

# ***The application of isotope techniques to the assessment of aquifer systems in major urban areas***

*Final report of a co-ordinated research project  
1997–2000*



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## FOREWORD

Increasing development and population migration to large cities and urban centers throughout the world has led to higher demands for water supply. As surface water diversions reach their maximum potential, the abstraction of groundwater within and near urban areas is being increasingly relied upon to meet growing water demands. Aquifer systems in most urban areas have been impacted to varying degrees by sustained exploitation and the future availability of water is being threatened by depleting aquifers or water quality degradation. This has become one of the main constraints on growth and quality of life in large cities. Improved methods for the assessment and management of groundwater resources in major urban areas, therefore, are issues of high priority for most countries.

The International Atomic Energy Agency (IAEA) has, over the last four decades, co-ordinated the development, adaptation, and testing of isotope techniques for hydrological applications. A number of techniques and methodologies that are now established for water resources management are potentially useful for characterizing the short and long term changes resulting from the use of extensive use of aquifers in and near urban areas. A number of publications describe the IAEA's activities in this field, which are also highlighted at a quadrennial symposium on isotope hydrology. The 10th symposium in this series was held in 1999. Proceedings of these symposia, available from the IAEA, describe the current state and emerging trends in isotope hydrology worldwide. The application of isotope techniques in urban hydrology was the focus of a co-ordinated research project (CRP) entitled "Application of Isotope Techniques to the Assessment of Aquifer Systems in Major Urban Areas" held from 1997 to 2000. Participants used a variety of isotope and geochemical tracers to characterize hydrological processes and changes in major urban centers in Africa, Asia-Pacific, and Europe.

This report provides the final results of the CRP, and is expected to be of interest to scientists, managers and planners involved in water resources assessment in urban areas. P. Aggarwal of the Division of Physical and Chemical Sciences was the IAEA technical officer responsible for this CRP. Y. Yurtsever conducted the second co-ordination meeting of the project and J.J. Gibson, also of the Division of Physical and Chemical Sciences, assisted in compiling this publication.

## *EDITORIAL NOTE*

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## SUMMARY

Most projections of future water demand indicate that in the next century, there may be a serious shortfall in water supply to meet the growing demands in many regions of the world. Rapid, unplanned population growth and deficiencies in proper planning for the development and management of freshwater resources are the principal factors for the projected shortfall. In many of the urban centers of the world, rapid population growth has placed a serious constraint on the available water resources. In addition, urbanization results in the degradation of the groundwater and surface water, further threatening the availability of the existing resources in many cities. The hydrological impacts of urbanization may be broadly categorized as follows:

- (A) Changes in water budget
- (B) Perturbation of hydraulic conditions
- (C) Pollution and degradation of water quality

### *Changes in water budget*

One of the most common hydrologic impacts of urbanization is a change in the quantity of surface precipitation that infiltrates the ground or runs off into surface water bodies. Conversion of open land reclaimed either from agricultural use or from wetlands, etc. to develop roads, pavements and buildings, results in an increase in surface runoff and decrease in recharge infiltration. Following the development of urban areas, an increase in recharge infiltration may occur mainly due to disposal of wastewater via in situ sanitation, leakage from water mains and sewers, or due to lawn over-irrigation.

### *Modification of hydraulic conditions*

A variety of activities related to the development and sustenance of urban areas produce changes in the hydraulic conditions and interactions between surface water and groundwater or shallow and deep aquifers. The additional runoff generated from urban areas may produce an increased sediment load and possibly alter the course and flooding frequency of surface water bodies. Abstraction of groundwater to meet water demand in urban areas may alter the hydraulic relationship between surface water and shallow groundwater aquifers. Groundwater withdrawal from deeper aquifers, either to meet demand or to avoid the use of polluted shallow groundwater, may alter the existing hydraulic relationships between the shallow and deep aquifers. This may result in leakage of contaminated shallow groundwater to deeper aquifers, threatening the quality of all groundwater available in the area. The changes in hydraulic conditions may also result in a sharp decline or increase in the groundwater levels. The development of buildings, roads, sewer networks, etc. may alter the groundwater flow conditions in the vicinity of an urban area. In addition, hydraulic changes induced in the vicinity of an urban area may influence the hydraulic conditions in downstream or downgradient areas. The most prominent manifestation of drastic changes in groundwater hydraulic conditions in and around an urban area is seen in large-scale land subsidence.

### *Pollution and degradation of water quality*

Urbanization results commonly in increased contaminant loading to surface and subsurface water bodies from industrial activities and septic tanks or sanitary sewer leakage. The resulting pollution and degradation of water quality of surface water also affects groundwater

due to the infiltration of polluted recharge. Contamination in surface water or infiltrating recharge may originate from a variety of activities on a wide scale and not be attributed to a specific activity (“non-point source” pollution). This may include leakage from sanitary sewers and effluents resulting from widespread industrial activities. Disposal of sanitary sewers in surface water bodies may significantly degrade the quality of water in the receiving waters. In contrast, a specific activity on a limited scale, such as landfills, sewage lagoons, septic tanks, leaking gasoline tanks and spillage, mining dumps, industrial sites, and cemeteries may constitute a “point source” of pollution to surface and ground water.

A Co-ordinated Research Project entitled “Application of Isotope Techniques to the Assessment of Aquifer Systems in Major Urban Areas” was implemented from 1997 to 2000. The project included participants from 8 countries, namely: Australia, China, Germany, India, New Zealand, Pakistan, South Africa, and the United Kingdom. To obtain a broad perspective on potential applications of isotope techniques, the project supported investigations in a wide range of urban areas including: Adelaide (Australia), Auckland (New Zealand), Calcutta, Jodhpur, Raipur (India), Dhaka (Bangladesh), Lahore (Pakistan), Munich (Germany), Pretoria (South Africa), and Shanghai (China).

*Adelaide, Australia:* Studies in Adelaide demonstrated tracing of artificial recharge and reclamation of stormwater using chloride and stable isotope tracers. A six year trial of aquifer storage and recovery (ASR) was conducted within the fringes of the Adelaide metropolitan area from 1993 to 1999. About  $250 \times 10^3 \text{ m}^3$  of storm water was injected during 4 separate events from 1993-1997 into a confined Tertiary limestone aquifer, and about half that retrieved during 1998 – 1999. The project was divided into two main objectives: 1) tracing of physical water movement and mixing within the zone of injection of surface water using conservative environmental tracers ( $\text{Cl}^-$ ,  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) and 2) evaluating the relative importance of various biogeochemical reactions induced by mixing of contrasting water types (e.g. organic matter oxidation, carbonate mineral dissolution, pyrite oxidation and sulphate reduction) using chemical mass balance,  $\delta^{13}\text{C}$ ,  $^{14}\text{C}$  and  $\delta^{34}\text{S}$ . Chemical parameters were monitored throughout study, whereas isotopic measurements were made primarily during in the injection phase of the project.

Chloride results show a high contrast between low salinity storm water and slightly brackish native groundwater. These data could be used effectively to estimate mixing proportions between injected water and native groundwater for the injection well and monitoring wells. Estimating the extent of mixing between two water types using  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  could be achieved for specific short-term injection events, but the high variability of stable isotopic composition of storm water makes it less useful than chloride. The use of both is recommended, but each has special value according to different field situations and/or the type of information required. For long-term, spatially averaged information, chloride ion data is preferred, provided there is sufficient chloride contrast between recharge waters and native groundwaters. For specific information on the fate and mixing of waters from a given injection event, stable isotopes of water may be more appropriate. This is the only option where chloride levels in both water types are similar.

Dissolution of carbonate minerals and oxidation of pyrite were considered to be the most important geochemical mass transfer reactions based on a comparison between concentrations expected *via* conservative mixing of waters, and concentrations actually measured. However,  $\delta^{13}\text{C}$  concentrations were essentially invariant before, during and after injection of storm water



despite net release of Ca, Mg and  $\text{HCO}_3^-$  into groundwater. This is thought to be due to the stoichiometry of the carbonate dissolution reaction, in which one equivalent of  $\text{CO}_2$  with a  $\delta^{13}\text{C}$  of approx.  $-22\text{‰}$  reacts with one equivalent of carbonate mineral of  $\delta^{13}\text{C}$  of  $0\text{‰}$  to yield a  $\delta^{13}\text{C}_{\text{DIC}}$  of about  $-11\text{‰}$  which is about that of the native groundwater.  $^{14}\text{C}$  data are more promising (but also more expensive) and show that oxidation of fresh (i.e., young) organic material is responsible for promoting the carbonate dissolution reaction. Given that carbonate dissolution and precipitation is likely to be a critical factor in determining viability of aquifer storage and recovery (due to expected changes in aquifer transmissivity), monitoring carbonate chemistry and  $^{14}\text{C}$  is essential during the development phase of such schemes.

Sulfur isotopes are very sensitive to processes involving pyrite oxidation and sulfate reduction. Addition of sulfate with relatively light  $\delta^{34}\text{S}$  values occurs immediately following injection, but very quickly the  $\delta^{34}\text{S}$  increasing due in part to mixing with native groundwater and sulfate reduction. Therefore, isotopes of sulfur (and possibly oxygen isotopes of sulfate molecule) may be especially useful where sulfur and associated mobilization of iron reactions are an issue in clogging of injection and recovery well screens.

*Auckland, New Zealand:* Isotopic analyses were combined with artificial neural network (ANN) models to determine the effect of storm water infiltration on water quality in a shallow unconfined basalt aquifer in the Mount Eden – Mount Albert areas of Auckland, New Zealand. Auckland is New Zealand's largest city and has over 1 million inhabitants. Groundwater is used as a drinking water supply for approximately 10% of the city, and storm water infiltration occurs up-gradient of the water supply wells.

Groundwater in the Mount Eden aquifer is used for small drinking water supplies, irrigation of parks and golf courses and for industrial uses. Sampling of heavy metals showed relatively high concentrations of total Pb and Zn in some groundwater samples and in sediments taken from the storm water drains some of which were above the maximum acceptable values (MAV) for New Zealand drinking water. Groundwater sampling detected polynuclear aromatic hydrocarbons (PAH) in some samples but these concentrations were below the MAV for PAHs. Intensive sampling of stable isotopes ( $^{18}\text{O}$  and  $^2\text{H}$ ) in both groundwater and storm water did not show any discernible patterns that could be used to identify storm water infiltration to the aquifer. This was because the groundwater isotopic composition showed little variation in isotopic composition, and the storm water had highly variable isotopic composition depending the direction from which the storm came. Tritium and CFC measurements of groundwater showed that in the southern part of the aquifer the water is very young ( $>3$  years old), but that when the water reached the area near the discharge zone the age of the water increased dramatically to  $47 \pm 2$  years old (using a piston flow model). Both the CFC and tritium dates for this well showed that the water is old, although the CFC age is likely to be slightly contaminated.

The ANN modelling was used to determine patterns of chemical concentrations and isotopic values after rainfall events. The results indicate that heavy metal concentrations increase after rainfall events, but that many of the major chemical constituents decrease after rainfall events due to dilution (for example nitrate decreases after rainfall events). Stable isotopes do not show any pattern after rainfall events and are not good indicators of storm water infiltration.

Analyses of sediment cores from drains indicate that most of the metals are bound to organic material in the drains and these materials need to be cleaned out regularly in order to maintain

the quality of the aquifer water. It is recommended that the storm water be treated before discharge to the aquifer and that clean adsorbent material be placed down the soakage pits to enhance recovery of metals before they are allowed to infiltrate into the aquifer.

The tritium and CFC measurements were important in helping to understand groundwater flow in the aquifer system and to establish a strategy for identifying vulnerable parts of the aquifer. Stable isotope measurements employed in the project did not help as variation in the isotopic composition of the groundwater was too narrow to detect storm water infiltration.

*Calcutta, Jodipur, Raipur, India:* Isotopic and geochemical methods were applied to study the impact of over-exploitation of groundwater on arsenic pollution of groundwater in Calcutta city, to identify water seepage sources in Jodhpur, and to study the impact of urbanization on a karstic aquifer in Raipur, India.

The Calcutta study was aimed at understanding the impact of over exploitation of alluvial aquifers in the urban areas of the Calcutta City on arsenic pollution of groundwater. Chemical analysis were used to classify groundwaters. Most were found to be Ca-Mg-HCO<sub>3</sub> and Na-Cl types. Arsenic concentration in most of the samples is below permissible level (0.05 mg/L). A few shallow zone samples in Jadavpur area show arsenic concentration in groundwater above permissible level. Isotopic study indicates that arsenic contaminated groundwater is depleted and has less residence times (less than 100 years). In contrast, deeper groundwater (depth ~ 150 m) is found to be arsenic-free and relatively old.

An isotope study was undertaken to locate the source of seepage water in the basements of a number of buildings in Jodhpur city (Rajasthan) in March 1998. On the basis of isotopic and chemical analyses and hydrogeological data, it is concluded that seepage from a lake, situated adjacent to the city was responsible. The lake water contribution to the seepage could be either due to direct seepage through the fractured rhyolite or seepage from pipelines carrying lake water. Increased consumption of lake water and decreased groundwater withdrawal has further aggravated the seepage problem.

Groundwater in Raipur, India is known to be susceptible to contamination by landfills, domestic and industrial waste disposal. Environmental isotopes (<sup>2</sup>H, <sup>3</sup>H, <sup>18</sup>O and <sup>13</sup>C) as well as chemistry of groundwater samples have been used to identify locations that are prone to contamination in the city. The isotopic and chemical analyses indicate that:

- groundwater recharge occurs mainly through canal network, pond seepage and direct infiltration of precipitation,
- groundwater shows contamination waste disposal sites and near dairy farms,
- shallow groundwater is more affected by contamination compared to the deeper groundwater, and
- deterioration of groundwater quality is localized and is not alarming at present.

*Dhaka, Bangladesh:* Carbon stable isotopes and geochemistry were used to confirm that extensive exploitation of groundwater under the city of Dhaka, Bangladesh has led to formation of an extensive cone of depression in the groundwater table, inducing infiltration of river water over several kilometers near the city centre.

Dupi Tila sand aquifer. Over-exploitation of the aquifer has led to a progressive decline in water levels. The resulting cone of depression is thought likely to be causing the infiltration of polluted surface waters. Stable isotopic techniques were used to characterize the hydrogeology and water sources the Dupi Tila aquifer beneath Dhaka.

The use of oxygen and hydrogen stable isotopes in tracing the present-day subsurface hydrology of the Dhaka area is somewhat constrained by the lack of 'baseline' data. On consideration of isotopic data from elsewhere in Bangladesh, it appears likely that the Dupi Tila beneath Dhaka must have had a 'natural' river water component even before groundwater abstraction began in modern times. Nevertheless it is clear from the samples obtained from representative tube wells across the city that additional, pumping-induced leakage is occurring, primarily from the Buriganga (a distributary of the Brahmaputra). This leakage extends for several kilometres into the city in places. Carbon stable isotopes and major-ion chemistry confirm this general picture, and support the view that groundwater in the Dupi Tila aquifer beneath the more central parts of the Dhaka 'island' is largely unpolluted. Although the Dupi Tila is regarded as a multi-layer aquifer, there is little evidence from stable isotopes or chemistry for depth-related stratification.

The coherent picture of progressive river infiltration presented by O, H and C stable isotopes demonstrates their usefulness as tracers. Perhaps their main benefit is that they are unaffected by pollution, and can therefore function where simpler tracers such as chloride or electrical conductivity are compromised. Future investigations should include sensitive indicators such as tritium and CFCs in order to define rates of movement of pollution fronts.

*Lahore, Pakistan:* Isotopes were applied to evaluate changes in aquifer dynamics in Lahore, Pakistan, with special emphasis on recharge mechanism, replenishment of the aquifer, pollution mapping, sources of nitrogen compounds and other contaminants, and vulnerability of the aquifer to pollution.

Lahore is the second biggest city of Pakistan having a population of more than 5 million. The aquifer under the area is composed of an unconsolidated alluvial complex (Pleistocene-Recent age) of more than 400 m thickness having mostly fine to medium sand with some clay/silt lenses. The aquifer is highly transmissive with coefficient of permeability ranging from 37.2 to 73.4 m/d and specific yield of 0.1 to 0.25. As water supply of the city has been based on the abstraction of groundwater, more than 400 high capacity public wells, in addition to a large number of shallow private wells (up to 50 m depth), are in operation. As a result the water-table is declining at high rate and aquifer dynamics are changing, and the flow of the river Ravi, which was one of the main sources of recharge to the aquifer has been reduced. The existence of saline groundwater in the nearby area south of the city is also a potential threat to the aquifer. There are some other sources like unlined sewerage drains containing untreated industrial and domestic wastes which can pollute the aquifer by induced infiltration.

Stable isotope data show that deep groundwater in the area from the river Ravi up to the center of the city has major contribution of the river water, while in the remaining area it comprises mainly base flow recharged by rains of a distant area to the North-East. High tritium values of deep groundwater fed by the river show its very rapid movement in the aquifers. The shallow groundwater at the locations near the river is found to be mainly recharged by the river water.

High nitrate accompanied by high  $^{15}\text{N}$  values show that shallow aquifer is being polluted by sewerage effluents.  $^{13}\text{C}$  data supports this evidence. Bacterial contamination of groundwater especially at locations near the drains also proves the penetration of urban recharge from sewerage drains. Owing to good connectivity between surface and deep groundwater systems, it is expected that pollutants will ultimately reach the deep water supply aquifer. Although the present municipal water supply is of good quality, proper management and remediation will be required to avert future contamination of this supply.

*Munich, Germany:* Isotopes were applied to establish the age distribution and recharge patterns of groundwater, and were used to calibrate a numerical flow and transport model of the water supply aquifer system in Munich, Germany. Tracers including tritium and argon-39 and their effectiveness at simulating migration of anthropogenic pollutants was evaluated.

Geologic strata underlying the urban area include two different Tertiary aquifers which are exploited for drinking and non-drinking water purposes, separated by a low-hydraulic conductivity layer of about 100 m of clay and silt. Isotope studies proved that the upper Tertiary aquifer belongs to the active and the lower aquifer to the passive recharge zone. In the active recharge zone more than 85 % of ground water recharge occurs whereas in the passive recharge zone less than 15 %. Since the beginning of this century the passive recharge zone aquifer has been used extensively by the Munich breweries and since the 1950's increasingly also by other industry.

From long-term investigations it has become evident that the isotopic composition of ground water abstracted even from the lowest aquifer changes continuously, indicating a non-steady state situation.  $^{39}\text{Ar}$  results support the assumption that the ground water age pattern of that aquifer is probably very sensitive to hydraulic conditions as well. Because the lower Tertiary aquifer is considered as Munich's potential subsurface reservoir of high quality ground water, adapted management strategies to contribute to ground water protection become of great importance. Hydrogeological data were used to develop and calibrate a transport model that qualitatively fit the isotope-derived age patterns, and that quantitatively reproduced the trends observed due to ground water exploitation. The model is still in provisional state and improvements are required such as extension to boundary conditions and 3D structures. In its current form, the model predicts that a hydraulic "steady state" is reached within less than 10 years whereas the age distribution pattern of all investigated scenarios does not converge to a "steady state" even after 200 years of abstraction of 20 % of total recharge. And though the tritium input was fairly high in the Northern Hemisphere, even with a "high-conductivity" scenario no tritium can be detected after 30 years of ground water abstraction out of the lower aquifer, in contrast to an important pollutant. Only  $^{39}\text{Ar}$  appears suitable to be used as precursor of anthropogenic pollutants. In any case, it is predicted that a fairly "conservative" exploitation of the passive recharge zone will not negatively impact migration of contaminants. Note that a final report on the Munich study is not included as it was not available at the time of publication.

*Pretoria, South Africa:* Nitrogen effluents from various industrial plants were investigated for the isotope ratios of nitrate and ammonia. It was found that large isotope fractionation occurs in cases where ammonia is involved in gas-liquid phase changes. This feature was found to occur in two coke oven plants where ammonia gas is removed from a gas stream by solution in water, in an ammonia sulphate plant where ammonia gas is absorbed in sulphuric acid and in a water treatment plant where ammonia is removed from (high pH) water by air blowing. In

all these cases  $^{15}\text{N}$  isotope enrichments ( in the range of 10 – 30 ‰) occurred. These enrichments are can be in excess of those found naturally.

The ammonia in such waste waters retains its high  $^{15}\text{N}$  content when it is converted to nitrate: which occurs rapidly in high oxidized conditions. Nitrate is a fairly conservative tracer and its contamination in water can be followed readily. In the low recharge environment in the central parts of South Africa evidence of waste management practices of 10-20 years earlier were still quite evident. The high  $^{15}\text{N}$  nitrate signal was used to distinguish industrial nitrogen pollution from pollution by local sewage disposal systems.

Vegetation that derives its nitrogen from such high  $^{15}\text{N}$  sources retains the isotope signature of its source. Grass and other annual plants have the isotope signature of the water of the specific year. Trees exhibit the isotope signature of deeper water which show the effects longer term pollution events. This approach enables the source apportionment of nitrogen derived pollution in these specific circumstances.

*Shanghai, China:* Shanghai City is supplied mainly by river water with low drinking water quality. To augment this supply, high quality groundwater water from a confined aquifer is also being considered for development, with supplies distributed in a separate network than normal tap water. To date, groundwater in such Quaternary aquifers in the Shanghai area have mainly been tapped for industrial use. Since 1965, the artificial recharge of the aquifers using tap water has been carried out in order to control the land subsidence. The influence of artificial recharge on the groundwater quality is important to assess if the aquifers are to be used for drinking water.

Isotope techniques, primarily tritium along with trace elements and organic tracers were used to study the impact of artificial recharge, based on a sampling program undertaken in 1998 and 1999. The results obtained show that tritium content is sensitive to presence of the artificially recharged water. Some major chemical constituents, such as sulphate and bicarbonate, and some volatile organic compounds, such as chloroform, bromo-dichloro-methane and 1,2-dichloro-ethane, and some trace elements are also good for tracing the recharge water. It was concluded that water quality degradation was likely if recharge and exploitation wells in the same aquifer were situated within a radius of about 1 km.

## Conclusions

The understanding and effective management of the hydrologic impacts of urbanization on groundwater aquifers is dependent upon the availability of specific hydrological information, such as:

- (i) source and amount of water contributing to surface runoff and subsurface infiltration
- (ii) rate and extent of changes in hydraulic conditions of groundwater aquifers
- (iii) changes in hydraulic interactions between surface water and groundwater or between shallow and deep groundwater aquifers
- (iv) origin, fate, and transport of pollutants in surface and subsurface environments.

A variety of well-established and developing isotopic techniques provide excellent means for obtaining this critical information. The widely used techniques of isotope hydrology based on stable oxygen and hydrogen isotopes can be used to differentiate the source of water contributing to increased runoff and recharge infiltration. These techniques may be supplemented with other commonly used isotopes, such as  $^{13}\text{C}$ ,  $^{34}\text{S}$ , and Tritium. In specific instances, other isotopic and non-isotopic tracers may also be useful for tracing the origin and movement of water in urban areas. Characterization of the rate and extent of changes in hydrologic conditions requires the quantification of small changes in the recharge, leakage between aquifers, or flow conditions. These time-dependent or transient changes can be most effectively understood with the use of isotopic or non-isotopic tracers for dating relatively young groundwaters.

Isotopic techniques most suitable for the source, fate and transport of pollutants in surface or subsurface environments are nitrogen and oxygen in nitrates, sulfur and oxygen in sulfates, oxygen in molecular oxygen, and carbon-13 in carbon dioxide and organic compounds.

The integration of isotopic techniques into a multi-disciplinary investigation is likely to be more effective, both economically and scientifically, in providing the required information. In particular, the time-dependent changes in aquifer conditions may be difficult to characterize by using non-isotopic techniques. This is because the hydraulic changes induced by urban activities are incremental in nature and may require monitoring at closely spaced locations over a long period of time in order to be detected. The use of isotopic techniques, however, can establish the pre-development or baseline hydraulic conditions and provide evidence and quantification of hydraulic changes at a comparatively minimal cost.

