6758	WQ94/105	14/5/94	OFF GREENHILL RD.	SPIKE
6555	WQ94/106	15/5/94	PICCADILLY RD.	
-	WQ94/106B	15/5/94		BLANK

SAMPLES ANALYSED FOR SCHEDULE C PESTICIDES

BORE NO.	AGSO LAB NO.	DATE SAMPLED	SITE IDENTIFICATION	QA/QC INFORMATION
6834	WQ94/58	20/4/94	SCHOCROFT RD.	
6835	WQ94/59	21/4/94	SCHOCROFT RD.	
11935	WQ94/60	21/4/94	PICCADILLY RD.	
6598	WQ94/61	22/4/94	GREENHILL RD.	
6567	WQ94/62	23/4/94	MT. LOFTY BOTANIC GARDENS	
6567	WQ94/63	23/4/94	MT. LOFTY BOTANIC GARDENS	DUPLICATE
6567	WQ94/64	23/4/94	MT. LOFTY BOTANIC GARDENS	SPIKE
8924	WQ94/65	24/4/94	PICCADILLY RD.	
12429	WQ94/66	24/4/94	PICCADILLY RD.	
15938	WQ94/67	25/4/94	SCHOCROFT RD.	
12827	WQ94/68	25/4/94	SCHOCROFT RD.	
7224	WQ94/69	26/4/94	ARBURY PARK OUTDOOR SCHOOL	
12045	WQ94/70	26/4/94	PICCADILLY RD.	
6776	WQ94/71	27/4/94	OFF BASIN RD.	
15410	WQ94/72	27/4/94	OFF BASIN RD.	
6750	WQ94/73	28/4/94	GREENHILL RD.	
6750	WQ94/74	28/4/94	GREENHILL RD.	DUPLICATE
6750	WQ94/75	28/4/94	GREENHILL RD.	SPIKE
6746	WQ94/76	29/4/94	BONYTHON RD.	
6742	WQ94/77	29/4/94	BONYTHON RD.	
13440	WQ94/78	1/5/94	BONYTHON RD.	
6759	WQ94/79	1/5/94	OFF GREENHILL RD.	
11934	WQ94/80	2/5/94	PERCIVAL RD.	
6627	WQ94/81	2/5/94	WILLSMORE PL.	
13253	WQ94/82	3/5/94	OFF RICHARDSON RD.	
13596	WQ94/83	3/5/94	OFF CAREY GULLY RD.	
12428	WQ94/84	4/5/94	SPRIGG RD.	
13906	WQ94/85	4/5/94	CAMPBELL RD.	
6828	WQ94/86	5/5/94	BROOKS RD.	
6771	WQ94/87	5/5/94	SWAMP RD.	
13543	WQ94/88	6/5/94	OFF CAREY GULLY RD.	
12921	WQ94/89	6/5/94	GREENHILL RD.	
6782	WQ94/90	7/5/94	URAIDLA SCHOOL	
6782	WQ94/91	7/5/94	URAIDLA SCHOOL	DUPLICATE
6782	WQ94/92	7/5/94	URAIDLA SCHOOL	SPIKE
14178	WQ94/93	9/5/94	SUMMIT RD.	
12825	WQ94/94	9/5/94	OFF SPRIGG RD.	
6811	WQ94/95	10/5/94	GORES RD.	
6809	WQ94/96	10/5/94	GORES RD.	
11601	WQ94/97	11/5/94	MT. LOFTY GOLF COURSE	
6709	WQ94/98	11/5/94	OFF SCHOCROFT AVE., NEAR GOLF COURSE	
12627	WQ94/99	12/5/94	OLD CAREY GULLY RD.	
6583	WQ94/100	12/5/94	PICCADILLLY RD.	
13537	WQ94/101	13/5/94	GREENHILL RD.	
12023	WQ94/102	13/5/94	OFF SPRING GULLY RD.	
6758	WQ94/103	14/5/94	OFF GREENHILL RD.	
6758	WQ94/104	14/5/94	OFF GREENHILL RD.	DUPLICATE
6758	WQ94/105	14/5/94	OFF GREENHILL RD.	SPIKE
6555	WQ94/106	15/5/94	PICCADILLY RD.	
13256	WQ94/107	15/5/94	OLD CAREY GULLY RD.	