An important outcome of the present CRP was the testing and identification of isotopic tracers that are particularly well-suited to specific studies in the urban environment, as shown below:

Tracer/ Approach	Main Application						
	source- water labelling and mass balance	ground- water dating	infiltration leakage/ artificial recharge	landfill leachate/ sewerage	industrial pollution	biogeo- chemical processes	pred- iction
$\delta^{18}\text{O}$ , $\delta^2\text{H}$	✓		✓			✓4	
$\delta^{13}\text{C}$			✓	✓		✓	
$\delta^{15}\text{N}$			✓	✓	✓	✓	
$\delta^{34}\text{S}$						✓	
$^3\text{H}$ , CFCs	✓	✓ 1					
$^{39}\text{Ar}$	✓	✓2	✓				
$^{14}\text{C}$	✓	✓3					
Chemistry	✓		✓	✓	✓	✓	
Modelling							✓

1- dating of recent recharge, 2- dating of recharge of  $10^2$ - $10^3$  years old, 3- dating of recharge  $10^3$ - $10^4$  years old, 4- refers to  $\delta^{18}\text{O}$  in sulphate and carbonate

Based on the results achieved from the CRP, the following conclusions were drawn:

- (i) stable isotopes can be used to distinguish multiple recharge water sources with distinct isotopic signatures. However, reliable definition of end-member sources is required in order to quantify mixing proportions,
- (ii) radioisotopes are essential to provide reliable ages of groundwater for flow model evaluation and calibration,
- (iii) measurement of suspended sediments and colloids are important to determine the mobility of pollutants in urban environments
- (iv) sampling precautions are needed to provide reliable data for chemicals and CFCs in urban environments because of the possibilities of atmospheric and down-hole contamination of samples, and
- (v) industrial processes can produce compounds with characteristic isotopic signatures that can be used for tracing of industrial wastes.





# Geochemical and isotopic tracers of recharge and reclamation of stormwater in an urban aquifer: Adelaide, South Australia

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## Abstract

Artificial recharge and reclamation of stormwater into groundwater is a newly developing strategy to augment water resources in the Adelaide metropolitan area of South Australia. Mixing between injected storm water and native groundwater can be most effectively using naturally occurring chloride ion. Stable isotopes of the water molecule are used more effectively during short term tests (i.e., immediately following injection events), and requires frequent monitoring of the surface water end-member. Biogeochemical processes involving geochemical reactions such as organic matter oxidation, carbonate mineral dissolution and sulfide mineral oxidation are very effectively traced by  $\delta^{13}\text{C}$  and  $^{14}\text{C}$  (of TDIC) and  $\delta^{34}\text{S}$  (of  $\text{SO}_4^{2-}$ ). The most important processes occurring in the Tertiary limestone aquifer in Adelaide were carbonate mineral dissolution which is induced largely by  $\text{CO}_2$  production during organic matter oxidation. Sulfide mineral oxidation is a minor process, and is accompanied by an equivalent amount of sulfate reduction after injection of the stormwater.

## INTRODUCTION

Increasing urbanisation throughout the world has resulted in additional demand for water near cities. Much of the available surface water has now been diverted, and very few new dams are being constructed. Exploitation of urban groundwater systems has increased enormously over the past few decades, and in many cases has reached near maximum potential, with many large urban areas observing enormous water draw-downs (eg., Mexico City, Sao Paulo, Bangkok, Las Vegas). Growing populations and increasing per capita water use are probably the single most important limitation to urban development (Gleick, 1999).

A potential solution to the problems of both deficit in water supply and disposal of stormwater in urban and suburban settings is through a process that is known as aquifer storage and recovery (ASR). The principle is one where rainwater is diverted through the stormwater system to temporary holding basins, and this water is recharged into groundwater aquifers. When needed in drier months, the water is recovered or pumped into reticulations systems or in some cases used for irrigation. ASR is therefore a form of artificial recharge, where the same water that is injected is intended to be recovered (rather than being used expressly to supplement existing groundwater supplies).

There are a number of unknowns in the whole ASR process that need to be addressed before its' sustainability can be fully assessed. One of the primary issues facing the viability of such schemes involves uncertainties when oxygenated surface waters, that may have substantial amounts of dissolved or particulate organic matter (i.e., high Biological Oxygen Demand) are injected into suboxic or anaerobic groundwaters that usually have higher salinity. The technical issues include:

- physical limitation for the soil and/or aquifer to accept or release water
- depth to which water will be injected below the land surface (greater depth generally results in increasing cost to inject and withdraw)
- The ability to contain groundwater within a specified area will depend on the topography of the groundwater table and hydraulic conductivity.
- Clogging of the aquifer, particularly near the intake (screen) intervals due to precipitation of iron oxyhydroxides, or growth of bacterial cell walls stimulated by the addition of organic matter to the system
- Dissolution of the aquifer matrix resulting in mobilisation of solid material (eg., sand grains) or collapse of the matrix near the vicinity of the well field
- In addition the water quality of the recovered water may be adversely affected by reactions such as the reductive dissolution of Fe and Mn oxides, H<sub>2</sub>S production and methanogenesis, that may result from the anoxification of the aquifer.

## 2 STUDY AREA

Adelaide is a city of approximately 1.1 million people located in the state of South Australia (Fig. 1). About half of the water supply comes from the River Murray, which as at the down-stream end of a very large agricultural catchment, and half from local catchments. Although there are a considerable number of private and municipal wells and boreholes within the metropolitan area, the contribution to the total consumption is relatively small. The surface water quality is renowned for being the worst in Australia, with projected salinity approaching WHO limits, high amounts of Ca and Mg, and high dissolved organic loads. Mean annual rainfall within the city environs is about 580 mm/yr, most of which falls in the cooler months from May–October, and that water has until now been diverted into the sea. Given that the demand for water is highest in the dry months, there seemed an excellent opportunity to harvest the excess winter rains, store it in the groundwater aquifers, and recover that water for the summer high demand.

ASR is becoming an increasingly attractive option in places where surface storages are not viable or are expensive, and in areas with dry summers and winter dominated rainfall. Many parts of Africa, middle east and western United States already use reclaimed and treated water. Gleick, 1999 estimated that up to  $2 \times 10^9 \text{ m}^3$  of water can potentially be reclaimed and reused by 2020. We can potentially solve the combined problems of insufficient available water in winter, and excess storm runoff in winter. Although ASR will not aim to replace the traditional water resource requirements of a modern city of this size, it does alleviate the need for increasing the infrastructure by offsetting demands from the mains water supply with on-site resources. Already, parks, golf courses and irrigators of vegetable and grape crops at the city fringes are using re-used storm water.

Three study sites were chosen out of a possible 20 field pilot projects within a 50 km radius of the Adelaide metropolitan area for detailed investigation. Of those three, one was selected for comprehensive study, including full chemistry and isotopes. The site is located about 15 km from the city centre and is locally as Andrews Farm. It is located within a new

housing development and is designed to eventually provide all the water needs for the surrounding household and municipal users. Also, the three holding basins (Fig. 1) are designed to provide environmental amenity and is a first order clean up step for the storm water. The first injection of water was in July 1993, and progressively more water was injected in the following five winters (Fig. 2).

The receiving aquifer is a confined, partly karstic Tertiary limestone aquifers (Fig. 3). The water is injected at a depth of about 120m, and samples retrieved from the injection well, as well as three monitoring boreholes located 25m, 65m and 325m down-gradient respectively. The native groundwater is a Na-Cl-HCO<sub>3</sub> type with salinity of about 1,800–2,150 mg L<sup>-1</sup>.

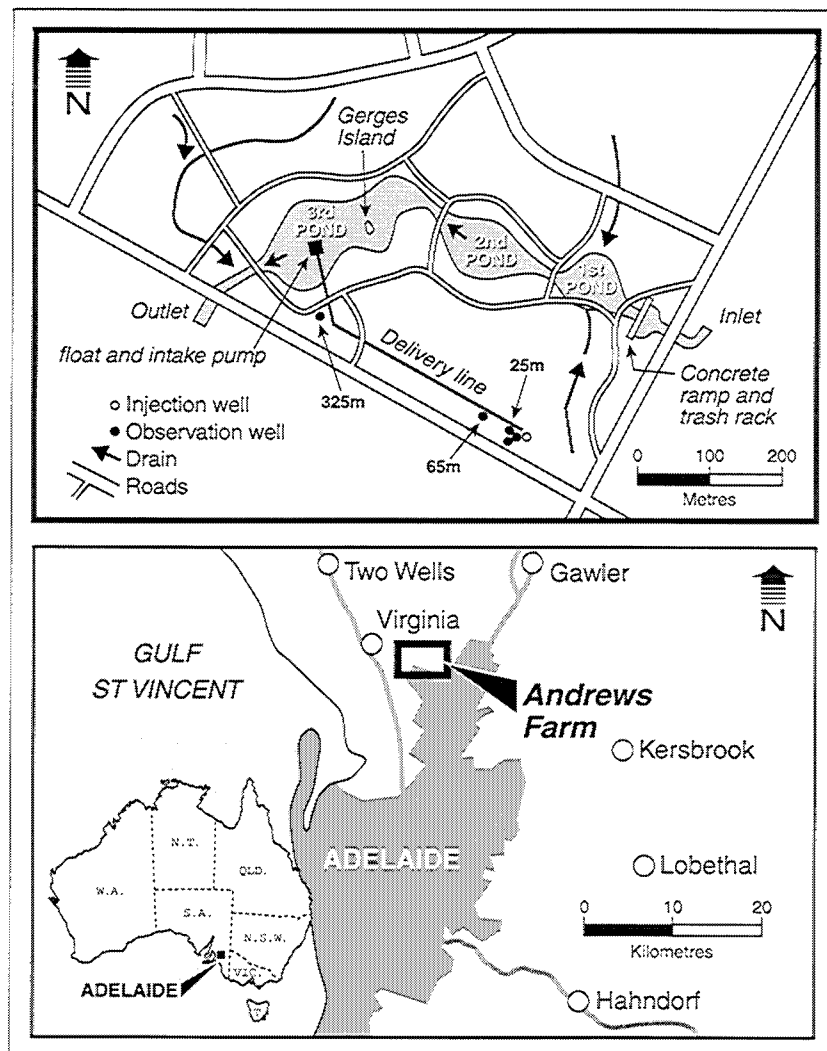
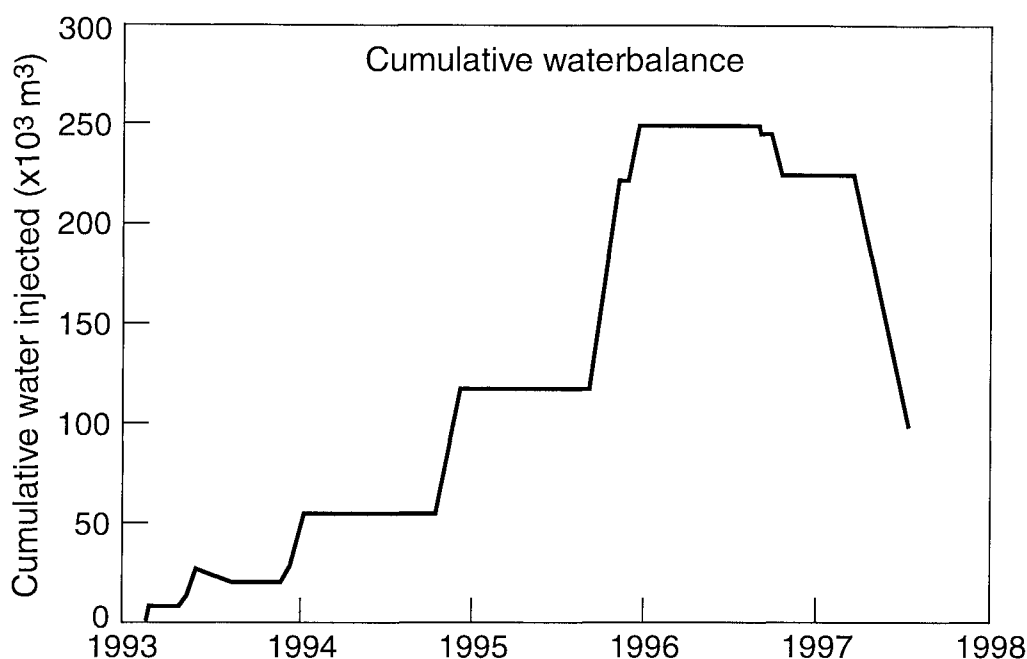


Fig. 1. Top Panel: Schematic map of the surface holding ponds, drains and location of injection well and observation boreholes at Andrews Farm. Bottom panel: Location map of Adelaide and that of the field study site (Andrews Farm).



*Fig. 2. Cumulative water balance of the Andrews Farm experimental site. The successive injection years shows that about half of the total injection volume took place in the 1995/1996 injection year. About half of all total volume of water injected was recovered in 1997.*

Injected water is storm water of salinity  $<100 \text{ mg L}^{-1}$ . Dissolved oxygen (DO) concentrations are zero, or very low in the native groundwater, whereas the injected waters tend to be high in DO and high in both dissolved and particulate organic carbon loads. Groundwaters from the injection wells and observation boreholes were sampled during and after injection of surface water. The sampling interval varied from weekly to over two months, with the sampling generally more frequent during and immediately following injection of fresh water. The last injection of storm water at Andrews farm was in 1997, and this was followed by an extensive long term recovery phase.

### 3 OBJECTIVES

We have divided our project into two main objectives. The first involves the tracing of physical water movement and mixing within the zone of injection of surface water using conservative water mass and the second involves evaluating the relative importance of the various biogeochemical reactions induced by mixing of contrasting water types. These are elaborated on in more detail below.

#### **3.1. What is the extent of mixing of injected water with the ambient groundwater?**

Evaluate different environmental tracers to estimate quantitative mixing proportions of injected stormwater and native groundwater. The conservative environmental tracers such as chloride concentration (for waters of different concentrations), stable isotopes of the water molecule ( $\delta^2\text{H}$  &  $\delta^{18}\text{O}$ ) and anthropogenic tracers chlorofluorocarbons (CFC-11, CFC-12) are applicable.

### 3.2 What types of geochemical reactions occur during the mixing process?

The addition of oxygen and organic matter (dissolved and particulate) to an anaerobic groundwater can induced a number of biogeochemical reactions. Furthermore, recharge water has a much lower salinity, and different chemical composition than the ambient groundwater, therefore inorganic reactions may also be taking place. That is, the ionic strength of the mixture may change as well as speciation of cations and anions.

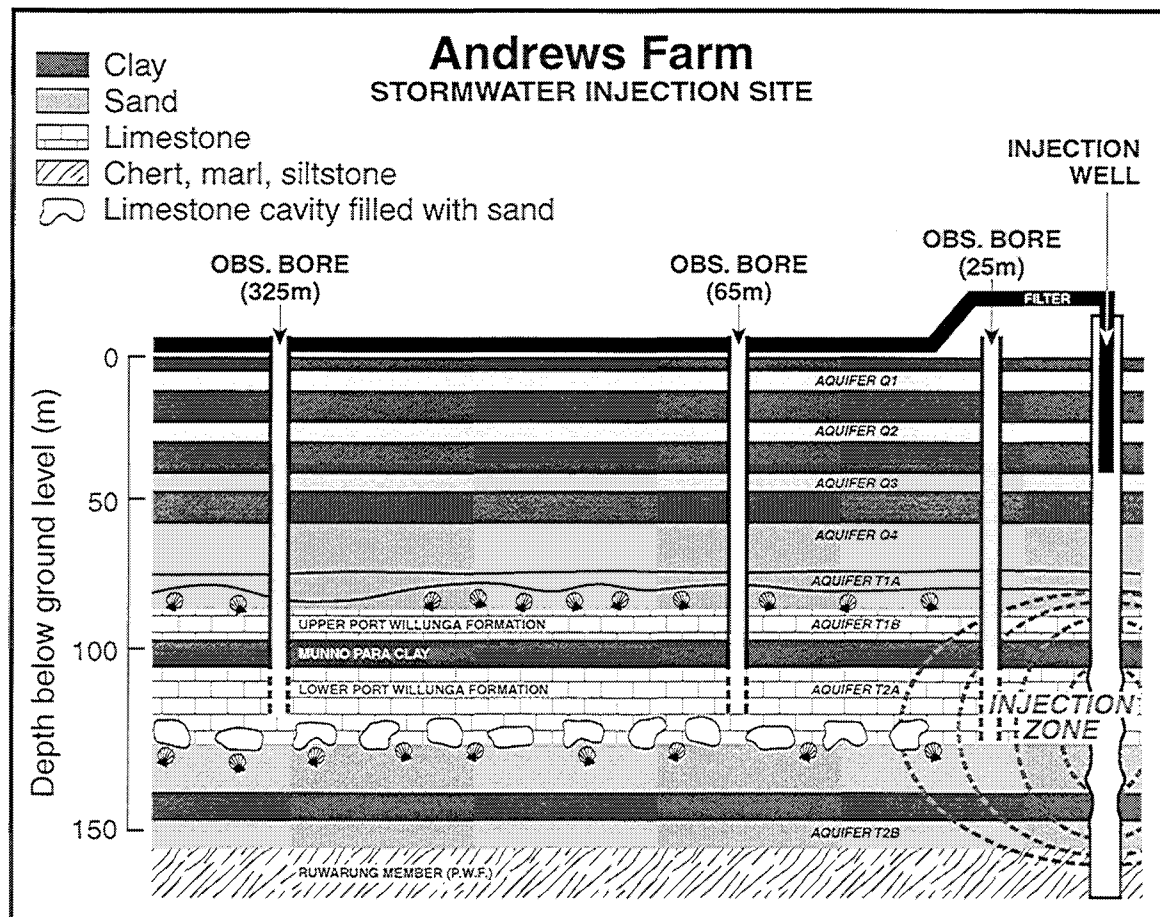


Fig. 3. Cross sectional schematic map of the Andrews Farm stormwater injection site. The injection zone is shown at approximately 120m below the land surface, and three observation bores used for sampling.

## 4 RESULTS AND DISCUSSION

### 4.1 Water mass tracers

#### 4.1.1 Stable isotopes of water

Deuterium and oxygen-18 measurements were made at the Andrews Farm site during the first 2 or so years of the injection phase of the study (Table 2). The isotopic composition of the native groundwater (i.e., the T2 aquifer) prior to any injection of surface water can be estimated from data recorded at the borehole located at 325 m. The Tertiary aquifer has a

uniform stable isotopic composition that is almost identical to the weighted mean composition of rainfall measured in Adelaide over a 12 year period ( $\delta^2\text{H}=-24\pm1.8\text{‰}$ ;  $\delta^{18}\text{O}=-4.3\pm0.3\text{‰}$ ). The isotopic concentrations of the injection well water show very large variability for two reasons. First, the variability of isotopic composition of rainfall from one event to another depends on a number of factors such as storm track and air temperature. The second factor is that the water held in three inter-connected ponds for different periods of time prior to injection. The longer the water is left in the open ponds, the greater the amount of evaporation, and this in turn depends on the season (i.e., summer time rain will undergo a greater degree of evaporation).

The stable isotope data demonstrate a very good and rapid connection between the injection well and the observation borehole at 25 m, but virtually no detectable breakthrough to 65m or at 325m. Interpretation of water mass mixing depends on there being a contrast between the injection water and that of the native groundwater. This situation does not always occur as can be seen in Table 1, where in general, injection waters in 1993, 1994 and July 1995 are enriched in  $^2\text{H}$  and  $^{18}\text{O}$  relative to the native groundwater. At other times it is similar to (June '96) or depleted in  $^{18}\text{O}$  (Aug. '95) relative to native groundwater.

The relationship between  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  (Fig. 4) shows that most data fall above the world meteoric water line. All data points excluding those from the injection well plot but close to the local meteoric water line defined by a slope of 7.6. Those data points from the injection well and the 25m well highlight the variability of rainfall isotopic composition.

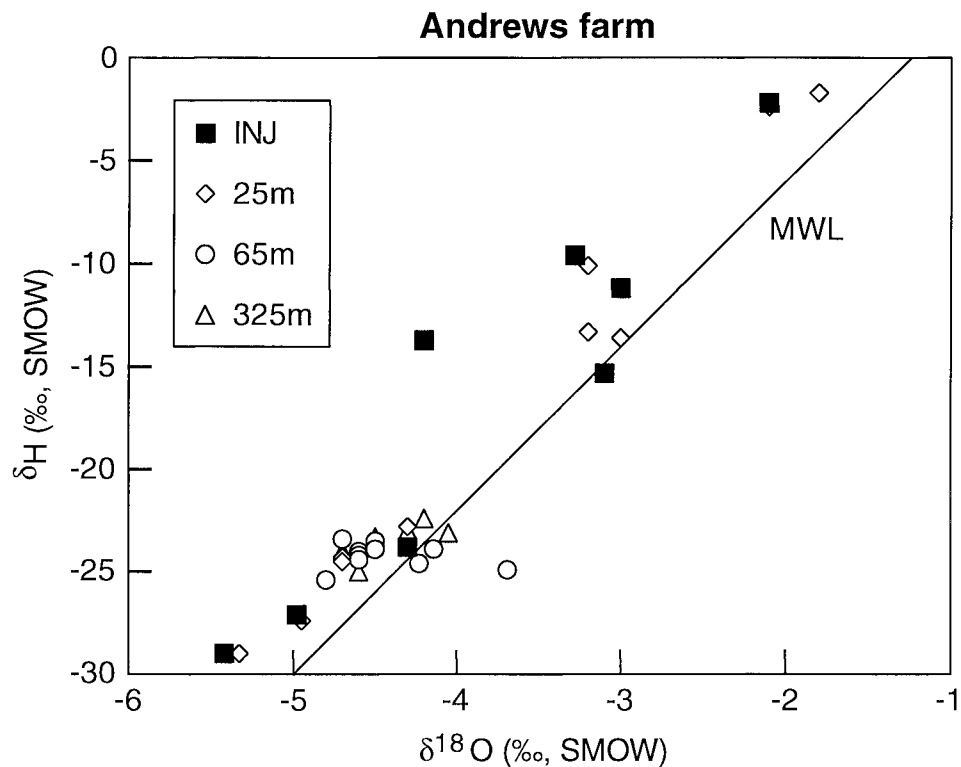
The use of stable isotopes of water is very useful for showing significant penetration of stormwater into the aquifer, but is not sensitive when the amount of stormwater penetration is <20% into the native groundwater, or when the isotopic values of injected water is not very distinct from the native groundwater. The best time to use these as tracers is after substantial residence time within the holding pond, and can be used as a tracer of discrete injection events.

**Table I.** List of some reactions that may occur during artificial recharge of surface water into an aquifer. Reactions 1–3 represent oxidation of organic matter in decreasing order of energy yield. Reactions 4–5 represent pyrite oxidation by  $\text{O}_2$  or  $\text{Fe(III)}$  reduction respectively (note the much higher yield of protons in the latter reaction). Reactions 6 and 7 are geochemical reactions that may occur due to perturbation of carbonate equilibria induced by reactions 1–5

1. $\text{O}_2 + \text{CH}_2\text{O} = \text{CO}_2 + \text{H}_2\text{O}$	Organic matter oxidation via $\text{O}_2$
2. $\text{FeOOH} + \text{CH}_2\text{O} = \text{Fe}^{2+} + \text{HCO}_3^-$	Organic matter oxidation via $\text{Fe(III)}$
3. $\text{SO}_4^{2-} + 2\text{CH}_2\text{O} = \text{H}_2\text{S} + 2\text{HCO}_3^-$	$\text{SO}_4$ reduction.
4. $15/4\text{O}_2 + \text{FeS}_2 = 2\text{SO}_4 + \text{Fe(OH)}_3 + 4\text{H}^+$	Pyrite oxidation via $\text{O}_2$
5. $14\text{Fe}^{3+} + \text{FeS}_2 + 8\text{H}_2\text{O} = 2\text{SO}_4^{2-} + 16\text{H}^+ + 15\text{Fe}^{2+}$	Pyrite oxidation via $\text{Fe(III)}$ reduction
6. $\text{CO}_2 + \text{H}_2\text{O} + \text{CaCO}_3 = 2\text{HCO}_3^- + \text{Ca}^{2+}$	Carbonate dissolution
7. $\text{X-Ca}^{2+} + 2\text{Na}^+ = \text{X-Na}_2 + \text{Ca}^{2+}$	Cation exchange

**Table II.** Stable isotope composition of water molecules for the injection well and three observation boreholes at andrews farm from 1993 to 1996. Injection events occurred in Oct. '93, June '94, June '95, and July '96

Date	INJ		Obs (25m)		Obs(65m)		Obs (325m)	
	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$	$\delta^2\text{H}$	$\delta^{18}\text{O}$
25/10/93	-15.3	-3.1	-13.3	-3.2	-24.0	-4.6	-23.4	-4.5
1/11/93	-2.2	-2.1	-2.4	-2.1	-23.4	-4.7	-23.0	-4.3
10/11/93			-1.7	-1.8	-23.5	-4.5	-23.3	-4.5
7/12/93					-23.9	-4.5		
24/6/94	-11.2	-3.0						
25/8/94			-24.3	-4.7	-24.3	-4.6		
14/9/94			-24.5	-4.7	-24.2	-4.6		
16/3/95			-22.8	-4.3	-24.4	-4.6	-24.0	-4.7
20/6/95	-23.8	-4.3	-23.5		-25.4	-4.8		
3/7/95	-13.7	-4.2	-13.6	-3.0	-25.5		-25.0	-4.6
20/7/95	-9.6	-3.3	-10.1	-3.2	-23.9	-4.1	-22.4	-4.2
3/8/95	-29.0	-5.4	-29.0	-5.3	-24.6	-4.2	-23.1	-4.0
23/8/95	-27.1	-5.0	-27.4	-5.0	-24.9	-3.7		
7/9/95						-4.4		-4.2
26/10/95		-5.0		-5.0		-4.0		
19/12/95		-4.9		-4.9				
26/2/96		-5.0		-4.7				-3.9



*Fig. 4. Stable isotope data for the injection well and observation boreholes for Andrews Farm during three injection events from 1993–1995.*

#### 4.1.2 Chloride

Because of its hydrophilic nature, the use of chloride ion as a water mass tracer can often be applied circumstances where there are no evaporite minerals within the aquifer or soils and where there can be assumed to be conservative behaviour (i.e., neither addition or removal during mineral-solution interactions). There is a high contrast between the low Cl stormwater ( $[Cl] = 30 \pm 12 \text{ mg L}^{-1}$ ) and higher salinity native groundwater ( $[Cl] = 1,200 \text{ mg L}^{-1}$  at 65m and  $870 \text{ mg L}^{-1}$  at 325m). Very little enrichment of chloride in the holding basins occurs prior to injection, which means that there is a relatively constant 'input' concentration that can be assumed when estimating mixing volumes. Following injection of stormwater into the aquifer, the relative proportions of injected water and native groundwater can be estimated from a simple mass balance in equation (1):

$$[Cl]_{\text{mixture}} = X[Cl]_{\text{inj}} + (1-X)[Cl]_{\text{gw}} \quad (1)$$

where X is the fraction of stormwater in any given groundwater sample at the injection well or observation borehole.  $[Cl]_{\text{inj}}$  and  $[Cl]_{\text{gw}}$  are end-member concentrations of Cl in the injection water and native groundwater respectively. The trend for chloride concentrations for the entire 5 year period is shown in Fig. 5, with injection events shown as shaded areas.

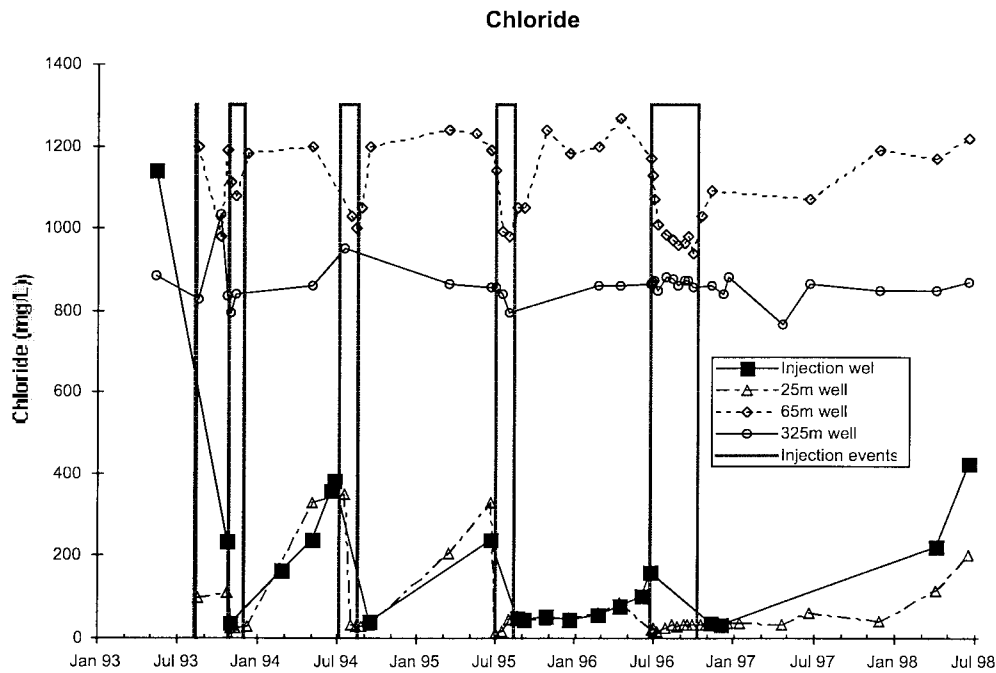


Fig. 5. Chloride concentrations at the injection well and three observation boreholes at Andrews Farm from 1993 to 1998. The injection periods are also shown as shaded areas. The Cl concentration of injectant was  $30 \pm 12 \text{ mg L}^{-1}$  throughout the entire 5 year period.

The trends in  $[Cl]$  for the injection well and the 25m observation borehole reinforces the stable isotope data that shows a direct hydraulic connection between the injection well and the 25 m observation borehole. Although there are small differences in the absolute magnitude of the values at the two sites, they move essentially identically which implies pseudo karstic behaviour. There is evidence from bore logs that drillers experienced loss of



circulation during drilling at this depth interval indicating very high hydraulic conductivity in this zone. There is clearly some penetration of injected stormwater through to 65m (shown as triangles) but none to 325m. The amount of stormwater that dilutes the groundwater at 65m is up to 15% so that is why it was not observed in the stable isotope signature. The variability of [Cl<sup>-</sup>] observed at 325 m is more likely to be an artefact of sampling technique (eg., pumping rate prior to sampling) and analytical uncertainty rather than penetration of stormwater to that borehole.

## 4.2 Biogeochemical processes

### 4.2.1 Mass balance calculations

Estimates of mass transfer of other major ions (Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, HCO<sub>3</sub><sup>-</sup> and SO<sub>4</sub><sup>2-</sup>) were done in the following sequence:

- (i) For each sample analysed, estimate the relative fraction of surface water and native groundwater using the Cl mass balance (Eq. 1).
- (ii) Using the calculated fractions estimated above, calculate what the concentrations for the all the major ions should be iff conservative mixing only was to take place,
- (iii) Compare the calculated values for Na, Ca, Mg, SO<sub>4</sub> and HCO<sub>3</sub> with those from ii). The net transfer between aquifer minerals and solution is the difference between the two numbers. For example, a higher measured value than calculated from mixing indicates transfer to solution (eg., dissolution or desorption). A lower measured value than that calculated from mixing indicates removal via precipitation of a minerals phase, or adsorption.

Calculated excess concentrations for Andrews Farm (Fig. 6) all indicate net transfer of ions into the solution as a result of mixing of storm water with the groundwater . Injection occurred from late June to mid Aug 1995 which resulted in substantial addition of HCO<sub>3</sub> and Ca+Mg into solution, and to a lesser extent Na and SO<sub>4</sub>. The increase in HCO<sub>3</sub> and Ca indicates calcite dissolution, caused by generation of CO<sub>2</sub> by oxidation of organic material plus a small amount of pyrite oxidation. Net transfer of Ca and HCO<sub>3</sub> occurred over the following 7 months. After about mid Feb 1996, the excess concentrations decreased and net fluxes approached zero by 26 July 1996 when further significant injection of surface water took place.

We can also calculate mass transfer of carbonate species using the mass transfer code PREEQEC. It is necessary to use these geochemical codes when more precise estimates are needed which involve calculation of ion activities and thermodynamic mineral equilibria data. The results of such calculations are shown as mass transfer of  $\Sigma$ Ca+Mg for the entire 4 year injection period (Fig. 7). Note the release of Ca+Mg after injection of stormwater (induced by carbonate dissolution due to CO<sub>2</sub> production). There is some, but in comparison relatively little carbonate precipitation after about 200 days after injection.

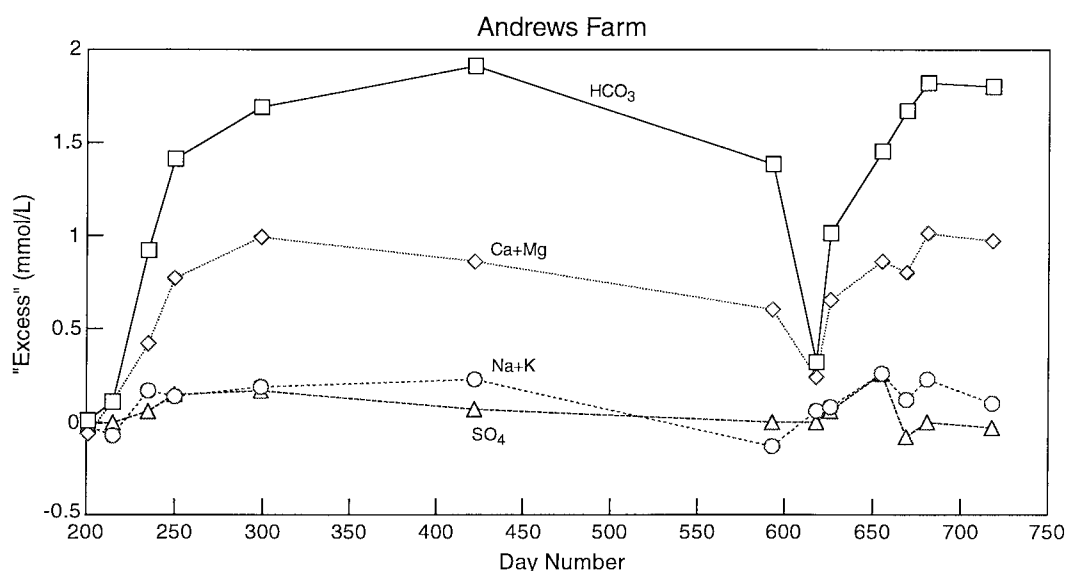


Fig. 6. Mass balance of major ions for a 1 1/2 year period at Andrews Farm (1995–96). The injection events occurred at day numbers 200 and 620.

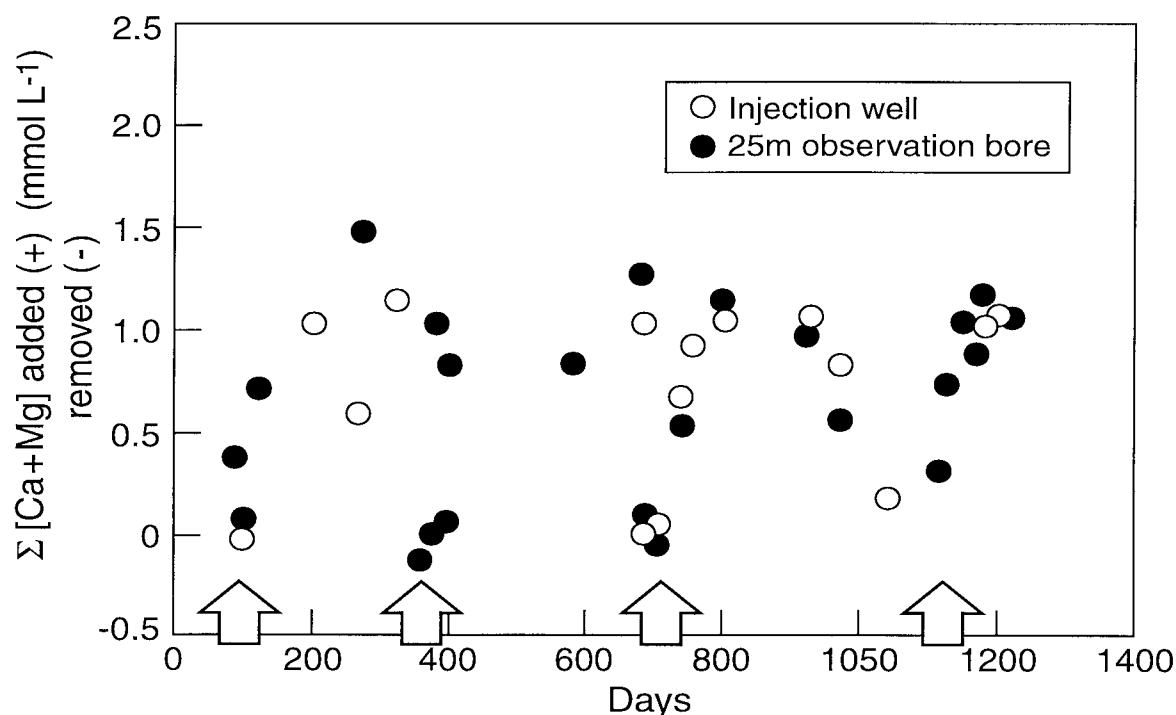


Fig. 7. Calculated mass transfer of Ca+Mg at Andrews Farm for the entire 4 year injection history 1993–1997. The arrows indicate injection of stormwater to the aquifer.

#### 4.2.2 Carbon isotopes ( $\delta^{13}\text{C}$ and $^{14}\text{C}$ )

The use of carbon isotopes were employed to trace the fate of organic matter and the source of carbon to fuel biogeochemical reactions.  $\delta^{13}\text{C}$  and carbon-14 are used as part of the chemical and isotopic mass balance to better understand the process of carbonate dissolution, organic carbon oxidation and possibly methane production (Back & Baedeker, 1989; Herczeg et al., 1993). For example,  $^{13}\text{C}/^{12}\text{C}$  ratios of carbonate minerals are about 0‰, those

of organic matter  $\sim -20$  to  $-30\%$ , and the  $\text{CO}_2$  produced as a by-product of methane generation is up to  $+20\%$ . In addition, the  $^{14}\text{C}$  concentrations indicate the amount of organic matter oxidised from young material, as opposed to old material (eg., old organic matter within the aquifer, or carbonate dissolution). It is important that a good understanding of the carbonate chemistry is necessary for such an approach to be used quantitatively. The  $\delta^{13}\text{C}$  concentration of 'native' groundwater at Andrews Farm is about  $-11.0 \pm 0.8\%$  while that of samples from the injection well and 25m obs bore are  $-13.4 \pm 1.1\%$ . The lowering of  $^{13}\text{C}/^{12}\text{C}$  ratios is indicative of oxidation of organic matter, but the signal is partly offset by dissolution of carbonate minerals that has a  $\delta^{13}\text{C}$  of  $0\%$ . Somewhat surprising is the high  $^{14}\text{C}$  concentrations measured in the injection well and 25m obs well which indicates that oxidation of young carbon is a significant contributor to the DIC pool, but this is not reflected in  $\delta^{13}\text{C}$  data. Carbon-14 is a very promising tool to assess the source and amount of carbon oxidised within ASR schemes.

**Table III.** Results for carbon isotopes sampled from andrews farm. Values for  $\delta^{13}\text{C}$  are given in per mill ( $\%$ ), relative to PDB. Values for  $^{14}\text{C}$  are in percent modern carbon (PMC)

	Date	$\alpha\delta^{13}\text{C}_{\text{DIC}}$	$\beta\delta^{13}\text{C}_{\text{DIC}}$	$^{14}\text{C}(\%\text{MC})$
<b>INJ</b>	20/7/95		-15.6	
	3/8/95			
	23/8/95	-10.6	-13.7	
	7/9/95			
	26/10/95	-11.6	-13.3	
	19/12/95	-11.8	-13.8	
	26/2/96	-11.5	-12.8	$58.5 \pm 2.7$
	5/6/96	-11.1	-12.0	
<b>Obs (25m)</b>	20/7/95			
	23/8/95		-15.1	
	7/9/95			
	26/10/95	-12.0	-12.9	
	19/12/95		-13.1	$74.7 \pm 1.8$
	26/2/96	-11.7	-13.2	$59.8 \pm 4.7$
	5/6/96	-11.1	-12.3	
<b>Obs (65m)</b>	20/7/95	-10.4	-11.3	
	3/8/95	-10.0	-11.0	$6.6 \pm 1.2$
	23/8/95	-10.8	-11.5	
	7/9/95		-10.8	$11.8 \pm 2.1$
	26/10/95	-10.9	-11.4	
	19/12/95	-12.6		
	26/2/96	-11.3	-12.5	$<5$
	16/4/96		-12.0	
	5/6/96	-11.5		
<b>Obs (352)</b>	20/7/95	-8.7	-9.7	
	3/8/95	-8.9	-10.0	
	26/2/96	-10.0	-10.4	$3.3 \pm 2.3$
	5/6/96	-10.1	-10.8	

<sup>a</sup>  $\delta^{13}\text{C}_{\text{DIC}}$  measured on  $\text{CO}_2$  evolved from the  $\text{SrCO}_3$  precipitate using  $\text{H}_3\text{PO}_4$ .

<sup>b</sup>  $\delta^{13}\text{C}_{\text{DIC}}$  measured on  $\text{CO}_2$  produced by high-temperature combustion of  $\text{SrCO}_3$  precipitate.

#### 4.2.3 Sulfur isotope data

Many redox reactions in groundwater often involve solid or dissolved sulfur in many forms. For example, addition of oxygen to a confined, reducing aquifer through injected surface water can oxidise reduced sulfur minerals, such as pyrite. The resultant release of acidity in turn can induce carbonate dissolution. Another type of reaction involves addition of organic matter which when mineralised to  $\text{CO}_2$  by bacteria requires energy from first dissolved oxygen, or  $\text{NO}_3$  or  $\text{SO}_4$  (see Table 1). Because dissolved oxygen and nitrate concentrations are usually very low, sulfate can be the most important electron acceptor in oxidation of dissolved or particulate organic matter injected into aquifers.

Sulfur isotopes are a very sensitive tool to investigate the above mentioned processes of sulfide mineral oxidation and sulfate reduction. There is a very large discrimination against  $^{34}\text{S}$  relative to  $^{32}\text{S}$  during many biogeochemical processes. In particular, sulfate reduction preferentially metabolises  $^{32}\text{S}$  resulting in progressive in  $\delta^{34}\text{S}$  values of residual sulfate as sulfate reduction progresses (Krouse and Mayer, 1999). The reduced sulfide is isotopically “light” which is why reduced sulfur minerals such as pyrite have quite negative  $\delta^{34}\text{S}$  values. Hence, dissolution of reduced sulfur minerals introduces light sulfate into the groundwater sulfate pool.

Sulfur isotope data on dissolved sulfate was monitored during one injection/recovery phase (see Fig. 8). We note from Fig 6 that there is relatively little net transfer of  $\text{SO}_4$  compared with other ions, but on the other hand can have a large impact on the redox status, and transfer of proton via pyrite oxidation and sulfate reduction (Table 1).

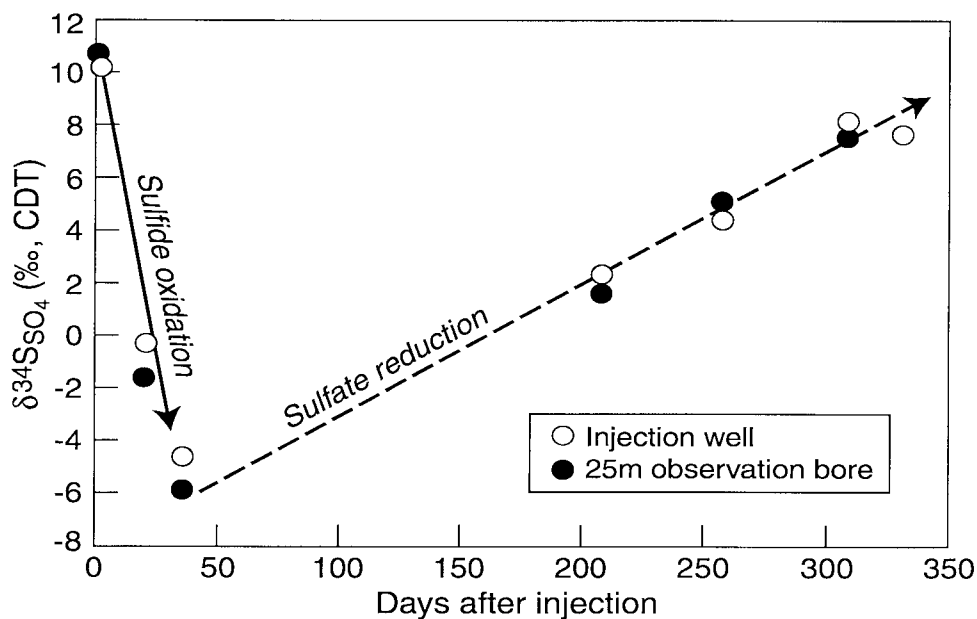


Fig. 8. Changes in  $\delta^{34}\text{S}$  of dissolved sulfate over a 1-year period following injection of stormwater to the aquifer at Andrews Farm.

There is an initial large negative shift in sulphur isotopic composition of about — 16‰ over a period of 40 days following injection of stormwater into the aquifer (Fig. 8). This is almost certainly due to oxidation of ‘light’ sulphur in sulphide minerals disseminated throughout the aquifer. At the same time, a substantial amount of Ca and Mg was released to

to dissolution of carbonate minerals, partly related to generation of acidity during sulfide mineral oxidation. For the remainder of the year of monitoring of sulfur isotopes, there was an increase in  $\delta^{34}\text{S}$ , which at face value indicates sulfate reduction, but only at the very end of the cycle was there any evidence of sulfate reduction (i.e., a negative calculated  $\text{SO}_4$  flux). The relationship between  $\delta^{34}\text{S}$  and amount of sulfate added or removed (Fig. 9) indicates a trend towards more positive  $\delta^{34}\text{S}$  values despite maintenance of a small, but significant net addition of sulfate to the aquifer.