E.3: METHODOLOGY

Sample extraction was based on USEPA Method 525.1 (Eichelberger et al., 1988), with modifications (Sandstrom et al., 1992) as described below. Briefly, samples were filtered and extracted on conditioned C_{18} solid phase extraction cartridges at the bore site to minimise analyte degradation. Pesticides were eluted with solvent in the laboratory and analysed by gas chromatography-mass spectrometry (GC-MS) in full scan and selected ion monitoring modes. Additional water samples were collected for paraquat, diquat and glyphosate analyses.

EXTRACTION

SCHEDULE A: Samples were filtered through glass fibre filters (47mm, 0.7µm). Approximately 400mL of filtered sample was weighed into a tared 1L teflon bottle. Methanol (3g) was added to the water sample. The weight of the filtered sample plus methanol was recorded. Surrogate mixture was added (100µL of ~5µg/mL solution) with a glass-tipped micropipette. The pre-cleaned cartridge was conditioned with 2mL of HPLC-Grade methanol, followed by 2mL of water. The cartridge was prevented from running dry; if this occurred the conditioning phase was repeated. A collection beaker was tared. The filtered sample was pumped through the conditioned cartridge at 20-25mL/min using a FMI-QB1 pump, or equivalent, collecting the spent water into the tared beaker. The processed water in the beaker was weighed. All residual water was removed from the cartridge with a Visi-1 (Supelco) syringe. Dried cartridges were stored in a labelled vial until laboratory analysis.

Blanks were processed similarly. Distilled water was passed through the pumping equipment, spiked with surrogate solution, extracted and analysed as for the samples.

Field spikes were processed as above, but 50µL of spike mixture (~ 5µg/mL solution) was added after the surrogate standard addition.

All bottles and pump lines were cleaned with phosphate-free detergent, followed by rinses with distilled water then methanol. Sample contact with plastic was minimised due to possible analytical interferences.

SCHEDULE B: Samples were filtered through glass fibre filters (47mm, 0.7µm). Approximately 400mL of filtered sample was weighed into a tared 1L teflon bottle. The pH of the water was adjusted to 2. The pre-cleaned cartridge was conditioned with 2mL of HPLC-Grade methanol, followed by 2mL of water at pH 2. The cartridge was prevented from running dry; if this occurred the conditioning phase was repeated. A collection beaker was tared. The filtered sample was pumped through the conditioned cartridge at 20-25mL/min using a FMI-QB1 pump, or equivalent, collecting the spent water into the tared beaker. The processed water in the beaker was weighed. All residual water was removed from the cartridge with a Visi-1

(Supelco) syringe. Dried cartridges were stored in a labelled vial until laboratory analysis.

Blanks were processed similarly. Distilled water was passed through the pumping equipment, extracted and analysed as for the samples.

Field spikes were processed as above, but 100µL of spike mixture (~ 10µg/mL solution) was added to the sample prior to extraction.

All bottles and pump lines were cleaned with phosphate-free detergent, followed by rinses with distilled water then methanol. Sample contact with plastic was minimised due to possible analytical interferences.

SCHEDULE C: Glyphosate samples were collected in clean 500mL polythene bottles and stored under refrigeration. Paraquat and diquat samples were collected in additional clean 500mL polythene bottles and stored, similarly, under refrigeration. Samples were filtered through 0.45µm filter using plastic filtration apparatus.

ANALYSIS

SCHEDULE A: Cartridges were gravity-eluted in the laboratory with 2x2mL of hexane:isopropanol (3:1). Eluates were concentrated to 500µL and an internal standard (phenanthrene-d_{10}) was added. Concentrated extracts were analysed by GC-MS in full scan electron impact (EI) mode to screen for the bulk of Schedule A compounds. The samples were reanalysed by GC-MS in selected ion monitoring mode (SIM) for twenty-one compounds. This mode has improved sensitivity, therefore lowers the limit of detection of these compounds tenfold. SIM analysis was performed particularly for triazine (eg. atrazine, simazine, desethylatrazine) and chloroacetanilide (eg. alachlor, metolachlor) compounds, which have frequently been reported in groundwater.