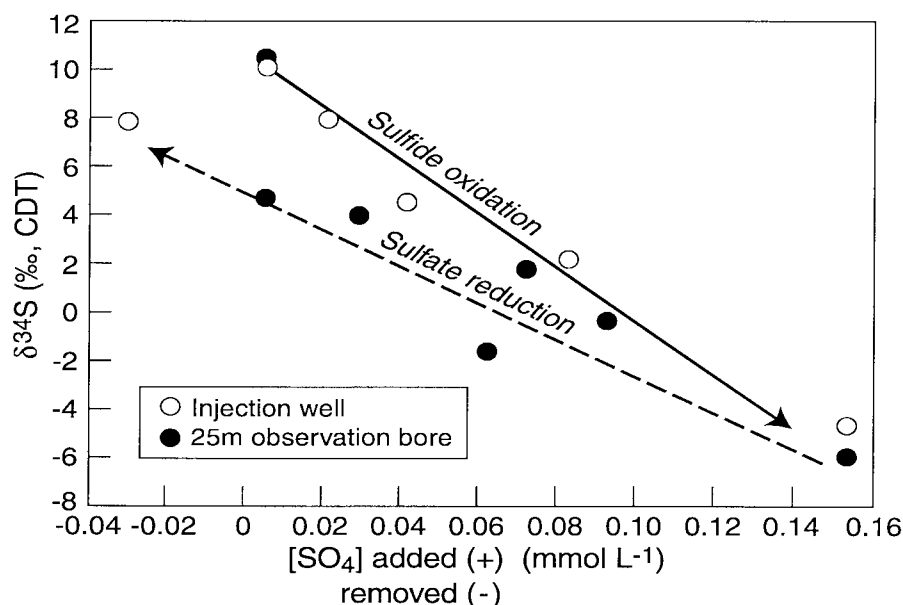


Fig. 9. Relationship between  $\delta^{34}\text{S}$  and mass transfer of sulfate following injection of stormwater to the tertiary aquifer at Andrews Farm.

The relationship shown in Fig 9 shows a negative inverse correlation between calculated  $\text{SO}_4$  excess concentrations and  $\delta^{34}\text{S}$  values. That is, higher values of  $\text{SO}_4$  excess concentrations correspond to more negative  $\delta^{34}\text{S}$  values. The increasing trend of  $\delta^{34}\text{S}$  concentration corresponds to a trend towards sulphate reduction (i.e., negative “excess” values), while maintaining net  $\text{SO}_4$  concentrations in the positive side of the ledger. Assuming that there is no error in the mass balance calculations (which is possible given the small  $\text{SO}_4$  excess residuals) the interpretation is not self-evident. There cannot be sulfide oxidation and sulfate reduction occurring simultaneously. It is possible that there are two processes occurring concurrently: net addition of sulfur during entrainment of native groundwater during the post recharge period, and sulfate reduction.

## 5 CONCLUSIONS

The combined use of geochemical and isotopic techniques in field investigations of aquifer storage and recovery operations are highly informative and essential for the assessment of such operations. These are used both for estimating the extent of mixing between two water types (using  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$ ) and chloride ion. The use of both is recommended, but each has special value according to different field situations and/or the type of information required. For long term, spatially averaged information, chloride ion data is preferred, provided there is sufficient chloride contrast between recharge waters and native groundwaters. For specific

information on the fate and mixing of waters from a given injection event, stable isotopes of water are preferred. Furthermore, this is the only option where Cl concentrations in both water types are similar.

As far as the biogeochemical reaction processes are concerned, the reaction sequence can be divided into two distinct phases:

- (1) During or immediately following injection there is an acid producing phase, (CO<sub>2</sub> production, sulfide oxidation and carbonate dissolution)
- (2) Further anaerobic organic matter oxidation accompanied by mobilisation of Fe, sulphate reduction and carbonate precipitation.

These processes can be traced using mass balance calculations (incorporating geochemical codes such as PHREEQC or NETPATH) as well as isotopes of carbon (<sup>12</sup>C, <sup>13</sup>C, <sup>14</sup>C) and sulfur (<sup>32</sup>S, <sup>34</sup>S). The isotope data provide special information regarding the main processes controlling minerals dissolution and redox processes. Particularly, sulfur isotopes hold great promise in situations where there is injection into an anaerobic aquifer.

As far as this field study site is concerned, there is apparent dissolution of carbonate matrix at Andrews farm inferred from the mass balance calculations, the amount of calcite dissolved due to that process alone is <0.001% of the total rock matrix to the dominance of rock mass over that of solutes dissolved in water. However, an increase in transmissivity may occur especially if the calcite acts as cement to bind minerals such as quartz, which may be mobilised especially during pumping. Changes in aquifer transmissivity could also be affected by the amount of particulate matter injected, and reactions involving Fe/Mn oxy-hydroxides.

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# **The combined use of chemical and isotopic information to model the effects of stormwater infiltration on groundwater quality in an urban fractured rock aquifer, Auckland, New Zealand**

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## **Abstract**

Disposal of storm water in the Mt Eden area of Auckland, New Zealand, is via “soak holes” drilled directly into the top of fractured basalt. Although this method of disposal has been used for at least 60 years, its sustainability with respect to groundwater quality has not been addressed. The groundwater has relatively low concentrations of dissolved heavy metals, although total metals are higher suggesting that the metals are bound to mobile particulates within the aquifer. PAH concentrations are also low in the aquifer, although sampling after rainfall events show small increases in PAH. Tritium measurements of the groundwater showed that all of the groundwater south of Chamberlin Park is less than 2 years old. This area has many soak holes. The data suggest that infiltration is very rapid and occurs throughout the area almost simultaneously after rainfall events. One well north of Chamberlin Park, where soak holes are absent has an age of 47 years  $\pm$  2 years. The groundwater here is low in dissolved oxygen and appears to be slow moving. CFC measurements indicate that all wells sampled south of Chamberlin Park are contaminated by excess CFCs. However, this result indicates rapid recharge from the surface via storm water. The same well north of Chamberlin Park that was dated using tritium, also has a CFC age of approximately 30 years. Thus, CFC dating may be useful in urban areas that are separated from atmospheric contamination by confining beds or slow circulation. A Kohonen self-organising feature maps (KSOFM) neural network was used to analyse the effect on storm water infiltration on groundwater quality, and determine the inter-relationship of the groundwater quality variables. The model shows that where the land use type is industrial or residential with many soak holes, there is a strong correlation of increased concentrations of heavy metals and storm water infiltration.

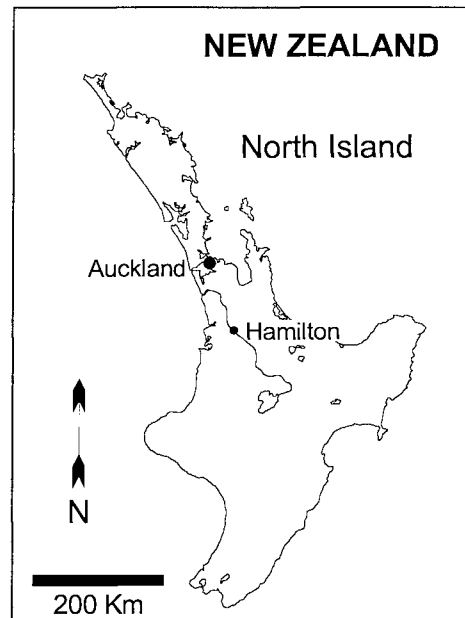
## **KEYWORDS**

Storm water infiltration, tritium, stable isotopes, CFC, heavy metals, PAH, groundwater quality, fractured rock, Auckland, urban setting, artificial neural network modelling

## **1. INTRODUCTION**

Disposal of storm water in the Mt Eden area of Auckland is via direct soakage into “soak holes” drilled into fractured basalt. Reticulation of the system is limited to short pathways under roads and gardens. Although surface water contamination is lessened the effects on groundwater quality are unknown. It has been suggested that there are benefits of direct soakage to the groundwater system as well as possible negative effects [1, 2, 3]. The main benefit is an increase in recharge to the shallow aquifer. This means that the resource is replenished at a much higher rate than most New Zealand aquifers due to the direct storm water soakage. The principle adverse effect is the cumulative point addition of contaminants to the groundwater system through the numerous soak holes. Soak holes collect sediment and storm water runoff from city streets throughout Mt Eden and Onehunga wherever shallow, highly permeable, fractured-rock basalt aquifers are available. Although this method of storm water disposal has been used for at least 60 years, its sustainability with respect to groundwater quality has not been addressed.

Auckland is located in the North Island (Figure 1), and is New Zealand's largest city, with a population of over 1 million people in the greater metropolitan area. The issue of storm water disposal and sewage reticulation infrastructure is important in the city because many areas of the city still have combined storm water and sewage pipelines, which need upgrading or replacing, and because resource consents for storm water and sewage discharge is currently being sought by the city council. In order to obtain resource consents for these discharges, New Zealand law requires that any adverse environmental effects are avoided or mitigated [4]. Therefore, the identification of the effects of storm water discharge to the Mt Eden aquifer is important in assessing the terms of these consents.



*Figure 1: The North Island of New Zealand showing the location of Auckland.*

This study aimed to determine the impacts of storm water runoff on the chemical composition of the groundwater by using several complimentary techniques including the use of naturally occurring stable and radioactive isotopes, chlorofluorocarbons (CFCs), hydrochemistry and modelling. In addition, analyses of sediments captured by the soak holes were examined to determine their effectiveness at trapping contaminants.

Because of the variety of variables observed as groundwater quality data (referred to as multivariate or multi-dimensional data), and the complexity and uncertainty involved in storm water infiltration, transport, and reaction mechanism into groundwater systems, it is necessary to use a modelling tool that can provide the analysis and visualization of multi-dimensional groundwater quality data. Indeed, it was impossible to determine the immediate effect of storm water infiltration to the Mt Eden aquifer using conventional observational and statistical methods because of the variability in the data [5]. The use of knowledge extraction and diagnosis techniques, in our case an artificial neural network (ANN) technique, can assist a decision-maker by analysing the multi-dimensional data and turning the information into simple visual information that can be used to manage the groundwater system sustainably.

## 2. PREVIOUS WORK

Few water quality evaluations have been conducted in the Mt Eden aquifer. Limited chemical analyses from 1925 and 1936 from an artesian spring in Western Springs Lake has been reported [6]. Additional springs, surface water and two new wells drilled into the basalt aquifer at Parrish Road and Eden Park were analysed [7]. Analyses for some heavy metals were conducted at that time. However,

groundwater sampling techniques used at the time did not allow for possible contamination from metal sampling gear and atmospheric contamination. Purging techniques for the groundwater wells were also inadequate to obtain representative samples.

Water was analysed from three new wells constructed as a possible drinking water supply at Chamberlin Park [8]. They found that the water quality was generally high, but that cadmium and bromate were present in excess of the New Zealand Maximum Acceptable Value (MAV) for drinking water. Chemical analyses, including total heavy metal analyses, from 7 new wells constructed down the groundwater flow gradient within the Western Springs aquifer were reported [9]. These wells are the same wells sampled for this study. [9] also conducted the first modelling of the Mt Eden aquifer using Visual MODFLOW. Much of the groundwater flow data used in this study is derived from this work.

### 3. GEOLOGICAL & URBAN SETTING

The study area is in Mt Eden, which is an inner suburb of Auckland on the North Island of New Zealand (Figure 2). The geology of the groundwater aquifer system is comprised of fractured basalt, scoria and tuff, from small volcanic cones (Mt Eden, Mt Albert, Three Kings) that were active about 20,000 years ago. Sandstone and siltstone sediments of the Miocene Waitemata Group underlie the basalt. Waitemata Group sediments have relatively low permeability and act as a barrier to groundwater flow [6]. Groundwater flows through the fractured basalt in a shallow, unconfined aquifer system that is channelled through topographic lows in the Mt Eden area. The aquifer system has two separate arms that meet at the Western Springs outlet (Figure 2). Groundwater flow is from south to north (Figure 3). Mt Eden and Three Kings craters are the recharge areas for the two arms of the basalt flows that are part of this study. Groundwater discharge from the basalt flows is at Western Springs, Meola Creek and offshore into Waitamata Harbour (Figure 3). Land use in the catchment is mostly residential housing, but significant pockets of industry also occur. The area includes some of the most heavily travelled roads in New Zealand [9].

Mt Eden is located in the Meola or Western Springs Catchment (Figure 2) and is one of the older suburbs of Auckland. Western Springs itself, located in the discharge area of the catchment, supplied water to the city of Auckland up until 1928 [7]. After 1928, the population of Auckland increased to a size that made the water supply from Western Springs unsuitable. In addition, contamination problems at the spring site made the water unfit to drink. Although most of Auckland now derives its drinking water from surface water held in dams around the city, groundwater is still an important water source for industry and certain residential areas, such as Onehunga. Approximately 10% of the city use groundwater for their drinking water supply.

Groundwater from the Mt Eden aquifer system has a relatively high through-flow and is used for small domestic water supplies and irrigation water for industrial uses such as nurseries and golf courses in the region. The transmissivity of the aquifer in the Three Kings cone area (Figure 2), which is the recharge area of the aquifer, has been calculated to be almost 24,000 m<sup>2</sup>/d [10]. It is estimated that in excess of 10<sup>7</sup> m<sup>3</sup> of groundwater is stored within the Three Kings volcanic cone itself. It was also estimated that the transmissivity of the basalt flow aquifers from Three Kings crater and Mt. Eden ranges from 68 to 4800 m<sup>2</sup>/d [3]. Pump tests conducted by the Auckland Regional Council indicate that hydraulic conductivity ranges from 6 m/d to 126 m/d, with an average of approximately 58 m/d. On average, 2500 m<sup>3</sup>/d is contributed by rainfall within the crater and a recharge has been calculated of 68800 m<sup>3</sup>/d for the whole aquifer based on the present recharge including storm water soakage [10, 3]. A calculation of pre-urbanisation recharge rates indicates that recharge to the aquifer has doubled because of the storm water soak holes [3].

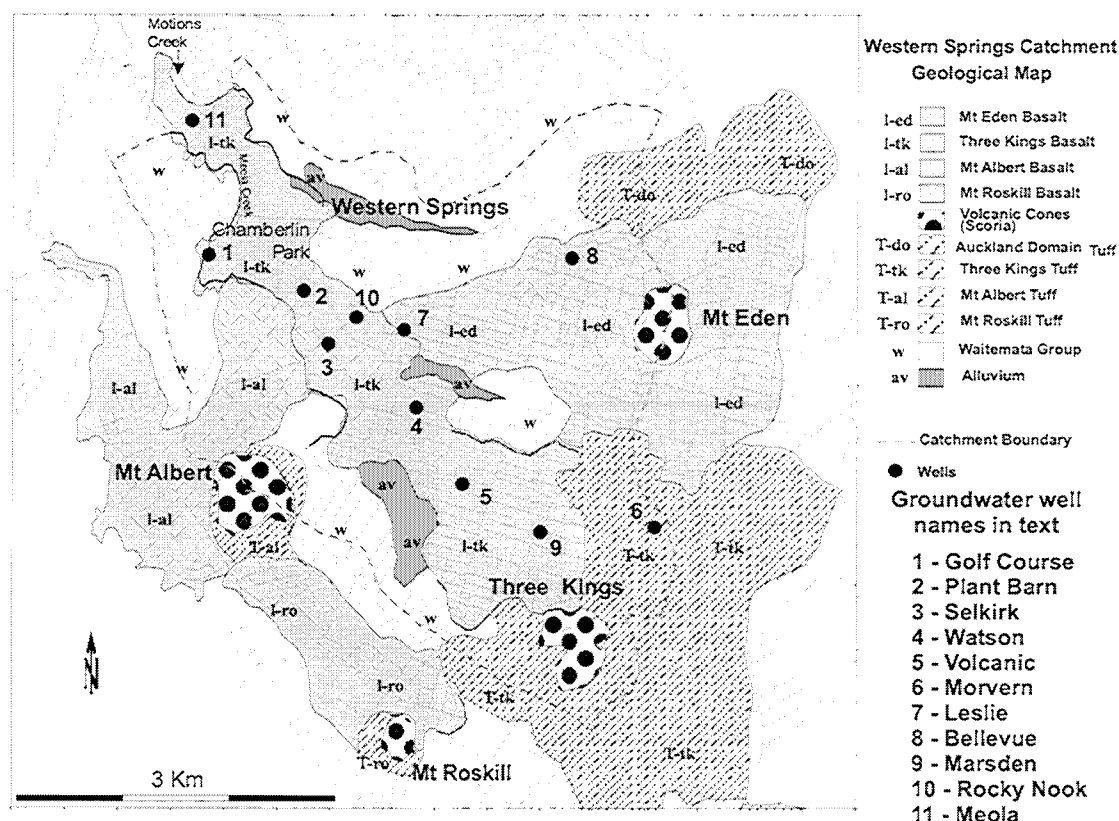


Figure 2: Geologic map of the Western Springs catchment and aquifer showing the location of groundwater sampling sites.

Urban residential dwellings with pockets of industrial activities and parks dominate Land use in the Western Springs catchment. Land use information has been compiled and is used here to illustrate the potential areas of contamination from storm water input [9]. Land use is divided into 3 categories; residential, commercial (or industrial) and parks and open land (reserves, sports fields). Storm water disposal via discharge from the area (via reticulated storm water pipes) occurs in areas of the catchment that are underlain by Waitemata Group sediments that have a low permeability. This area accounts for 47% of the catchment. Disposal via ground soakage (either into soak holes or through the surface) occurs in the rest of the catchment, which is underlain by volcanic rocks. The total catchment area is approximately 21 km<sup>2</sup> [9] and the total area where ground soakage occurs within the catchment is 11.2 km<sup>2</sup>. The soakage area is made up of 8.3 km<sup>2</sup> of residential housing, 0.7 km<sup>2</sup> of commercial activities, 2.2 km<sup>2</sup> of parkland.

## 4. METHODS

### 4.1 Groundwater sampling

Clean sampling techniques were used to avoid contamination of samples by sources outside of the groundwater environment [11]. These techniques involved the use of two people in the sampling team to avoid contamination, the use of clean suits and gloves to minimise contamination from the samplers, acid washed sample bottles, and pre-cleaned teflon sampling gear where possible when collecting samples for heavy metals. Blind duplicate samples and field blanks were taken on all sampling rounds and all wells were purged until at least 3 times the casing volume was evacuated from the well. Some samples were collected using a teflon bailer, and other were taken using a submersible pump. The submersible pump was made of stainless steel, but contact with the groundwater sample was minimal. Duplicate samples using both techniques on the same well were taken to determine which method was more suitable.

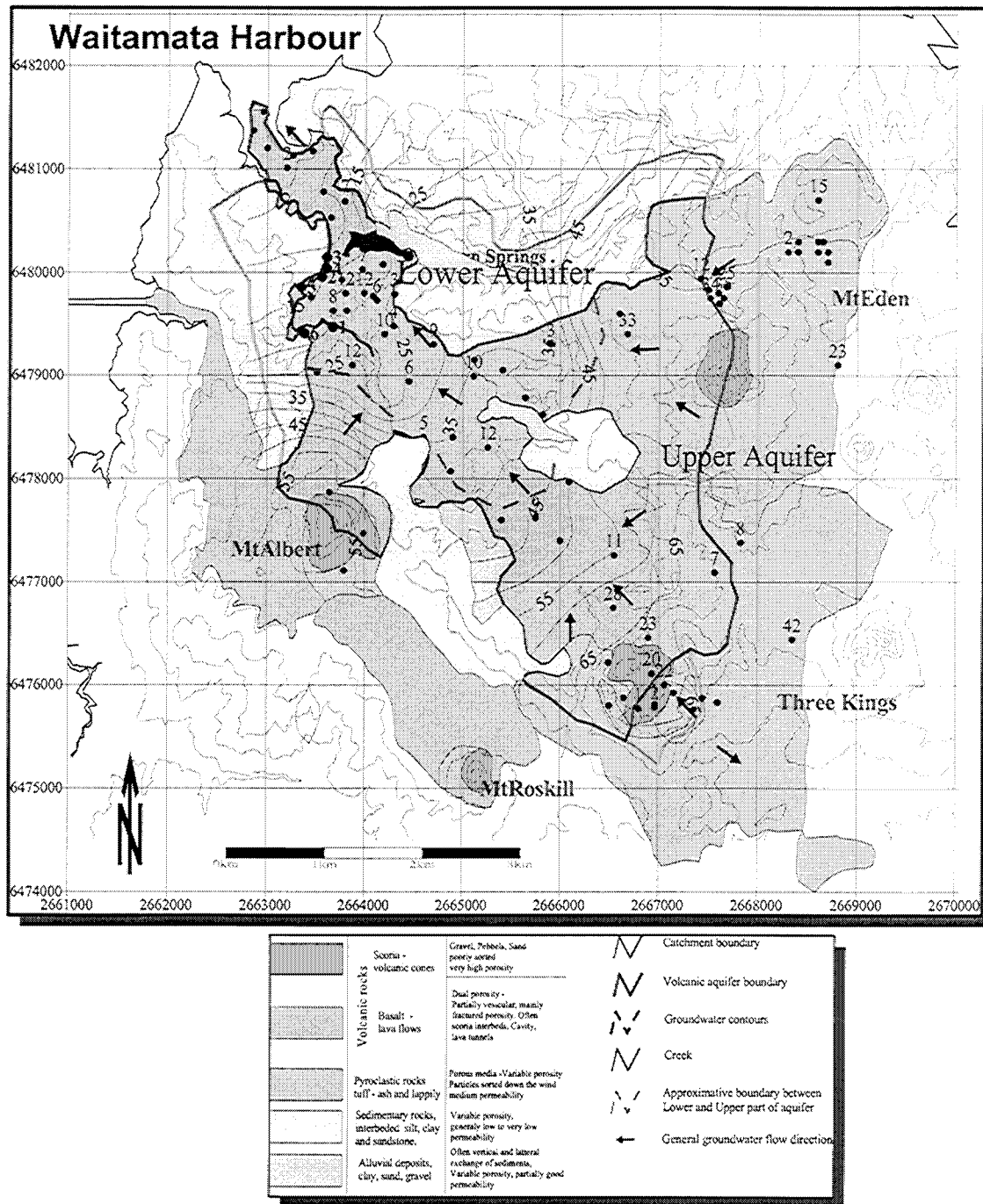


Figure 3: Geology and groundwater flow directions for the Mt Eden aquifer. Numbers by the wells represent the thickness of the aquifer. Groundwater flow is generally to the north. Not wells used for water levels could be sampled for chemistry. Drawing modified from [9].

The results from these trials are presented in Section 5.2. Conductivity, pH, dissolved oxygen and temperature were measured in the field, and samples for dissolved metal analyses were field filtered and acidified.

In addition to baseline sample collection (4 collections), samples were collected after 3 rainstorm events one in October 1998 (22 mm of rain), one in April 1999 (8 mm of rain), and the last in August 1999 (26 mm of rain). Samples were collected from the same well on three consecutive days after the rainfall event.

Samples were analysed for major cations and anions, nutrients (NO<sub>3</sub>-N, PO<sub>4</sub>, NH<sub>4</sub>-N) total and dissolved metals (Cu, Cr, As, Pb, Ni, Zn, Cd), polyaromatic hydrocarbons (PAH), stable isotopes ( $\delta^{18}\text{O}$ ,  $\delta^2\text{H}$ ), tritium and CFCs. Alkalinity measurements were made by titration on the evening after sample collection. Not all of the parameters mentioned were analysed on every sample. Samples were analysed by ICP-OES and AA (major cations), ion chromatography (anions), and ICP-MS (heavy metals). PAH groundwater samples were analysed using a GC-MS in SIM mode after either solid phase or liquid-liquid extraction (depending on the sediment load in the sample).

Samples for stable isotope analyses were collected directly into clean, 28 mL glass McCartney bottles. Analyses of  $\delta^{18}\text{O}$  in water samples were carried out by isotopically equilibrating the water with carbon dioxide gas at 29°C, and analysing the carbon dioxide using an NAA mass spectrometer [12]. Analyses of  $\delta^2\text{H}$  in water samples were conducted by quantitatively converting the water to hydrogen gas by reaction with zinc at 500°C in individual reaction tubes [13]. The hydrogen was isotopically analysed using a Micromass 602C mass spectrometer. Results are reported in  $\delta$  notation relative to V-SMOW (Vienna-standard mean ocean water; [14]) where

$$\delta^{18}\text{O} \text{ ‰} = [({}^{18}\text{O}/{}^{16}\text{O})_{\text{sample}}/({}^{18}\text{O}/{}^{16}\text{O})_{\text{V-SMOW}} - 1] \times 1000 \quad (1)$$

and similarly for  $\delta^2\text{H}$ . The standard deviation of measurement is  $\pm 0.1\text{‰}$  for  $\delta^{18}\text{O}$  and  $\pm 1\text{‰}$  for  $\delta^2\text{H}$ . The results have been normalised assuming  $\delta^{18}\text{O} = -55.5\text{‰}$  and  $\delta^2\text{H} = -428\text{‰}$  for SLAP (standard light Antarctic precipitation) relative to V-SMOW.

Samples for tritium analysis were collected in clean 1.1 L glass containers with teflon sealed lids. Counting was achieved using liquid scintillation counters. Concentrations of  $^3\text{H}$  are reported as Tritium Ratios (TR) at the date of sample collection  $\pm 1$  standard measurement error, using the scale recommended [15]. TR = 1 corresponds to a T/H ratio of  $10^{-18}$ .

Sufficient sensitivity and accuracy for detection of tritium is necessary to make use of low-level natural tritium as a tracer of the hydrologic cycle. Because of the low tritium concentrations prevailing in New Zealand's surface waters we have established at the Institute of Geological & Nuclear Sciences Ltd. (GNS) a tritium measurement system with extremely high detection sensitivity. The lower detection limit is 0.03 TU using Ultra Low-level Liquid Scintillation Spectrometry, and electrolytic enrichment prior to detection. One litre of water is required for analysis. Reproducibility of a standard enrichment is 2%, and an accuracy of 1% can be achieved via deuterium calibrated enrichment [16].

CFCs Chlorofluorocarbons or CFCs are entirely man-made contaminants of the atmosphere and hydrological systems. CFCs are used industrially for refrigeration, air conditioning and pressurising aerosol cans. Their concentrations in the atmosphere have gradually increased from zero in 1940 to the present as CFC use increased. Because the gases (CFC-11, CFC-12 and CFC-113) are relatively long-lived, they are widely distributed in the atmosphere. CFCs are slightly soluble in water and enter groundwater systems along with water during recharge. Their concentrations in groundwater record the atmospheric concentrations when the water was recharged. However the solubility of CFCs is controlled by temperature. Therefore it is important to know the recharge temperature of the water entering the aquifer. The average temperature of the groundwater in the Mt Eden aquifer is known to be 12.5 °C. This temperature was used for all ages determined. This allows the recharge date of the water to be determined.

Water samples for CFC concentration measurements were collected in such a way as to prevent contact with the atmosphere or with plastic materials, either of which could contaminate the sample with CFCs. The samples are preserved in the field by sealing them into 62 mL borosilicate glass ampoules at the well site. The sampling apparatus is connected to the well outlet by copper tubing. All other tubing in contact with the water during sampling is stainless steel. The ampoule is attached to the sampling apparatus and flushed with ultra-high-purity nitrogen gas. The well water is then allowed to flow through the tubing and valves and into the bottom of the ampoule displacing the nitrogen. The ampoule is rinsed

with several hundred ml of water, then nitrogen is forced into the neck to displace some of the water. The ampoule is then fused shut about 1-2 cm above the water level with an oxy/acetylene gas torch. Nitrogen flows continually across the union to prevent any contamination with air. Five ampoules are normally collected at each sampling site. The CFC samples were analysed at GNS by gas chromatography.

CFC age determinations were made on groundwater from all wells except Morvern and Marsden. These wells did not have a continuous supply of water that could be pumped without allowing atmospheric contamination.

The results of all chemical and isotopic analyses are presented in Appendix I.

## **4.2 Soak hole sediment sampling**

Sediment cores from four storm water sediment traps (soak holes) were collected by pushing or gently hammering 40 mm PVC into the top of the sediment. The depths of the cores varied widely from 90 cm at the Bellevue-D soak hole to only 10 cm at the Morven-D soak holes. This variability was determined by the depth of sediment in the catch-pits together with an inability to penetrate very dense sediment in very confined circumstances.

The tubes were sealed immediately upon withdrawal and placed in containers with ice-packs for transport to the laboratory and refrigerated until sampled. The outer layer of the core, where smearing and cross-contamination was likely, was removed (usually to a depth of 5 mm) to expose the undisturbed sediment. Large included components, such as leaves, stones and any debris from the sampling or sub-sampling process (particularly saw cuttings of PVC) were removed and the loosened layers which contained such material were rejected. The surface layers were primarily composed of such material and the rejected material is not considered to contain significant chemical contaminants. Only plastic tools were used. No metal tools or objects were allowed to contact the samples at any stage prior to analysis. Control samples were taken from sub-soils at various locations throughout the catchment. The samples were taken at what appeared to be pristine soils in the sides or base of trenches or cuttings open on the day of sampling. Other exposures in cliff-faces or slip sites were also sampled. Sub-soils only were sampled, and there is a strong possibility that some sites had been disturbed or affected by construction or other activities.

Sub-samples were taken for analysis for inorganic and organic components. The samples for inorganic analysis were dried in an oven at 60°C then sieved to remove material >2mm and the finer fraction retained. The pH and conductivity of the sediment was determined by adding deionised water to a dried, sieved sample (10 grams in 25 mL of water) and inserting the respective calibrated electrodes [17]. A further 20 g of sample was ground and analysed for major and trace element components, using X-ray fluorescence and by ICP-MS for Cd and Hg after digestion. A further 5 g of sample was analysed for C and N analysis.

Leachable trace metal components were determined on some sub-samples by shaking 1 g of dried sample with 25 mL of 0.1 M HCl. The leachates were decanted and analysed by ICP-MS. The sub-samples were selected to detect differences between base, mid and surface sediments in the cores.

The results of all sediment analyses are presented in Appendix II.

## **4.3 Modelling**

Generally, multivariate analysis methods such as factor analysis [18, 19], and principal component analyses (PCA) [20] have been used for modelling contaminant transport in hydrological and groundwater systems. Due to the rapid innovation of computer technology, the artificial neural network (ANN) technique, which is a powerful tool for multivariate, nonlinear analysis and modelling, has recently attracted considerable attention in analysis and diagnosis of dynamic systems. ANN is one of a group of intelligence technologies for data analysis and modelling that differ from other classical analysis techniques by learning about user's chosen subject from the given data, rather than

being programmed by the user in a traditional sense. ANN offers the ability of gathering its knowledge by detecting the patterns and relationships from a given data set, learning from relationships and adapting to change. ANN techniques outperform current methods of analysis because they can successfully: (1) deal with the non-linearities of the system, (2) be developed from data without requiring the mechanistic knowledge of the system, (3) handle noisy or irregular data, (4) be easily and quickly updated, and (5) interpret information from multiple variables or parameters [21].

The aim of the current model is to analyse the effect on the storm water infiltration due to rainfall events on the groundwater quality.

#### 4.3.1 Kohonen's Self-Organising Feature Maps (KSOFM) Neural Network

Neural networks are used for two main tasks in engineering applications: 1) function approximation and 2) pattern classification. In function approximation, the neural network is trained to approximate a mapping of its inputs and outputs. Many neural network models have been proven to be universal approximators, *i.e.*, the network can approximate any continuous function arbitrary well. The pattern classification application can be regarded as a specific case of the function approximation. The mapping is done from the input space to a finite number of output classes.

Currently, there have been a wide variety of neural networks that are being studied. Based on characteristics, such as the class of inputs, the method of training, and weight updating procedures. Neural network architectures have been classified into three categories based on models of the human nervous system [22] (Figure 4). In Figure 4, *feedforward networks* transform sets of input signals into sets of output signals. The desired input-output transformation is usually determined by external, supervised adjustment of the system parameters. In feedback networks (recurrent), the input information defines the initial activity state of a feedback system. After state transitions, the asymptotic final state is identified as the outcome of the computation. In competitive, unsupervised or self-organizing category cells (neurons), the neighbouring cells (neurons) in the network compete in their activities and develop iteratively specific detectors for different input signal patterns.

Competitive neural networks are designed to solve the type of problems where the output we require is unknown (unsupervised learning) the output required in such a situation are clusters or categories into which the input falls depending on its similarity with other input. If we use the unsupervised learning algorithm and place the neurons in some sort of order such as a line or a grid, we may wish to use information regarding the locations of the nearby winning output units to determine the similarity of input vectors in  $n$ -dimensional space. For example, if  $E_1$  and  $E_2$  are two input vectors, and  $U_1$  and  $U_2$  are the locations of the corresponding winning outputs then  $U_1$  and  $U_2$  should get closer as  $E_1$  and  $E_2$  get closer. Neural Networks such as this are called feature maps. The principle idea behind feature maps is to create a neural network with topology preserving characteristics. A topographic map attempts to preserve the neighbourhood relationships between the input and output spaces. This is of course not entirely possible when the input space is of a higher dimension than the output space. Feature maps are trained on input vectors using rules that aim to iteratively arrange the neurons in the maps so as to approximate the aforementioned properties. Thus the paradigm is often referred to as self-organizing maps. The ideas behind the model were first suggested [23] as a method of solving the retinotopic map problem. A simplified and more widely used model was developed [22, 24].



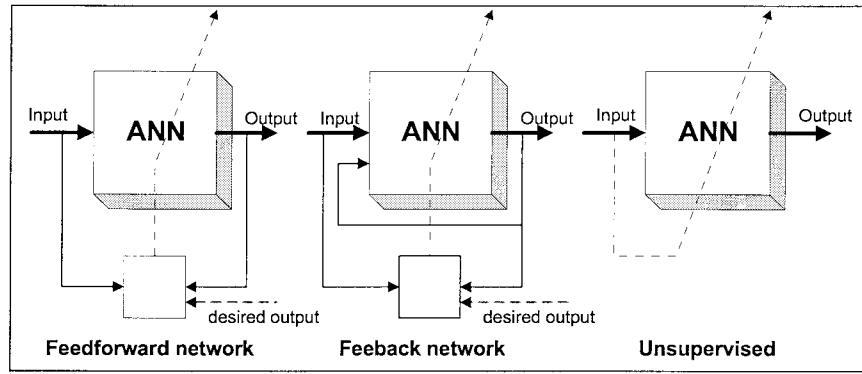


Figure 4: Neural network models (dotted line illustrates the training scheme).

Details of how the model for this project has been developed and applied can be found in [25].

#### 4.3.2 Visualisation of neural networks

Because of the important role that humans have in the process of knowledge extraction from the data, visualisation plays an essential role in analysing the results or reporting the results based on the knowledge extracted. The most important features of the KSOFM are its visualisation capabilities. There are a variety of different kinds of visualisation techniques available for the KSOFM. Two different kinds of presentation of the map: (1) the component planes [26] and (2) the U-matrix [27] are commonly used for the KSOFM.

Component plane representation visualises relative component values of the weight vectors. The illustration can be considered as a sliced version of the map, where each plane shows the distribution of one weight vector component. This representation gives information on the distribution of the component values, and allows direct visual inspection and helps to see correlation between components by viewing several component planes at the same time.

The U-matrix is also a good method for visualising the clusters in KSOFM. In the U-matrix method, a matrix of distances between the weight vectors of map units and their neighbours is calculated. By showing this matrix, the relative distances between map nodes on the whole map can be seen.

In this work, the component planes and the U-matrix are used to diagnose which of the groundwater quality variables are affected by the storm water infiltration and to see how the groundwater quality variables relate to each other. All simulation is done using SOM Toolbox ([www.cis.hut.fi/projects/somtoolbox/](http://www.cis.hut.fi/projects/somtoolbox/)) for use with MATLAB<sup>TM</sup>.

#### 4.3.3 Data pre-processing

Raw data obtained from the field collection of chemical data from the Mt Eden aquifer system consists generally of many groundwater quality variables (in our case, over 20 variables) such as concentrations, pH, rainfall, groundwater level, etc (Appendix I). Each of these variables is measured in different units having different magnitudes. If raw data are fed into the KSOFM, then variables having a larger magnitude are given unequal importance due to the nature of the weight update procedure. Standardising the dynamic range of each variable in the input vector by using data transformation techniques is required and ensures that any movements in a given direction in feature space are co-measurable. In this work, if  $X_i$  [ $i=1,2, \dots, n$ ] is an input variable sequence, then the scaled values  $U_s$ , are obtained as:

$$U_s = \frac{X_i - X_{mean}}{X_{st.dev}} \quad (2)$$

This scaling results in the data being scaled with zero mean and unit variance. The output of the KSOFM is recalled to return data to its original mean and variance.

## 5. RESULTS

### 5.1 Water samples

#### 5.1.1 Inorganic parameters

The dissolved components of Mt Eden water are dominantly Na, Ca, Mg,  $\text{HCO}_3$  and Cl and so the water can be classified as a sodium-bicarbonate-chloride-type water. Water from the Morvern St well, which is taken from volcanic tuff is characterised as a calcium-sodium-bicarbonate-type water. Sodium is enriched relative to the seawater concentration-dilution line (SCDL), but storm water plots along the SCDL (Figure 5a). The major element composition of the groundwater shows a strong correlation between sodium and potassium (Figure 5b), which indicates dissolution of feldspars and reflects the basaltic nature of the aquifer. Calcium and magnesium are present in solution at about the same equivalent concentration except in the Morvern well, which contains Ca as the dominate cation (Figure 5c).

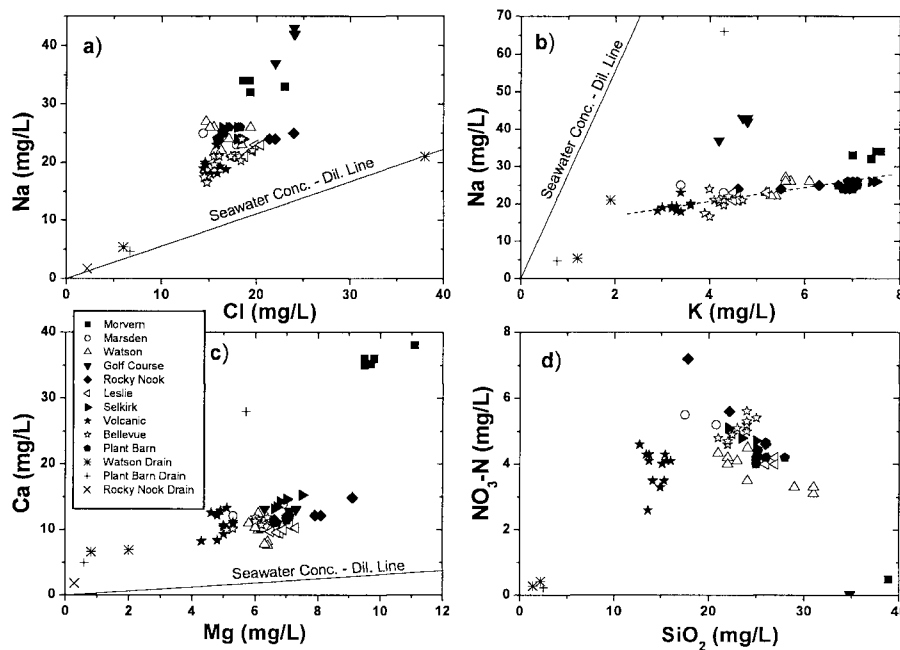


Figure 5: Cross plots of a) Na versus Cl, b) Na versus K, c) Ca versus Mg, and d)  $\text{NO}_3\text{-N}$  versus silica for groundwater wells and storm water drain samples. The seawater concentration-dilution line is plotted for reference in a-c.

Water quality in the Mt Eden aquifer is generally of good quality. However, samples collected from the Meola well show an unusual chemical composition of the groundwater that is unlike the water collected from all other wells (see Appendix 1). There is a closed unlined landfill near this well and it is likely that the chemical and isotopic composition of the water from this well has been effected by landfill leachate. The exceptionally high alkalinity, chloride, and potassium concentrations point to leachate as the cause of the different chemical composition. For this reason, the water from the Meola well will not be considered in the discussion and will not be plotted.

It has been recognised that nitrate concentrations were higher than natural background nitrate concentrations [7] (Figure 5d). Interestingly, the relatively high nitrate concentrations (approximately 5 mg/L NO<sub>3</sub>-N) have not changed significantly from 1925 to the present (1999). Total heavy metals were first analysed by [7] and then by [8] and [9]. Dissolved metals were not measured in any of the previous studies. Heavy metal concentrations are generally low (Figures 6a-d) for groundwater collected in an urban aquifer, and all but certain total and dissolved Pb concentrations (Figure 6a) are below maximum acceptable values (MAV) [28]. Heavy metal concentrations are higher in the eastern arm of the aquifer (Bellevue and Leslie wells) than in the southern arm (from Three Kings cone). Metal and PAH concentrations do not increase down the groundwater gradient towards Western Springs. Nitrate concentrations do, however, increase towards the north in the southern arm of the aquifer up to the Golf Course well. Nitrate concentrations also show a curious antithetic relationship with silica (Figure 5d) for many wells. An explanation for this relationship is not obvious. Measurements of storm water NO<sub>3</sub>-N in the Mt Eden area indicate that storm water does not contain much nitrate (Figure 5d). Nitrate concentrations in the Golf Course well are low (<1 mg/L NO<sub>3</sub>-N), but dissolved oxygen concentrations are also low in the water in this well.

Wells react to storm water input in various ways depending on location and chemical species. Total Pb concentrations generally increase during the first day and then decrease in the next two days (Figure 6a). Nitrate concentrations are more stable, but generally decrease after rainfall (Figure 6b). Total Zn concentrations vary depending on the well (Figure 6c), and PAH concentrations generally increase by the second or third day after rainwater input (Figure 6d). Because of the complex pattern of heavy metal concentrations after rainfall events, the KSOFM modelling described above was employed to determine if rainfall influenced metal concentrations (see Section 5.4).

Dissolved metal concentrations are much lower than total metal concentrations (Figure 7a) except at high Zn concentrations, dissolved concentrations are approximately equal to total Zn concentrations (Figure 7b). At low concentrations, total Zn concentrations are greater than dissolved Zn concentrations.

### 5.1.2 Isotopes

Stable isotopes were measured on groundwater under baseline conditions (no rainfall) and during rainfall events (storm water recharge events). It was hoped that a distinct isotopic signature would occur after storm water recharge events due to temperature differences between the groundwater and the rainwater. Unfortunately, this was not the case as the isotopic signature of the groundwater was not different from baseline conditions after rainfall events. A few measurements of the isotopic composition of storm water showed large variations between rainfall events (Figure 8), but the isotopic composition of the groundwater didn't change much. The Meola well plotted above the local Pukekohe Meteoric Water Line (PMWL) (Figure 8), but the chemical and isotopic composition of the water in this well has been influenced by leachate from a nearby closed landfill (see Section 5.1.1). When groundwater samples were compared with regional rainfall isotopic compositions from Pukekohe (located approximate 50 km south of Auckland), no differences could be distinguished and the isotopic composition of the Mt Eden aquifer water fell on the PMWL (Figure 8).

The stable isotopic composition of groundwater after rainfall events did not vary significantly or show definitive trends (Figures 9a and b). This was because both deuterium and oxygen varied less than the error in the analyses (see Appendix 1) so it is difficult to attribute changes to any actual trend. In general, the isotopic composition of the groundwater reflected the regional rainfall input. Storm water infiltration could not be distinguished isotopically.

Sampling of selected wells for tritium isotopes indicated that all of the wells south of Chamberlin Park (see Figure 2) are less than 1 year old. The Bellevue well has an age of 1 year although the age may be between 0 and 1.5 yrs, but is most likely 1yr. Selkirk/Volcanic/Watson Ave. wells have an age of 1 year but may be between an age of 0 and 3 years. Theoretically it is possible for these tritium concentrations to represent the bomb-tritium peak increase, in which case the water would be 39 years old, or the bomb-tritium peak decrease, in which case the water would be 21 years old.

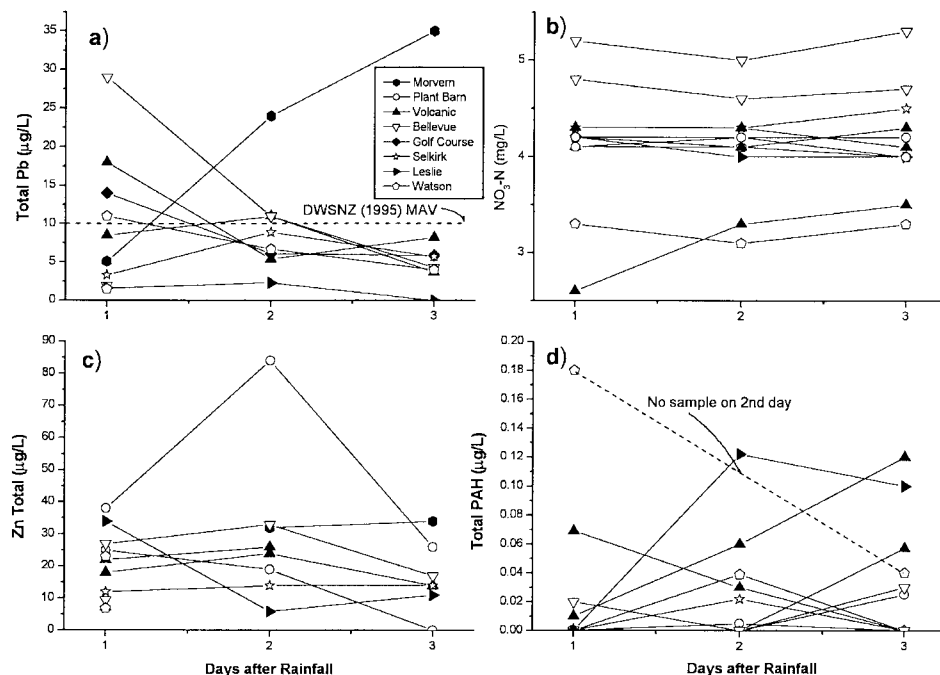


Figure 6: Concentrations of a) total Pb, b) NO<sub>3</sub>-N, c) total Zn, and d) total PAH after rainfall events. Not all wells were sampled during each rainfall event. Some wells were sampled during more than one rainfall event. Wells have the same symbol on each graph (µg/L = ppb).

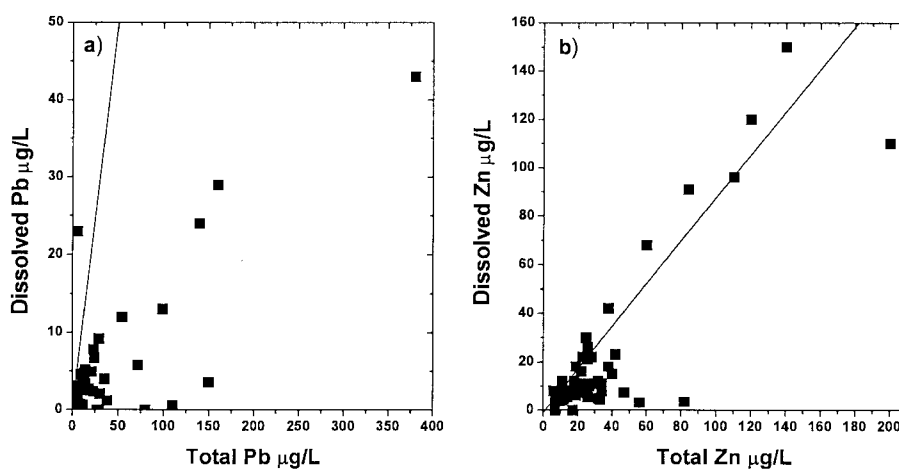


Figure 7: Dissolved metal concentrations a) Pb and b) Zn plotted against total metal concentrations for the same element. Straight line represents 1:1 correlation. Total Pb concentrations are higher than dissolved concentrations, whereas total Zn concentrations are higher than dissolved concentrations only at low concentrations (µg/L = ppb).