SCHEDULE B: Cartridges were gravity-eluted in the laboratory with 2x2mL of methanol. Eluates were concentrated to 200µL prior to derivatization. Schedule B compounds were analysed by GC-MS in full scan EI mode after derivatization of the extracts. These compounds, because of their acidic nature, are not amenable to gas chromatography without derivatization.

SCHEDULE C: Paraquat and diquat analysis was performed by High Performance Liquid Chromatography (HPLC) using photodiode array detection. Glyphosate analysis was also performed by HPLC using post-column derivatization with fluorometric detection.

E.4: QUALITY ASSURANCE/QUALITY CONTROL

BLANKS: Field equipment blanks (with suffixes of "A" following sample numbers) were extracted on five occasions for Schedule A and four for Schedule B analytes, throughout the sampling period. These blanks ensured that the rinsing procedure between sampling was efficient and that there was no contamination from the sampling equipment.

An additional blank was performed (WQ94/2002) for Schedule A extraction only. Distilled water was extracted after deliberate contamination (~10µg/L) of the pesticide extraction apparatus with the spike mixture, followed by the routine rinsing procedure. This was included to determine whether there would be carry-over contamination from one sample extraction to the next following a more heavily contaminated sample.

REPLICATES: Duplicate extractions (four samples each for Schedule A and C compounds) were analysed. The duplicate results monitor precision of sampling, extraction and analytical methods. Duplicates were stored under identical conditions as the original sample.

SPIKES: Four triplicate samples were spiked with a range of compounds representing those pesticide groups of interest from Schedule A. These spikes occurred throughout the sampling period, at a level of ~0.625µg/L.

Duplicate acidified cartridges were spiked (at a level of ~ 2.5µg/L) on three occasions with a mixture of acid herbicides.

The calculated recoveries give an indication of extraction efficiency of a range of compounds, matrix affects and degradation of analytes with storage.

Triplicate samples were spiked (at ~30µg/L) on four occasions for Schedule C compounds. The calculated recoveries give an indication of extraction efficiencies of a range of compounds, matrix affects and degradation of analytes with storage. Four laboratory spikes of selected samples were also performed on Schedule C compounds, to compare recoveries between field and fresh laboratory spikes. This comparison highlights recovery losses based on degradation due to extended time before analysis and storage conditions.

SURROGATES: All samples, including blanks, duplicates and spikes were adulterated with a known quantity of surrogate standards prior to extraction of Schedule A compounds. This solution consisted of the following compounds: difluoro-DDE; dibromo-DDE; deuterium-labelled terphenyl (d_{14}). The recovery of these compounds indicates the efficiency of individual cartridge extractions. These results also indicate matrix, processing and storage affects. The consistency of these results is important in identifying problems with specific cartridges.

RECOVERY OF FIELD-SPIKED SAMPLES (SCHEDULE A)

COMPOUND	MEAN (%)	S.D. (%)*	R.S.D. (%)*
SIMAZINE	72	17.3	24
ATRAZINE	62.5	14.8	24
CARBARYL	60.5	70.5	117
LINDANE	112	25.6	23
DIAZINON	100.8	30.5	30
CHLORPYRIFOS	45.8	42.9	94
CHLORPYRIFOS METHYL	72	32.8	46
FENITROTHION	99.5	29.6	23
CHLORFENVINPHOS 1	79	17.6	22
CHLORFENVINPHOS 2	83.8	28.1	34
PENDIMETHALIN	67	12.8	19
HEPTACHLOR	32.3	37.7	117
HEPTACHLOR EPOXIDE	95.5	28.3	30
CAPTAN	17.8	23.7	133
CHLORDANE CIS	72.3	21.3	30
CHLORDANE TRANS	65	21.3	33
DIURON	254.3	311.6	123
FENAMIPHOS	35.5	71	200
DDE	64	18.2	28
DDT	52	13.6	26
DIELDRIN	108.5	34.7	32
HEXAZINONE	34.8	20.5	59
PERMETHRIN 1	42.8	13.3	31
PERMETHRIN 2	44.5	8.6	19

n=4

RECOVERY OF FIELD-SPIKED SAMPLES (SCHEDULE B)