But there are two reasons why this is unlikely. First, the steep in/decrease at the bomb peak allows us to obtain very exact dates in this range ( $\pm 1$  year). It is very unlikely that all four samples are exactly 39 or 21 years old. The second reason is that the hydrologic situation probably does not allow this high age in this part of the aquifer.

The Golf Course well has a tritium age of  $47 \pm 2$  years. There is no other age possibility to explain this low tritium concentration. If the hydrologic situation for this sample is more represented by mixing, than the age will turn into a mean residence time (which will be much higher than 47 yrs).

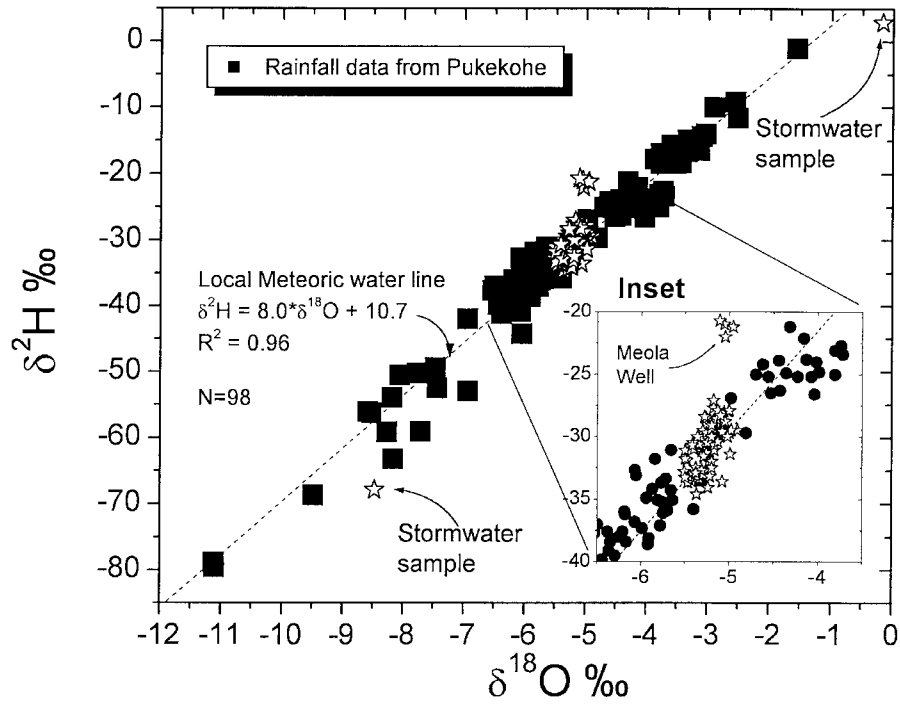


Figure 8: Plot of  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}$  for rainfall from Pukekohe (squares, circles in inset) and groundwater and storm water from the Mt Eden area (stars). Note the relatively consistent composition of groundwater and variable composition of rainwater and storm water. The Pukekohe meteoric water line (PMWL) is plotted for reference. The PMWL is almost identical to the Global Meteoric Water Line. The isotopic composition of the Meola well (see inset) is probably effected by landfill leachate.

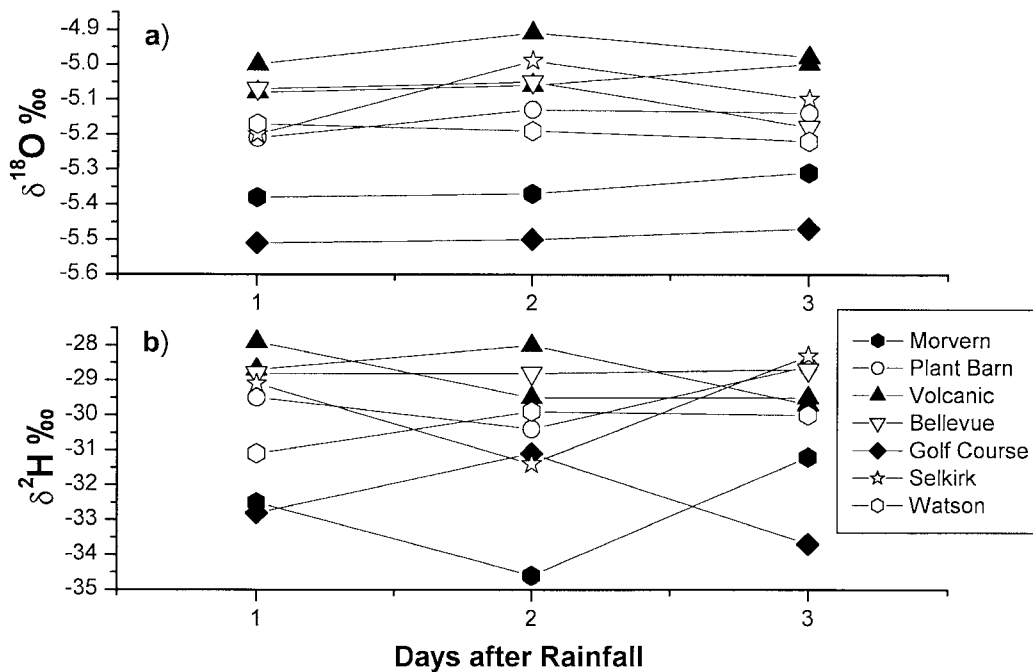


Figure 9: Trends of a)  $\delta^{18}\text{O}$  and b)  $\delta^2\text{H}$  for three days after rainfall events. There are no consistent trends and variations are generally less than the error of the measurement ( $\pm 0.1$  ‰ for  $\delta^{18}\text{O}$ , and  $\pm 1$  ‰ for  $\delta^2\text{H}$ ).

In the ages obtained a model using a combination of 85% piston-flow and 15% diffusive flow (exponential model) was used. The exponential model represents mixing, so the combination of the two models allows some mixing. In nature, there is no pure piston flow in groundwater. The 15% mixing is a result of using a model adapted from data from the Hutt Valley aquifer near Wellington, where long-term tritium data are available. This aquifer represents probably the maximum possible piston flow in nature, and is a good approximation for the piston-flow like nature of storm water infiltration in the Mt Eden aquifer system.

Measurement of CFCs indicated that most of the wells are contaminated by excess CFCs that are common in urban environments. However, a few of the wells (Volcanic, Golf Course and Watson) give useful ages. Volcanic and Watson give modern CFC ages, which are in agreement with the modern tritium ages. The Golf Course well indicates an age of at least 25 years (CFC-12), and possibly almost 40 years (CFC-11) depending on whether the CFC-11 or CFC-12 age calculation is used. Experience in New Zealand and elsewhere has shown that the CFC-12 ages are more reliable [29, 30]. In either case however, the CFC dates for the Golf course well suggests water being pumped from the well is older than the samples analysed from the rest of the aquifer south of Chamberin Park. This conclusion is in agreement with the tritium age determinations.

### **5.3 Comparison of bailed and pumped sample collection techniques**

In order to determine the best sampling technique to recover representative samples for heavy metal analyses. Sampling from the same well was done using both manual and automated methods. A teflon® bailer lowered down the well on a teflon® string was used for the manual method, and a Grundfos® stainless steel submersible pump with a teflon® hose attachment was used for the automated method. Although the submersible pump did have stainless steel in contact with the water, the ability of the pump to deliver water constantly and with minimal disturbance of the sediment in the well seemed like a promising sampling technique.

Figures 10a-d illustrate the difference in sampling techniques for total metal concentrations for four wells (Golf Course, Leslie, Selkirk and Bellevue). Although the manual technique had no metal in contact with the sample during sampling total metal concentrations of lead and copper were always much higher for the bailed samples than the pumped samples. Zinc, which is a main component of stainless steel, should have been higher in the pumped samples, but in 2 of the 3 samples tested, Zn concentrations were higher in the bailed sample. The Bellevue sample in particular had much higher concentrations of total metals from the bailed sample than the pumped sample (Figures 10a-d). The Zn concentrations were greater than 4 times higher in the bailed sample, the Pb was 10 times higher and the Cr was 5 times higher.

The results indicate that the more gentle action of pumping the well using a submersible pump will yield better results for metal concentrations of the groundwater than bailing, even when a teflon® bailer is used. This is because the act of bailing the well disturbs sediment that has accumulated at the bottom of the well. The metals bound to the sediment are incorporated into the sample and analysed. These sediments may not be representative of the entire aquifer condition, but may represent the accumulation of metals associated with either the drilling of the well, or because of storm water infiltration carrying contaminated sediment directly to the well.

### **5.4 Sediment samples**

The major component analyses are typical of soils/sediments derived from the basaltic lava underlying the catchment [31]. The total carbon and nitrogen concentrations vary greatly in the soak hole cores. They are generally higher in the surface layers except for the Plantbarn core, which is more “organic” at its base. Except for some surface sub-samples, all soils are very mildly acidic.

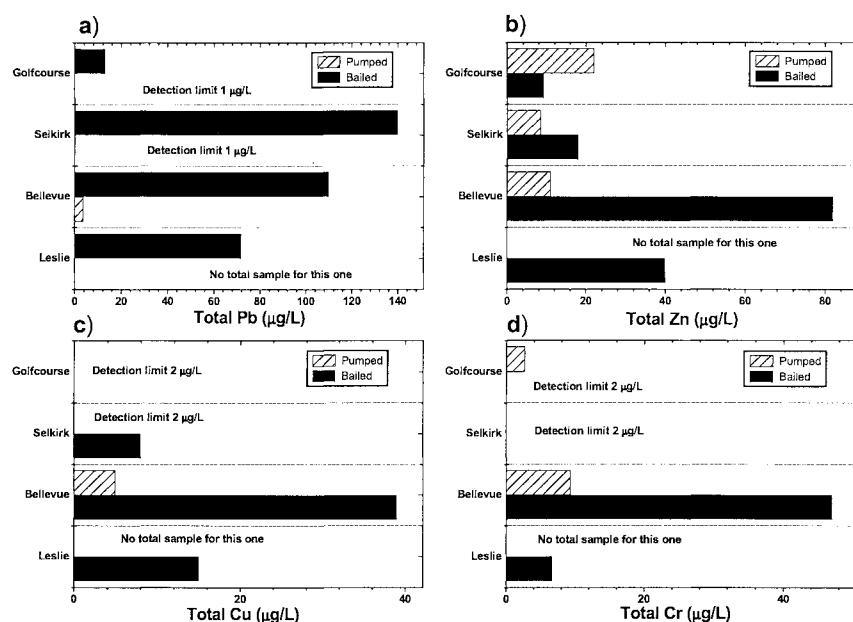


Figure 10: Comparison of the total heavy metal concentrations of a) Pb, b) Zn, c) Cu, and d) Cr, in groundwater using a bailer and a submersible pump ( $\mu\text{g/L} = \text{ppb}$ ).

The total levels of trace metals in the sediments (Figures 11a and b) may be compared with the ANZECC high and low Interim Sediment Quality Guidelines (ISQG) for total metal contents [32]. On the basis of the ISQG, the metals of concern in the soak hole sediments are Pb, Cu and Zn, and to a lesser extent the metalloid As, being intermediate and significantly higher than the controls.

It is recommend the development of guidelines be based upon leachates, and suggested 1.0 M HCl be the leaching acid [32]. Guidelines have yet to be developed, hence the use of total concentrations. The need for guidelines based on leachates is to differentiate between bio-available and immobile metals of which the former is of most concern. In this study, the issue is the potential for the sediments in the soak holes to contribute contaminants to the underlying aquifer, so the mild leach of 0.1 M HCl was used as some compromise strength. Figures 12a-d compare the total and the leached metal concentrations in the sediments and the controls.

Leached As concentrations falls in the same range as the controls for all but the single sample from the Morvern soak hole, which is from 5-10 cm below the surface. It is very much an outlier, with the total concentration being one of the highest. Most control samples gave similar leached Cd concentrations. Most other samples analysed gave values of leached Cd higher than the control samples, and indeed many were considerably higher ( $> 2x$ ). The implication is that the sediments have accumulated small quantities of Cd in all soak holes sampled except Morvern, and that this Cd is potentially mobile.

Lead in all soak hole samples (Figure 12a), with the exception of that from Morvern, is considerably higher than in the native sub-soils and the leachable fraction is proportional to the total Pb content. Zinc gives a similar picture, albeit not so clearly (Figure 12b).

Samples from the Plantbarn and the Bellevue soak hole cores have considerably higher ( $> 7x$ ) leached Cu contents compared to the control samples, and there is a strong positive relationship between total and leached Cu (Figure 12c). Leached Ni is higher than the controls in all the Bellvue sediment samples analysed, and marginally higher in the surface sample from the Plantbarn soak hole (Figure 12d). Ni, like Cr, is naturally concentrated in basaltic minerals, but like Cr, it is potentially more mobile in the soak hole sediments than in most of the native soils. There is no clear relationship between total and leachable Ni concentrations.

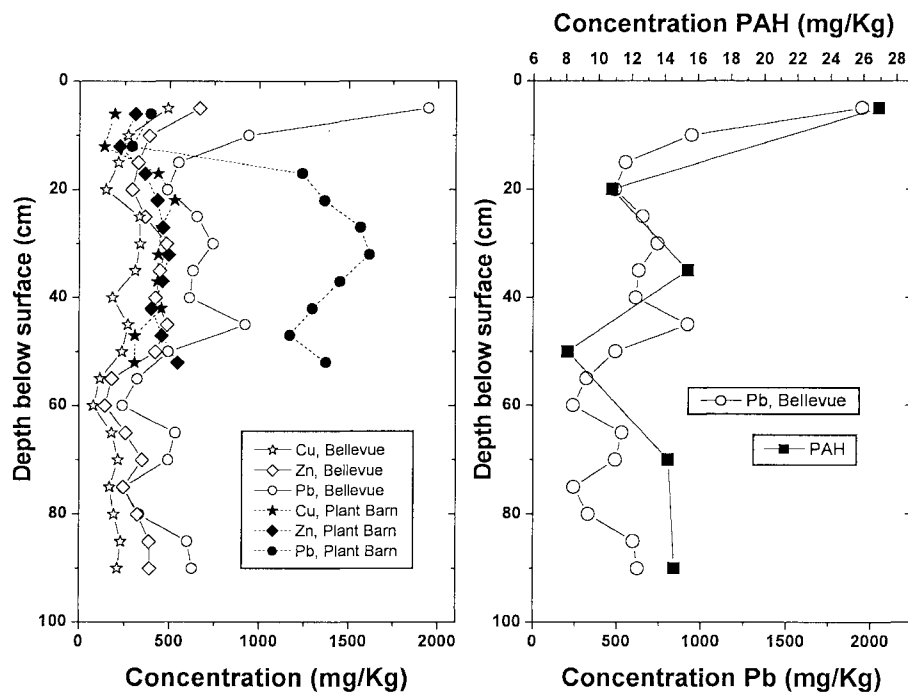


Figure 11: Depth profiles of a) Cu, Pb and Zn from two sediment cores taken from soak holes, note the similar curves for each element in each core, and b) comparison of PAH profiles with Pb concentrations from the Bellevue core (Plant Barn profile is similar). (mg/Kg = ppb).

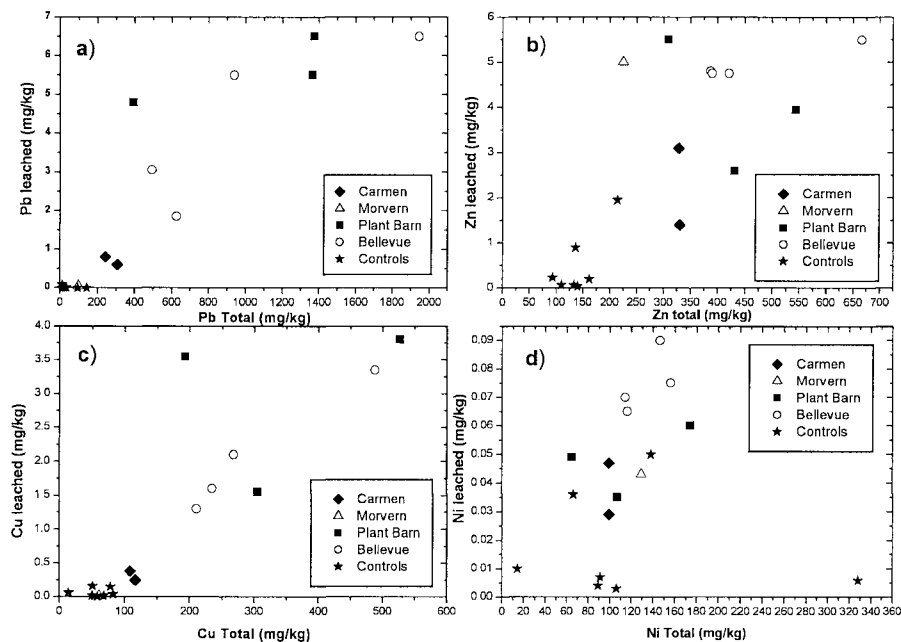


Figure 12: Leaching tests of sediment using 0.1 M HCL: a) Pb, b) Zn, c) Cu, and d) Ni. Results for As, Cd, and Cr are not shown (mg/Kg = ppb).



## 5.4 ANN modelling

Initially, the data set collected from Watson Ave. site (Figure 2) was used to analyse the effect on the storm water infiltration through soak holes on groundwater quality variables after the rainfall events and to understand the dependencies between the groundwater quality variables. The data set collected from the Watson Ave. site has 21 variables or components. These 21 components in the data file were used to create the map. The Watson data set consisted of 21-dimensional vectors.

The size of the map gradually grows to 10x7 in size during the training process. The total number of nodes (70) in the hexagonal grid is displayed. After a map has been created, the component planes are placed serially to analyse the dependencies between components. The component planes for the Watson site, which is a mix of residential with commercial and minor light industrial activities, are displayed in Figure 13. In each component plane, each hexagon represents one map node, and its colour tells the value of the component in that node. Hexagons in each place on different component planes correspond to the same map node and show the values of the components in the weight vector of that node. Each component plane window represents the local average component value at each node in a certain colour. The colour beside the picture shows the relationship between colour and component values. In Figure 13 the nodes that represent the high values are in red and those representing the low values are coloured blue.

From Figure 13 of special interest are correlations between rainfall and heavy metals concentration and the distribution of values in the components corresponding to the relatively high rainfall. By comparing component planes, component planes of heavy metals (Cu-t, Pb-t, Cu-d, Pb-d, Zn-d, and Cd-d) have similar distributions over the map with the rainfall plane. It means that heavy metal components in Watson site are highly correlated with rainfall. Areas of the map with high values of those heavy metals show high rainfall values indicating that the heavy metals are influenced by the rainfall event. An increase in the heavy metals due to rainfall indicates that storm water is a major source that increases the concentration of heavy metals observed in the groundwater aquifer.

For illustration, let us take a look at component windows for Zn-d and rainfall in Figure 13. In Figure 13, Zn-d and Zn-t denote dissolved Zn and total Zn, respectively. The baseline concentrations of Zn-d (deep blue colour in top right of Zn-d plane corresponding to group A in U-matrix), which represents the concentration at no rainfall event (deep blue colour in top right of rainfall plane corresponding to group A in U-matrix) are recorded in the range of 7.5 to 24 ppb. When the rainfall is low within the range of mean 0 to 5 mm/hr (blue marked area corresponding to group B and C in U-matrix), the concentration of Zinc-d has not changed much. However, the concentration of Zn-d is significantly affected and increased up to 130 ppb (deep red colour in top left of Zn-d plane corresponding to group D) in the case of the high rainfall event (deep red colour in top left of rainfall plane corresponding to group D). The concentrations of Cu-d have fluctuated from 2.8 to 4.48 ppb with the lower rainfall, and have varied up to 12 ppb with the higher rainfall. In the case of Cd-d, it is seen that the concentration of Cd-d is stable (with the range of approximately 0.06 to 0.9 ppb) and increased as the rainfall increased. For Pb-d, the baseline concentrations have fluctuation between approximately 1.5 and 5 ppb whereas the high concentrations are in excess of 10 ppb according to the value of rainfall.

The KSOFM was applied to the Volcanic Rd. site, which has the same aquifer conditions as for the Watson site shown in Table 1. From Figure 14, heavy metal concentrations, in particular dissolved metal concentrations, are strongly associated with the high rainfall events. Ca, Mg, Silica, NO<sub>3</sub>-N, and SO<sub>4</sub>, are inversely related to rainfall. Because of the similar aquifer condition, pattern analysis of the groundwater quality variables at the Volcanic Rd. site (Figure 14) shows same inter-relationships as found in the Watson Ave. site.

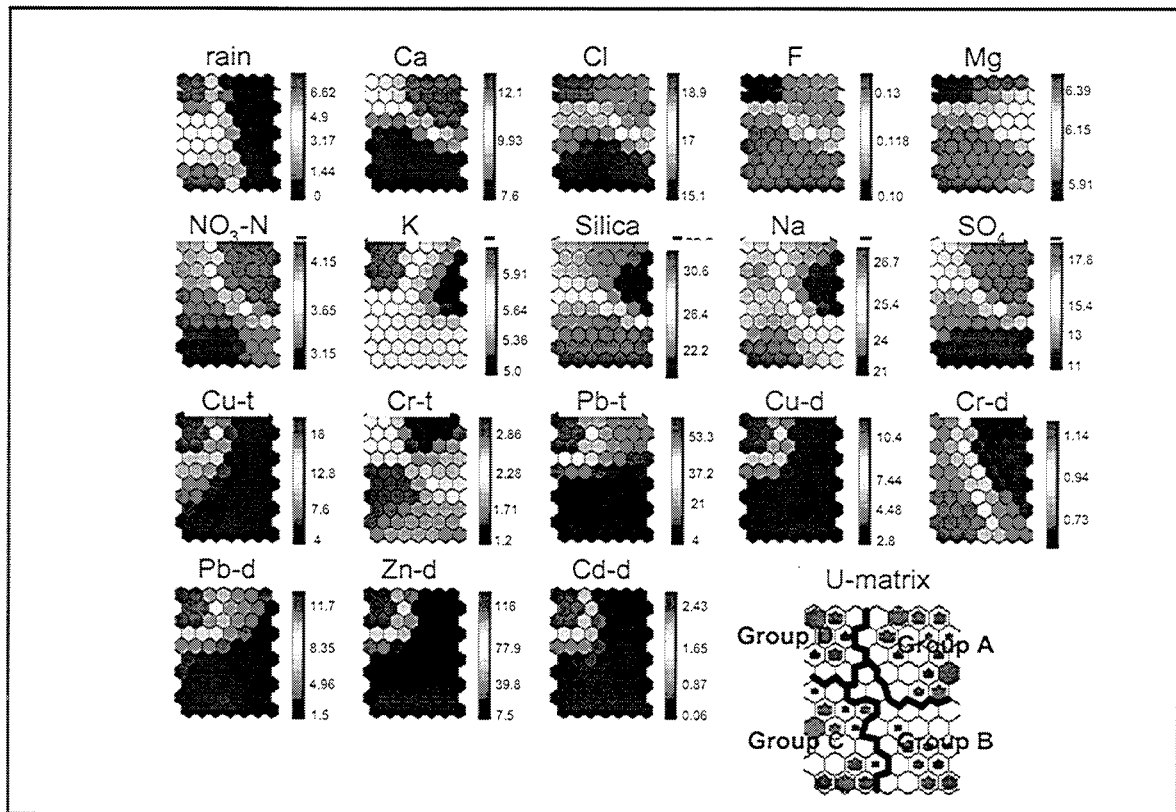


Figure 13: Component planes and U-matrix visualisations for the Watson Ave. site. (*t* and *d* denote total and dissolved, respectively). Units for rainfall are millimetres and for metals are ppb.

The simulation was also done for other monitoring sites (Leslie Ave. and Bellevue Res.). Only the results of the Watson and Volcanic sites are displayed because the pattern distributions of the groundwater quality variables from Leslie Ave. and Bellevue sites are similar to those of the Watson and Volcanic sites.

The Ca, Cl, SO<sub>4</sub> and NO<sub>3</sub>-N component planes have similar patterns to each other and do not follow the pattern distribution of the heavy metals. These ions show an obvious inverse relationship with rainfall. In the component plane of nitrate-nitrogen, areas of the map with the highest values of nitrate show low rainfall values and vice versa. It can be seen that the baseline concentration of nitrate has a mean of 4.30 mg/L (deep red colour in top right of nitrate plane) whereas the nitrate concentrations with high rainfall decrease in the range of 3.0 to 3.15 mg/L. This relationship was also noted based on graphical analysis of the NO<sub>3</sub>-N data [33, 5]. They concluded that nitrate concentrations are being diluted by storm water input that is low in nitrogen. This is because it has been shown that nitrate concentrations in New Zealand storm water are a generally low [34]. Therefore, the likely source of nitrate-nitrogen to the aquifer is from leaking sewerage pipe connections or fertiliser applied to gardens and sports fields in the area. Each component of Mg, Na, F, and silica of a similar pattern to each other, but do not appear to be related to rainfall or other obvious forcing functions. Potassium does not follow any of the patterns exhibited by the other parameters and also does not correlate with rainfall.

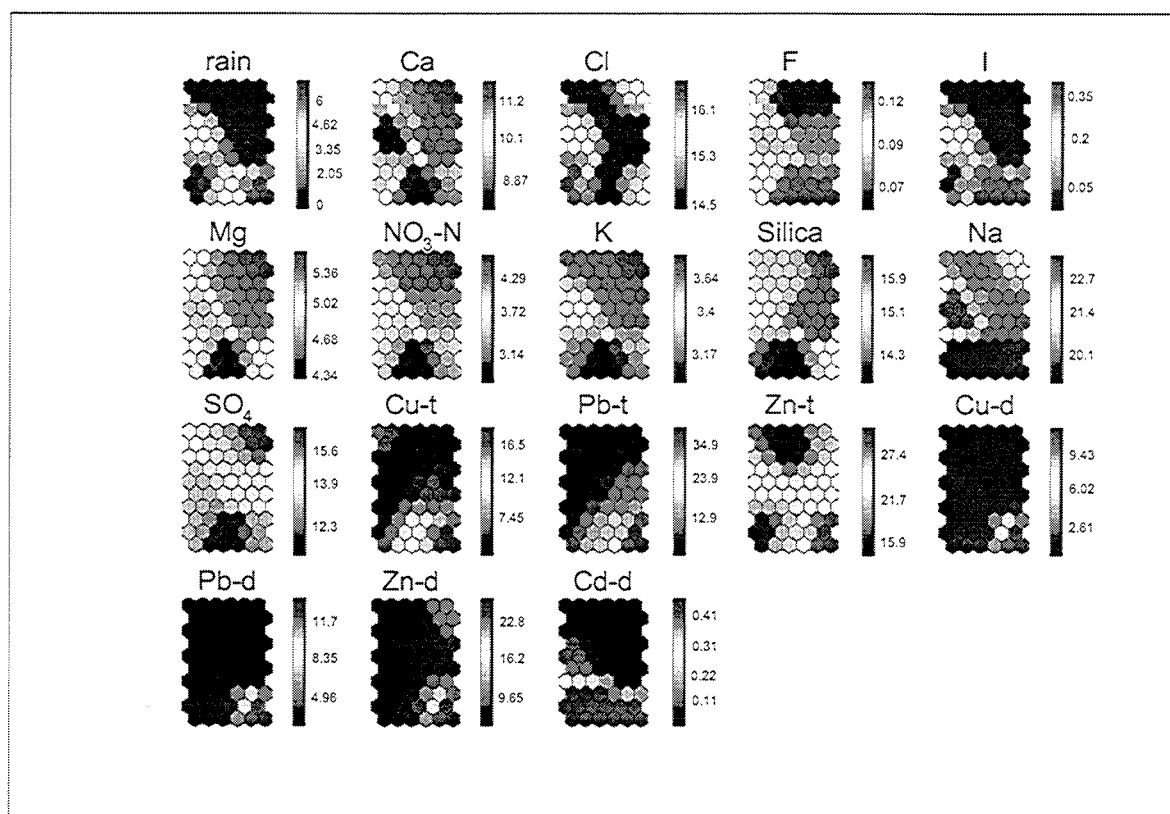


Figure 14: Component planes for Volcanic site. (t and d denote total and dissolved, respectively). Units for rainfall are millimetres and for metals are ppb.

## 6. DISCUSSION

### 6.1 Hydrochemistry

Comparison of major ions, metals and nutrients in groundwater samples taken during our study with the few samples analysed [7] indicates that water quality has not changed significantly in the Mt Eden aquifer for over 25 years, at least with respect to major components and nitrate, even with the loads caused by storm water infiltration. Indeed, for nitrate concentrations, they have not changed much since 1925. Although quantities of storm water infiltration would have been similar in 1976 to 1999, the contaminant loads may have been different. However, any changes in contaminant loads have not changed the chemical composition of the groundwater significantly. Sampling of groundwater after rainfall events appears to show short-term variations in groundwater chemistry, particularly for total metal concentrations and PAH. These variations tend to stabilise within the three day sampling period (Figures 6 a-d, see also modelling sections).

The concentration of nitrate (approximately 5 mg/L  $\text{NO}_3\text{-N}$ ) in the Mt Eden aquifer is similar to other areas of urban Auckland such as Onehunga to the southwest of Mt Eden and Three Kings volcanic cone [2, 35]. Higher nitrate levels throughout the area suggest a relatively ubiquitous source, possibly from a combination of sources such as leaks from the sewerage system, application of fertilisers in gardens and sports fields. However, nitrate concentrations in storm water are relatively low [34] indicating that storm water is not a major contributor to the high nitrate concentrations observed in the groundwater.

The Morvern Street well and Golf Course wells appear to have different chemical compositions to the other wells. The Morvern Street well has higher metal concentrations, lower nutrient concentrations and higher calcium concentrations than the other wells sampled. Although the

variation in major element composition may be due to the different aquifer materials at this site (tuff rather than basalt), the higher metal and lower nutrient concentrations may be due to a larger influence of storm water infiltration at this well. The aquifer is particularly thin at this location and there is a small saturated thickness at this point in the aquifer. The Golf Course well has much lower dissolved oxygen and nitrate concentrations than the other wells and higher dissolved iron concentrations (Appendix I). The age of the water based on tritium measurements is also much older (>40 years) than the rest of the wells sampled [36, see isotope sections]. The reason for this is not clear, but the data suggest that reducing conditions have become established in this part of the aquifer and it is possible that nitrate is lost via denitrification processes. A source of carbon is necessary for denitrification to proceed. The lithology of the Golf Course well is not known, so it is impossible to say if a significant carbon source exists. However, storm water infiltration from soak holes upgradient of the well may be a source of carbon (see below). Regardless of the source of carbon, the low concentrations of both nitrate and ammonium suggest that denitrification is possible.

Analysis of the cores taken from the soak holes indicates that high concentrations of contaminants occur in the sediments collected. The contaminants are mostly associated with the organic fraction of the cores [36] suggesting that they are present due to storm water runoff (Figures 15a-d). Copper, As, Pb, Cd and Zn in particular are closely correlated with the organic fraction in the sediment (Figures 15b and c), but Cr and Ni show inverse trends (Figure 15a). Sodium, which is derived mostly from the basalt and sediment is inversely correlated with the organic fraction (Figure 15d) indicating that the bulk of the contaminants are not associated with the rock material, with the exception of Cr and Ni. Although many of the contaminants are leachable (particularly Pb, Zn and Cu) it is the build up of contaminated sediments in the soak holes that transfers suspended solids to the aquifer via fractures. These suspended solids are then analysed as total metal concentrations in the groundwater samples collected, although relatively high dissolved loads of Zn also occur. Storm water infiltration is also indicated by the presence of low concentrations of PAH in the groundwater analyses, because PAHs do not occur naturally in groundwater.

Although the solubility of PAH compounds is very low, their solubility in water can be significantly increased in the presence of dissolved organic carbon, at environmentally feasible concentrations [37]. Furthermore, this dissolved organic carbon also has the ability to enhance desorption of PAHs from low organic carbon sediments [38], such as the Mt Eden basalt aquifer. Analyses of the soakage pit sediments demonstrate that high concentrations of PAHs are correlated with high metal concentrations such as Pb (Figure 11b) and organic matter in the cores. This suggests that organic matter accumulations in soak holes could be important in determining the mobility of PAHs into the low organic carbon basalt aquifer.

Sediments are removed from soak holes at regular intervals in order to prevent flooding and to ensure rapid infiltration. It is this maintenance of the soak holes that appears to be critical in ensuring that contaminants don't build up in the aquifer. Accumulation of suspended sediments in the aquifer material must be avoided to prevent clogging of the aquifer and to ensure metal concentrations do not increase.

## **6.2 Isotopes and CFCs**

The stable isotope data collected for the study has not been able to be used to trace storm water infiltration into the aquifer. The main reason for this is because the groundwater isotopic composition is relatively uniform regardless of the composition of the rainwater falling on the catchment. Rainfall and storm water entering the groundwater in the Mt Eden area has a relatively large isotopic variation, but despite this the groundwater isotopic composition is essentially an average of all the recharge entering the aquifer. The reason for this is the relatively high storage of water in the aquifer compared with rainfall recharge at any given time. This means those large variations in the rainwater and storm water isotopic compositions can be easily assimilated into the average isotopic composition of the aquifer without changing the aquifer isotopic composition.

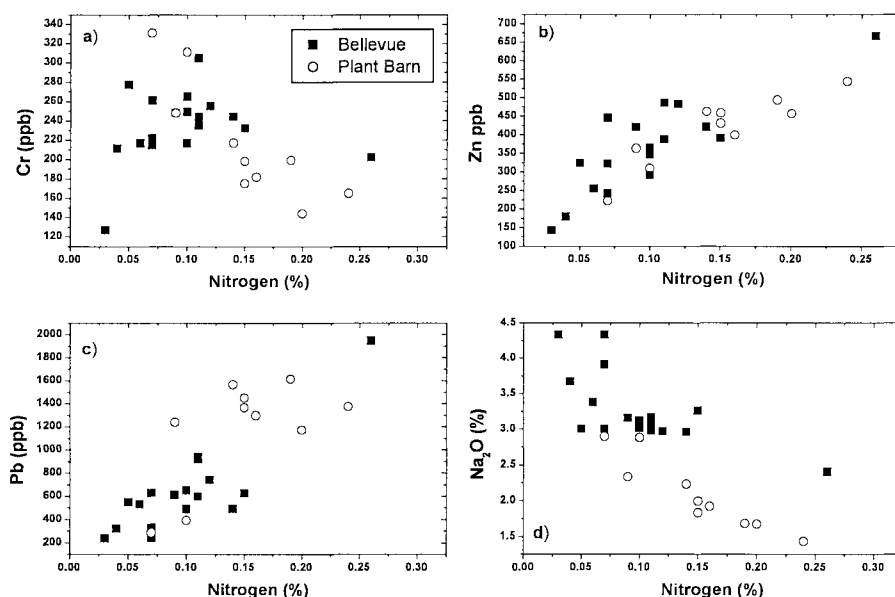


Figure 15: Plots of a) Cr, b) Zn, c) Pb and d) Na<sub>2</sub>O versus nitrogen for drain sediment core samples.

In addition, some rainfall events have isotopic compositions that are similar to the aquifer isotopic composition. During a rainfall event in October 1998 the isotopic composition of the groundwater in the Watson Ave. well was -5.2 ‰ for  $\delta^{18}\text{O}$  and -30 ‰ for  $\delta^2\text{H}$ , over the three day period of sampling (Appendix 1). But the storm water collected from the drain at Watson Ave. had an isotopic composition of -5.3 ‰ and -28 ‰ for  $\delta^{18}\text{O}$  and  $\delta^2\text{H}$  respectively. The difference between the groundwater and storm water was not sufficient to be able to detect it in the groundwater sampling.

There is very little spatial variation in isotopic composition between wells in the aquifer. The average  $\delta^{18}\text{O}$  composition of all wells sampled is between -5.1 ‰ and -5.3 ‰, except for the Golf Course well, which has an average  $\delta^{18}\text{O}$  value of -5.5 ‰. The Meola well (the one effected by the landfill) has an average  $\delta^{18}\text{O}$  composition of -5.0 ‰. The more positive value for this well is probably related to chemical reactions associated with landfill processes. The average  $\delta^2\text{H}$  composition of all wells lies within a narrow range of -29 ‰ to -34 ‰ (excluding Meola, which is -21 ‰). No systematic spatial variations can be seen in the  $\delta^2\text{H}$  data.

The tritium and CFC age determinations are similar for most wells sampled. The wells to the south of Chamberlin Park (Figure 2) all have modern tritium ages and either modern CFC dates or excess CFCs, which suggests the water is young. The Golf Course well has a model tritium age of 47 years but a CFC-12 age of less than 30 years, and CFC-11 age of almost 40 years. Atmospheric concentrations of CFC-12 and CFC-11 in the Southern Hemisphere in 1953 were lower than the measured concentrations in the sample. If the model tritium age is correct, this suggests that CFC ages represent some amount of contamination of CFCs at the time of recharge (1953). CFC-12 is more sensitive to contamination than CFC-11, which explains why the CFC-12 age appears to be younger than the CFC-11 age. In general, both the CFC and tritium dates indicate that the groundwater north of Chamberlin Park is much older than water to the south. The reason for this is not well understood, but two possibilities are that the aquifer becomes wider and deeper at this point and may allow for much slower movement of groundwater at this point in the aquifer. The other possibility is that the aquifer becomes confined at this point and water is slowed down because of a lack of space to accommodate new recharge water. The discharge of groundwater at Western Springs (Figure 2) suggests that some confinement of the aquifer is possible near this location. Although the CFC dating did not provide accurate ages of the groundwater, it did produce the same general pattern determined using the tritium method. This suggests that the CFC technique could be useful in limited situations in urban settings.

### 6.3 Modelling

We examine how the different land use type affects the groundwater quality. The well located at the Golf Course (Figure 16) shows different patterns to the other wells analysed (Figures 13 and 14). By comparing the component planes of heavy metals in Figures 13 & 14 and the component planes of heavy metals in Figure 16, we can investigate the effect of different land use types on the groundwater quality. From Table 1, we can see that the land use at the Golf Course site does not contain soak holes (no streets are present near the well) and the land use is mainly recreational (golf course) while that at Watson Ave. is industrial with many soak holes.

TABLE 1. INFORMATION ON SAMPLING WELLS

	Golf Course	Watson Ave.	Leslie Ave.	Bellevue Res.	Volcanic Rd.
RL casting	24.	40.5	36.5	67	46
Well diameter (mm)	100	100	50	50	100
RL Depth of well	-8	1.5	11	31	35.5
RWL	11.63	28.18	26.41	34.2	37.3
Aquifer thickness (m)	30	38.3	24	34.3	9
Land use type	park (golf course)	commercial	commercial	residential	residential
Stromwater & rainfall drainage type	Percolation of storm water into ground (no soakholes)	Storm water directly disposed into ground mainly through the soakholes	Storm water directly disposed into ground mainly through the soakholes	Storm water directly disposed into ground mainly through the soakholes	Storm water directly disposed into ground mainly through the soakholes

RL= relative level, RWL= relative water level

Unlike Watson and Volcanic sites, it is observed that component planes of Zn-d, Pb-d, and Cd-d in Golf Course site have a different pattern distribution with rainfall, indicating that they are not associated with the strong relationship with rainfall as found in Watson and Volcanic sites.

For example, the base concentration of Zn-d in Watson site in Figure 13 varies within a range from 7.7 to 12 ppb and at the Golf Course site in Figure 16 varies with a range from 1.8 to 5 ppb during the same sampling period. The Zn-d concentration in Watson site increases with high rainfall and reaches 137 ppb, which is the highest value found in the study. The Zn-d concentrations at the Golf Course site, however, varied slightly within a range of 4.2 to 8.5 ppb with the high rainfall, which is only slightly greater than the baseline concentrations. It seems to be that heavy metals concentration at the Golf Course site are not significantly related to the infiltration of storm water and may be affected by another source, for example, the lateral transport from other areas with soak holes. This result also shows that the difference of land use types and the existence of soak holes affect the heavy metals concentrations in the aquifer. Furthermore, these data suggest the importance of proper soak hole management, particularly of sediments in the soak holes, in order to prevent the transport of contaminants into the aquifer after rainfall events.

Like the Watson Ave. site, the pattern distribution of Na and Silica at the Golf Course site resembles each other. The component planes of Na and Cl in Figure 16 show that these elements at the Golf Course sites, which is close to the sea, are higher, respectively, by 37 to 43 mg/L and 22 to 24 mg/L than those in Watson site. It is interesting that a relatively high iron concentration (range of 1.8 to 3.3 mg/L) at the Golf Course site is detected while that in Watson Ave. is below 0.01 mg/L.

Furthermore, the nitrate concentration at the Golf Course site is very small (below 0.05 mg/L) while that in Watson and Volcanic sites is relatively high as shown in Figures 13 and 14. The relationship between high iron and low nitrate at the Golf Course site is caused by the relatively low dissolved oxygen concentration in this part of the aquifer. These data combined with the analysis of the component planes indicates that different aquifer conditions from those at the Watson and Volcanic Ave. sites control metal concentrations and water quality at the Golf Course site.

Like the Watson Ave. site, the component plane of Pb-t among the heavy metals at the Golf Course site has similar pattern distributions over the map with the rainfall plane indicating that it has a positive relationship with rainfall events. This may result from a possibly mixed effect of the storm water infiltration and transport from other sites.

Stable isotope data was also compared to all other chemical parameters and rainfall patterns to see if there is any complex relationship between isotopic signatures and rainfall in particular that could not be distinguished by visual inspection. Although there is limited data available for many sites, the ANN technique did not show any significant correlation between isotopic compositions and rainfall or chemical parameters.

#### *Clustering by U-matrix*

One important technique often used in knowledge extraction is a cluster analysis that generates the classifications automatically from the raw data. In this work, by comparing component planes with the U-matrix, the relationships between the variables within each cluster are analysed and the major characteristics of a cluster are also identified by applying statistical analysis.

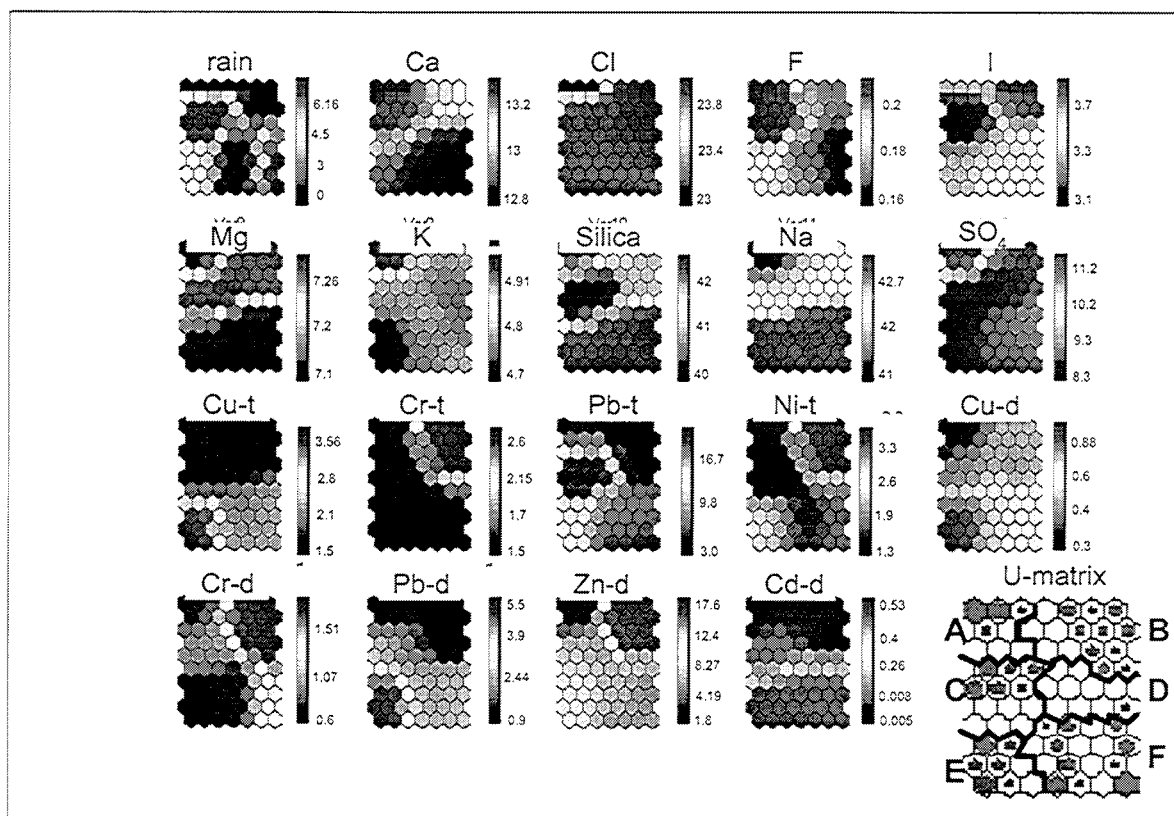


Figure 16: Component planes and U-matrix visualisations for Golf Course site. (t and d denote total and dissolved, respectively). Units for rainfall are millimetres and for metals are ppb.

The clustering of the maps is based on visual inspection of the U-matrix shown in Figure 13 supplemented by the knowledge of the distribution component values. For Watson site, 4 clusters are extracted corresponding to different responses with respect to the rainfall. The statistical descriptions of each cluster for the Watson Ave. site are shown in Table 2.

From Figure 13 and Table 2, it is noted that Group D is characterised by the high values in Cu-t, Pb-t, Cu-d, Pb-d, Cd-d, and relatively low value of NO<sub>3</sub>-N with high rainfall. Group A corresponds to no rainfall (mean 0.001 mm/hr) with high Ca, high Cl, and high NO<sub>3</sub>-N, high SO<sub>4</sub>, low Silica, and low Na. Group B and group C resemble each other. They are characterised by high Silica, high Na, and high Mg with low Ca and low Cl. The data patterns of heavy metals (Cu-t, Pb-t, Cu-d, Pb-d, Zn-d, and Cd-d) in groups B and C generally are similar to those in group A.

The data for Golf Course site can be divided into 6 groups as shown in Figure 13. Group C consists of high Pb-t and relatively medium values of heavy metals with high rainfall. Group E resembles group F with the difference that Pb-d, Cu-d, and Cu-t are relatively high. Comparing Figure 13 with Figure 16, it can be seen that the properties of each group in the Golf Course site are different from those for the Watson Ave. site.

It is worth noting that the KSOFM can provide a powerful means of visualising the multi-dimensional data, and help to understand the dependencies between the groundwater quality variables and to diagnose the effect of the storm water on the groundwater qualities. By using the component planes and U-matrix which are the visualisation capabilities of the KSOFM, the results are readily explainable, simple, and highly visual. In addition, the greatest advantage is that the component planes show some detailed local relationship between the variables, e.g., different responses of the groundwater quality variables under different rainfall conditions.

This result can not be obtained from traditional statistical methods such as factor analysis and PCA which just reveal the global relationship between the variables. Those features of the KSOFM provide useful information with a decision-maker who is faced with characterisation or understanding of the dynamic in the groundwater quality for sustainable groundwater management.