COMPOUND	MEAN (%)	S.D. (%)*	R.S.D (%)*
DICAMBA	126.5	3.5	3
MCPP	115	1.4	1
DICHLORPROP	114	2.8	3
2,4-D	152	4.2	3
TRICLOPYR	109	7.1	7
2,4,5-T	91	9.9	11
2,4-DB	94	4.2	5

n=4

* S.D. denotes Standard Deviation.

R.S.D denotes Relative Standard Deviation, $R.S.D. = \frac{S.D. \times 100}{MEAN}$

RECOVERY OF FIELD-SPIKED SAMPLES (SCHEDULE C)

COMPOUND	MEAN (%)	S.D. (%)*	R.S.D (%)*
PARAQUAT	60.7	13.3	22
DIQUAT	97.7	8.1	8
GLYPHOSATE	48.0	1.7	4

n=3, excluding data from spiked sample Bore 6758

RECOVERY OF LABORATORY SPIKED SAMPLES (SCHEDULE C-PARAQUAT & DIQUAT)

AGSO LABORATORY NUMBER	SPIKE LEVEL (µg/L)	PARAQUAT (%)	DIQUAT (%)
WQ94/59	2	30	60
WQ94/79	20	80	81
WQ94/88	40	86	104
WQ94/101	100	97	109

RECOVERY OF LABORATORY SPIKED SAMPLES (SCHEDULE C-GLYPHOSATE)

AGSO LABORATORY NUMBER	SPIKE LEVEL (µg/L)	GLYPHOSATE (%)
WQ94/65 & 59	2.5	32
WQ94/89 & 79	5	30
WQ94/93 & 88	50	74

RECOVERY OF SURROGATE ANALYTES

AGSO LAB NO.	RECOVERY (%)		
	Difluoro-DDE	Terphenyl-d_{14}	Dibromo-DDE
WQ94/58	44	9	9
WQ94/58A	45	8	11
WQ94/59	47	5	5
WQ94/60	40	6	7
WQ94/61	41	4	5
WQ94/62	44	5	8
WQ94/63	44	9	13
WQ94/64	26	11	22
WQ94/65	36	5	7
WQ94/66	41	7	9
WQ94/67	32	4	6
WQ94/68	36	5	7
WQ94/69	30	3	4
WQ94/70	43	6	9
WQ94/71	36	4	5
WQ94/72	39	4	5
WQ94/72A	30	3	3
WQ94/73	28	4	7
WQ94/74	35	5	8
WQ94/75	42	4	10
WQ94/76	38	7	10
WQ94/77	28	3	4
WQ94/78	34	3	4
WQ94/79	26	6	7
WQ94/80	23	4	5
WQ94/81	20	4	7
WQ94/82	27	4	5
WQ94/83	24	5	8
WQ94/84	12	2	3
WQ94/85	24	4	8
WQ94/86	19	3	5
WQ94/86A	17	2	3
WQ94/87	16	3	4
WQ94/88	15	2	4
WQ94/89	34	5	10
WQ94/90	32	4	3
WQ94/91	45	9	18
WQ94/92	50	8	30
WQ94/2001	38	7	12
WQ94/93	38	5	6
WQ94/94	33	5	6
WQ94/95	39	4	7
WQ94/96	43	5	8
WQ94/97	35	4	6
WQ94/98	34	3	4
WQ94/98A	31	7	7
WQ94/99	37	4	6
WQ94/100	40	6	9
WQ94/101	39	4	6
WQ94/102	19	2	3
WQ94/103	33	6	8
WQ94/104	37	7	15
WQ94/105	34	4	13
WQ94/2002	18	2	2
WQ94/106	31	6	9
WQ94/106A	21	4	5
WQ94/107	19	2	3
MEAN (%)	32.7	4.8	7.6
S.D. (%)*	9.3	2.0	4.8
R.S.D. (%)*	28	41	63

DISCUSSION OF QA/QC DATA

BLANKS: Blank extracts were free from pesticides, verifying that cleaning of sampling and processing equipment was efficient and carry-over contamination was unlikely to occur. Pesticides were not detected in the blank extract which followed deliberate contamination, proving that the methanol rinse was effective in removing previous contaminants.

REPLICATES: Duplicate extractions produced identical results as original extractions. In all cases no pesticides were detected in duplicate or original samples.

SPIKES: Analysis of recovery data shows acceptable recoveries for simazine and atrazine. The last spiked sample (WQ94/105) produced lower recoveries than earlier spikes, indicating that there may have been a problem with extraction or storage of this sample. Excluding the spiked sample WQ94/105, simazine and atrazine mean recoveries were 80 and 69% respectively, with relative standard deviations less than 10%. This proves that extraction of triazine herbicides on C_{18} cartridges is efficient.

Many of the spiked compounds produced acceptable recovery levels for all four spiked samples (lindane, diazinon, chlorpyrifos methyl, fenitrothion, chlorfenvinphos, pendimethalin, heptachlor epoxide, chlordane, DDE and dieldrin). Other compounds produced poor or inconsistent extraction efficiencies (carbaryl, chlorpyrifos, heptachlor, captan, diuron, fenamiphos, DDT, hexazinone and permethrin). Diuron produced inflated recoveries (>100%), most probably due to analytical difficulties associated with gas chromatography of urea herbicides. Similarly, captan produced very low mean recoveries due to the poor chromatography of this polar compound. It is possible that HPLC would be a more suitable analytical method for these particular compounds. Some of the spiked organophosphate compounds, such as fenamiphos and chlorpyrifos also produced low mean recoveries, with large standard deviations.

Acid herbicide spikes resulted in satisfactory recovery levels and excellent reproducibility of recoveries (<11%). Certain compounds (2,4-D, dicamba, MCPP and dichlorprop) produced slightly inflated (ie >100%) recovery levels. This was due to the enhanced GC response of these compounds relative to their standards, possibly caused by sample matrix effects.

Recovery levels of paraquat (mean = 61%) were consistently lower than that of diquat (mean = 98%). The same trend was observed in laboratory spikes of field samples at various concentrations. This indicates that paraquat was extracted less efficiently than diquat at all spike levels. Recoveries were low for paraquat at 2µg/L spike level, but acceptable recoveries (>80%) were achieved for both compounds at 20, 40 and 100µg/L levels. Field spikes of paraquat produced lower recoveries than laboratory spikes at equivalent spike levels, implying that there had been some degradation in the field samples. Samples were stored under refrigeration, but were sent in bulk for analysis, hence there was a variable delay before analysis. Degradation of paraquat and diquat may be matrix dependent, given that recoveries from spikes collected earlier in the field trip were equivalent to those at the end of the field trip.

Recoveries of glyphosate at 30µg/L spike level were, on average, 48% and consistent throughout the entire field trip. This consistency indicates that significant degradation did not occur over the sampling period. Laboratory spikes of field samples produced low recoveries at the 2.5 and 5µg/L levels for glyphosate (~30%), but an acceptable recovery was achieved at 50µg/L (74%). As the earliest field spike results are similar to those of the latter, it appears that the low field recoveries may be due to the relatively low spike level and/or binding to particulates in the sample which have passed through the filters.

SURROGATES: Recoveries from surrogate additions were consistently low, indicating that they are poorly extracted using our C_{18} extraction procedures. Difluoro-DDE recoveries were slightly higher than those of the other two analytes (mean = 33%). Terphenyl-d_{14} and dibromo-DDE recoveries were extremely low (means < 10%), indicating that their extraction efficiency on C_{18} cartridges is poor. As a result, alternative surrogate compounds were selected for future use.