The main drawback of the KSOFM is that its result can not be expressed explicitly by mathematical forms. The development of useful algorithms to produce a more structured and interpreted solution by combining the KSOFM with other artificial intelligence (AI) techniques with the KSOFM will be preferred for further analysis. Recently, other AI techniques [39, 40, 41] based on machine learning algorithm and fuzzy logic techniques [42] have been developed to construct and to infer variables from a data set. These techniques have the abilities of learning algorithms like neural networks and are able to derive rule-based models using an “If...Then” rule, which produces the interpretation rules. Therefore, a new method is under development to produce rule-based models by combining fuzzy logic and KSOFM. This technique can search for functional dependencies hidden in data and express the discovered knowledge explicitly in the “If...Then” rule.

It has been shown that the KSOFM is capable of capturing the complex relationships between the groundwater variables and the storm water infiltration with no *prior* knowledge about the complex mechanism of infiltration and transport occurring in a fractured rock aquifer. It is demonstrated that the KSOFM is useful technique for characterising and diagnosing the groundwater quality for a given aquifer system providing the detailed local information as well as global information. This KSOFM is also computationally efficient, accurate, and reliable simultaneously, and may have the potential to be applied to other environmental problem as well.

Using the KSOFM technique, information from various databases can be integrated, e.g., using KSOFM in a hierarchical way. For instance, land use pattern, groundwater usage pattern, and geological data can be combined. This allows the analysis and simulation of various effects on the groundwater quality in different areas. This technique is under development.



TABLE 2. STATISTICAL DESCRIPTIONS OF EACH CLUSTER FOUND IN WATSON SITE.

Component	Group A			Group B			Group C			Group D		
	Mean	Std. D	Min.	Max.	Mean	Std. D	Min.	Max.	Mean	Std. D	Min.	Max.
rain	0.001	0.005	0	0.042	0.001	0.07	0	0.83	5.04	1.79	3.32	8.39
Ca	12.42	0.65	9.82	13.48	8.14	0.60	7.12	10.48	7.6	0.45	6.81	8.67
Cl	17.45	0.35	15.89	18.55	15.47	0.51	14.45	17.02	14.64	0.37	13.97	15.33
Mg	5.88	0.11	5.70	6.12	6.25	0.05	6.13	6.34	6.40	0.047	6.28	6.48
NO <sub>3</sub> -N	4.30	0.11	3.82	4.52	3.32	0.11	3.07	3.72	3.11	0.086	2.90	3.31
K	5.19	0.11	5.0	5.38	5.41	0.13	5.31	5.61	5.64	0.08	5.46	5.92
Silica	22.22	1.41	19.17	26.59	29.61	1.28	26.09	33.15	31.07	0.84	29.01	32.81
Na	23.80	0.61	22.63	25.18	25.97	0.30	25.17	26.75	28.86	0.34	26.30	27.79
Cu-t	5.68	1.24	2.81	8.92	5.09	1.52	2.00	8.22	6.42	1.62	2.37	10.91
Cr-t	1.35	0.16	1	1.76	2.27	0.347	1.61	2.99	2.82	0.21	2.22	3.19
Pb-t	23.6	4.87	13.8	32.0	13.65	4.26	4.85	24.98	11.89	4.96	1.22	21.78
Cu-d	3.48	0.5	2.42	4.65	2.97	0.73	0.65	4.16	3.34	0.85	1.58	5.15
Cr-d	0.70	0.04	0.61	0.79	0.76	0.05	0.63	0.89	1.13	0.07	0.921	1.25
Pb-d	4.83	0.87	2.47	6.31	3.091	1.01	0.83	5.35	3.93	1	1.02	5.98
Zn-d	24.0	7.0	12.1	39.9	22.7	5.3	10.0	36.0	21.8	9.8	1.1	45.8
Cd-d	0.38	0.11	0.065	0.64	0.52	0.15	0.23	0.98	0.65	0.154	0.2	0.964
Frequency	0.318	0.465	0	1	0.2	0.4	0	1	0.21	0.42	0	2
Quantization error	3E-4	1E-3	0	7E-3	3E-5	1E-4	0	1E-3	2E-4	1E-3	0	1E-2
U-matrix	0.2	0.22	0.07	1.93	0.19	0.12	0.003	1.1	0.25	0.21	0.003	1.54
									0.36	0.40	0.02	1.88

## 7. CONCLUSIONS

The data from this study incorporating groundwater sampling after rainfall events and soak hole sediment sampling indicate that even with more than 60 years of storm water infiltration into the Mt Eden aquifer, there has only been a minor effect on groundwater quality. Particulate organic matter adsorbs much of the contaminant load. Although long-term binding of contaminants to particulate matter is not certain, the soak holes appear to be cleaned frequently enough to remove much of the adsorbed contaminants. The possibility of leaching of Pb, Zn and Cu from the sediments appears to be the most likely cause for concern. Total Pb and Zn concentrations in groundwater are higher than natural background concentrations and total Pb concentrations are greater than the New Zealand Drinking Water Standard in some wells at certain times. Dissolved Zn concentrations are also relatively high. PAH concentrations are low, but increase after rainfall events suggesting some direct infiltration of storm water into the aquifer. Management of the sediment load entering the soak holes is a key strategy for controlling contaminant input and reducing clogging in the fracture network of the aquifer.

Concentrations of nitrate are relatively high in the aquifer, but are similar to concentrations recorded in other parts of the city. Nitrate concentrations have not increased in over 25 years, and storm water does not contribute much nitrogen to the mass load. Nitrate contamination comes from ubiquitous sources, possibly from a combination of sources such as small leaks in the sewerage system and fertiliser applications to gardens and sports grounds. The stable isotopic composition of the groundwater reflects the regional isotopic pattern for the upper part of the North Island of New Zealand. Although some storm water events had diagnostic isotopic signatures, others did not differ substantially from the groundwater. In addition, those events that did have distinct isotopic compositions were not useful for tracing storm water infiltration because the average stable isotopic composition of the groundwater overwhelmed the storm water signature. Overall, sampling after rainfall events did not show patterns that were diagnostic of storm water infiltration.

In areas that have many soak holes (south of Chamberlin Park), tritium measurements of the groundwater was shown to be less than 2 years old. The data suggest that infiltration is very rapid and occurs throughout the area almost simultaneously after rainfall events. Where soak holes are absent (north of Chamberlin Park), the age of the groundwater is 47 years  $\pm$  2 years. The groundwater here is low in dissolved oxygen and appears to be relatively slow moving.

CFC measurements show a similar pattern to the tritium measurements, although CFC contamination of wells in the young water (south of Chamberlin Park) was prevalent. The same well north of Chamberlin Park that was dated as 47 years old using tritium, also has an age of approximately 30 years using the CFC technique. Thus, although the CFC date may not be completely accurate in urban areas, the pattern of ages in the aquifer is similar to tritium and so the CFC technique may be useful in urban areas that are separated from atmospheric contamination by confining beds or slow circulation.

We have demonstrated that KSOFM, a type of unsupervised neural network, is an efficient tool for determining the effect of storm water infiltration on the groundwater quality and for extracting the dependencies between variables in a given groundwater quality data set. By applying the KSOFM technique, the following results are obtained as:

- (1) In Watson and Volcanic Ave. sites where the land use type is industrial or residential with many soak holes, the strong correlation of heavy metals to storm water infiltration due to rainfall is obvious. But only a high rainfall value (over 6 mm/hr) has an impact on the heavy metal concentrations.
- (2) At the Golf Course site where the land use type is recreational with no soak holes, the relatively weak correlation of heavy metals to rainfall indicates that the land use pattern and the lack of soak holes may affect the groundwater quality dynamic. The limited infiltration of storm water in this area suggests that storm water is not a major source of heavy metals observed at the Golf Course site.

- (3) Generally, Ca, NO<sub>3</sub>-N, and SO<sub>4</sub> have similar pattern distributions showing an inverse relationship with rainfall regardless of monitoring site. Thus, the lower concentrations observed may result from the dilution effect of infiltrating storm water.
- (4) The pattern distribution of silica and Na resembles each other regardless of monitoring site, but the patterns are not related to rainfall.

The Mt Eden aquifer system does show the effect of rapid storm water infiltration after rainfall events in some parts of the aquifer. Water quality has been effected in some areas, but in general the water quality is good considering the quantity of storm water discharge that has occurred in the area for the past 60 years. The relatively high quality of the water may be attributed to the ability of the sediment in the soak holes to trap contaminants.

Further research is need to determine if continued use of the groundwater system as a conduit for storm water infiltration will lead to clogging of the fractures at the top of the aquifer and the transport of particulates and colloids into the aquifer.

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The use of brand names in this report is for informational purposes only and does not represent endorsement of any product by the organisations involved in this study.

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## **APPENDIX 1**

### **CHEMICAL AND ISOTOPIC ANALYSES OF WATER**

**Table 1.** Field measurements of pH, conductivity, dissolved oxygen and temperature for groundwater

Hole ID	Date	pH	Conductivity mS/cm	T°C	Dissolved Oxygen (ppm)
MORVERN-D	17/08/1998 10:55				
MORVERN	17/08/1998 13:10	7.11	0.433	17.7	4.8
MARSDEN	17/08/1998 14:45	6.5	0.264	18.7	6.6
VOLCANIC	17/08/1998 16:00	6.45	0.136	17.2	7
BELLEVUE	18/08/1998 09:40	7.12	0.247	17.3	9.5
BELLEVUE-D	18/08/1998 10:20				
WATSON_AVE_1	18/08/1998 12:10	6.62	0.251	17.5	7.3
GOLFCOURSE	18/08/1998 15:30	7.24	0.324	16.4	1.8
SELKIRK	19/08/1998 09:30	6.68	0.297	17.1	7.2
ROCKYNOOK	19/08/1998 10:40	6.74	0.327	16.6	6.8
ROCKYNOOK-D	19/08/1998 11:10	6.59	0.011	11.5	8.4
MEOLA	19/08/1998 12:40	6.88	5.21	18.5	0.4
PLANTBARN	19/08/1998 14:10				
LESLIE	19/08/1998 15:20	6.8	0.235	17.1	7.1
MORVERN	14/09/1998 10:15	7.31	0.412	17.9	3.5
MARSDEN	14/09/1998 12:00				
VOLCANIC	14/09/1998 17:15	6.07	0.217	16.7	4.9
SELKIRK	15/09/1998 09:55	6.71	0.268	16.9	7.2
ROCKYNOOK	15/09/1998 10:45	6.75	0.295	17	6.4
GOLFCOURSE	15/09/1998 12:55	7.2	0.334	16.7	2.8
WATSON_AVE_1	15/09/1998 16:10	6.8	0.265	16.9	5
WATSON_AVE_1	15/09/1998 16:45	5.73		17.4	7.1
LESLIE	16/09/1998 09:55	7.01	0.249	17.2	5.5



Table 1. (cont.)

Hole ID	Date	pH	Conductivity mS/cm	T°C	Dissolved Oxygen (ppm)
BELLEVEUE	16/09/1998 12:20	7.16	0.239	17.1	6
PLANTBARN	16/09/1998 15:00	7.06	0.268	18.9	6.5
PLANTBARN	16/09/1998 14:50				
MEOLA	16/09/1998 16:45	6.93	4.18	17.5	1.9
PLANTBARN-D	17/09/1998 09:30				
MORVERN	21/10/1998 00:00	6.95	0.425	16.9	3.8
MORVERN	22/10/1998 00:00	7.07	0.428	16.7	4.5
MORVERN	23/10/1998 00:00	7.21	0.412	16.9	4.3
VOLCANIC	21/10/1998 00:00	6.55	0.142	17	6.4
VOLCANIC	22/10/1998 00:00	6.54	0.152	17.1	6
VOLCANIC	23/10/1998 00:00	6.54	0.213	16.9	6
GOLFCOURSE	21/10/1998 00:00	6.77	0.336	16.6	1.9
GOLFCOURSE	22/10/1998 00:00	6.96	0.333	16.4	3.9
GOLFCOURSE	23/10/1998 00:00	6.87	0.333	16.4	2
WATSON_AV_1-D	22/10/1998 00:00	6.41	0.148	19.2	6.9
WATSON_AVE_1	21/10/1998 00:00	6.67	0.248	17.6	5.5
WATSON_AVE_1	22/10/1998 00:00	6.67	0.244	17.2	7.1
WATSON_AVE_1	23/10/1998 00:00	6.61	0.244	17.3	6.9
LESLIE	20/10/1998 00:00	6.86	0.248	17.1	7.2
BELLEVEUE	20/10/1998 00:00	6.88	0.236	16.9	7.22
PLANTBARN-D	22/10/1998 00:00	6.47	0.486	18.8	8.4
VOLCANIC	21/10/1998 00:00	6.55	0.142	17	6.4
WATSON_AVE_1	23/10/1998 00:00				
BLANK	23/10/1998 00:00				

Table 1. (cont.)

Hole ID	Date	pH	Conductivity mS/cm	T°C	Dissolved Oxygen (ppm)
LESLIE	17/11/1998 00:00	6.77	0.258	16.9	8.9
GOLFCOURSE	17/11/1998 00:00	6.88	0.337	16	2.5
WATSON_AVE_1	17/11/1998 00:00	6.39	0.263	17.3	5.7
GOLFCOURSE	17/11/1998 00:00	6.88	0.337	19.8	2
BLANK	17/11/1998 00:00				
SELKIRK	18/11/1998 00:00	6.58	0.278	17.1	8.2
VOLCANIC	18/11/1998 00:00	6.42	0.231	18.3	5.9
BELLEVUE	18/11/1998 00:00	6.9	0.258	20.6	8.6
PLANTBARN	18/11/1998 00:00	6.6	0.275	21.3	5.9
MEOLA	18/11/1998 00:00	6.73	3.58	20.1	0.2
LESLIE	19/11/1998 00:00	6.85	0.259	16.4	7.2
ROCKYNOOK	19/11/1998 00:00	6.52	0.264	16.9	8.1
PLANTBARN-SOIL	20/10/1998 11:40				
WATSON_AV_SOIL	20/10/1998 15:05				
MARSDEN	17/11/1998 11:50				
SELKIRK	15/02/1999 14:10	6.62	0.304	16.7	6.2
SELKIRK	15/02/1999 14:50	6.38	0.298	17.9	6.4
BLANK	15/02/1999 15:15				
LESLIE	16/02/1999 10:10	6.89	0.275	16.3	7.4
MORVERN	16/02/1999 11:55	6.81	0.462	17.8	3.8
VOLCANIC	16/02/1999 14:30	6.25	0.251	16.6	5.4
MEOLA	16/02/1999 16:40	6.83	4.61	18.4	2.4
BELLEVUE	17/02/1999 10:15	6.93	0.264	16.2	8.2
BELLEVUE	17/02/1999 11:10	6.79	0.262	18.4	8

Table 1. (cont.)

Hole ID	Date	pH	Conductivity mS/cm	T°C	Dissolved Oxygen (ppm)
WATSON_AVE_1	17/02/1999 13:00	6.64	0.274	16.8	5.6
GOLFCOURSE	17/02/1999 16:00	7.11	0.356	16.6	3.1
ROCKYNOOK	18/02/1999 08:40	7.25	0.287	17.7	
PLANTBARN	18/02/1999 09:10	7.13	0.284	17.7	4.7
ROCKYNOOK	18/02/1999 09:40	6.9	0.289	17.9	
MARSDEN	16/02/1999 13:15				
CARMEN-D	17/02/1999 16:45				
BLANK	26/04/1999 17:45				
VOLCANIC	27/04/1999 09:50	6.55	0.138	16.5	
SELKIRK	27/04/1999 12:00	6.66	0.284	16.5	
PLANTBARN	27/04/1999 13:40	6.89	0.268	18.3	
BELLEVUE	27/04/1999 15:50	7.02	0.226	16	
BLANK	27/04/1999 16:20				
VOLCANIC	28/04/1999 09:40	6.63	0.14	16.3	
SELKIRK	28/04/1999 11:35	6.68	0.282	16.5	
PLANTBARN	28/04/1999 12:35	6.72	0.265	17	
BELLEVUE	28/04/1999 16:15	6.88	0.224	15.9	
VOLCANIC	29/04/1999 09:30	6.46	0.216	16.4	
SELKIRK	29/04/1999 11:30	6.71	0.282	16.4	
PLANTBARN	29/04/1999 12:05	6.92	0.265	17.1	
BELLEVUE	29/04/1999 14:40	7.11	0.228	15.9	
VOLCANIC	17/08/1998 09:00	6.17	0.172	17	10.3
WATSON_AVE_1	17/08/1998 10:30				
WATSON_AV_1-D	17/08/1998 10:00				

Table 1. (cont.)

Hole ID	Date	pH	Conductivity mS/cm	T°C	Dissolved Oxygen (ppm)
PLANTBARN	17/08/1998 11:20	6.98	0.167	17.4	9.6
PLANTBARN-D	17/08/1998 11:40				
BELLEVUE	17/08/1998 14:15				
BLANK	17/08/1998 14:30				
LESLIE	17/08/1998 15:35				
VOLCANIC	18/08/1998 08:50				
WATSON_AVE_1	18/08/1998 09:50				
WATSON_AVE_1	18/08/1998 09:50				
PLANTBARN	18/08/1998 10:40				
BELLEVUE	18/08/1998 11:45				
LESLIE	18/08/1998 15:30				
VOLCANIC	19/08/1998 08:55				
WATSON_AVE_1	19/08/1998 10:10				
PLANTBARN	19/08/1998 10:50				
BELLEVUE	19/08/1998 11:45				
LESLIE	19/08/1998 13:30				
MARSDEN	19/08/1998 14:40				

9800265	Volcanic	1998/10/22;10:20	-5.06	-28	50.02	0.07	0.09	9.3	14.4	0.11	0.36	5	0.05	3.3	3.3	3	13.6	19	10.9	12	3	10	18	22	<1
9800266	Volcanic	1998/10/23;10:30	-5	-29.7	57.34	<0.01	0.09	10.7	16.8	0.09	0.03	5	<0.01	3.5	<0.1	3.2	14.1	18.8	13.4	5	2.8	2.3	8.2	<20	<1
9800277	Volcanic	1998/10/21;10:15																		12	3.3	7.9	18	24	<1
9800403	Volcanic	1998/11/18;00:00	-5.01	-28	51.24	<0.01	0.1	13.3	16.2	0.1	<0.01	5.1	<0.01	4.01	<0.1	3.3	15.1	19.3	16.3						
9900825	Volcanic	1999/02/16;13:15	-5.42	-33.6	56.12	<0.01	0.11	11.5	15.8	0.07	<0.02	5.5	<0.02	4.5	<0.1	3.7	16.2	21	16.9	4.7	<2	3.4	80	21	<0.5
9901239	Volcanic	27/04/1999	-5	-27.9	65	<0.01	0.1	10.4	14.6	0.09	<0.2	5	<0.02	4.1	<0.1	3.6	15.5	20	14.7	6.5	<2	3	8.5	18	<0.5
9901244	Volcanic	28/04/1999	-4.91	-29.5	67	<0.01	0.1	11.2	14.6	0.08	<0.2	5.3	<0.02	4.1	<0.1	3.6	16	19.6	14.7	5.8	<2	2.8	11	24	<0.5
9901248	Volcanic	29/04/1999	-4.98	-29.5	60	0.01	0.11	10.9	14.7	0.07	<0.2	5.3	<0.02	4.3	<0.1	3.6	15.4	19.6	15.1	4.2	<2	2.2	3.7	14	<0.5
898/2/6	Golfcourse	1998/08/18;15:30	-5.31	-32.7	117	<0.01	0.09	13.2	22	0.29	1.8	6.3	0.1	0.04	<0.1	4.2	34.8	37	9.3						
9800049	Golfcourse	1998/09/15;00:00	-5.46	-33.4	142.7	0.1	0.1	13.2	24	0.2	3.1	7.3	0.1	<0.05	<0.1	4.8	40.2	42	8.6	<2	<2	23	20	<1	
9800267	Golfcourse	1998/10/21;15:25	-5.51	-32.8	139.08	0.14	0.12	12.9	24	0.18	3.3	7.1	0.1	<0.05	<0.1	4.7	42	43	8.8	3.5	<2	<2	14	<20	<1
9800268	Golfcourse	1998/10/22;16:10	-5.5	-31.1	137.86	0.15	0.127	12.8	24	0.16	3.4	7.1	0.1	<0.05	<0.1	4.8	42	43	9.1	2.2	<2	2.3	6.1	<20	<1
9800269	Golfcourse	1998/10/23;15:00	-5.47	-33.7	136.64	0.14	0.12	12.8	24	0.17	3.4	7.1	0.1	<0.05	<0.1	4.8	42	43	9.1	2.1	<2	<2	5.9	<20	<1
9800398	Golfcourse	1998/11/17;12:00																		<2	<2	13	9.3	<0.5	
9800400	Golfcourse	1998/11/17;16:00	-5.5	-33.3	140.3	0.13	0.1	13.1	24.1	0.17	3.7	7.3	0.1	<0.05	<0.1	4.8	41	42	9.06	<2	2.7	<2	<1	22	<0.5
9900830	Golfcourse	1999/02/16;14:30	-5.48	-31.9	139.08	0.15	0.12	13.3	23	0.2	3.3	7.1	<0.02	<0.05	<0.1	5	42	41	11.2	<2	<2	4.4	6.8	<0.5	
898/2/5	Watson_Ave_	1998/08/18;12:10	-5.29	-30.9	57	<0.01	0.1	10.1	17.1	0.11	0.01	6.5	<0.01	4.5	0.1	5.5	24.1	24	16.6						<0.5
9800050	Watson_Ave_	1998/09/15;14:29	-5.26	-31.3	69.5	<0.01	0.1	11	19.4	0.1	<0.01	5.8	<0.01	3.5	<0.1	6.1	24.1	26	16.5	19	2.2	<2	54	120	3.4
9800271	Watson_Ave_	1998/10/21;12:30	-5.17	-31.1	71.98	<0.01	0.09	8.2	15.5	0.13	0.01	6.4	<0.01	3.3	<0.1	5.7	29	26	13.2	7	3	<2	11	23	<1
9800272	Watson_Ave_	1998/10/22;12:50	-5.19	-29.9	75.64	<0.01	0.09	7.6	14.7	0.13	<0.01	6.4	<0.01	3.1	<0.1	5.6	31	27	11.6	4.8	2.6	<2	6.7	<20	<1
9800273	Watson_Ave_	1998/10/23;12:30	-5.22	-30	70.76	<0.01	0.09	7.8	15.1	0.13	<0.01	6.3	<0.01	3.3	<0.1	5.6	31	26	12.1	4	2.6	<2	4	<20	<1
9800278	Watson_Ave_	1998/10/23;12:30																		3.3	<1	<1	4	<20	0.27
9800399	Watson_Ave_	1998/11/17;00:00	-5.08	-29.7	67.1	<0.01	0.1	12.5	18.5	0.11	<0.01	6.1	<0.01	4.34	0.14	5.2	21	23	18.2						
9900829	Watson_Ave_	1999/02/16;11:50	-5.3	-29.5	67.1	<0.01	0.11	12.5	18.4	0.11	<0.02	5.9	<0.02	4.3	0.13	5.6	23	24	18	5.8	<2	<2	21	18	<0.5
898/2/11	Leslie	1998/08/19;15:20	-5.4	-31	68	<0.01	0.1	9.7	18.8	0.09	0.1	6.5	0.01	4	0.11	4.5	26	21	16.6						
9800051	Leslie	1998/09/16;00:00	-5.22	-33.2	53	<0.01	0.1	9.5	19.9	0.2	<0.01	6.8	<0.01	4.2	0.1	5.2	26	23	18.9	23	6.9	<2	380	42	1.9
9800274	Leslie	1998/10/20;10:50	-5.08	-29.6	68.32	<0.01	0.1	10.7	19.6	0.11	0.21	7.1	<0.01	4.2	<0.1	4.6	27	22	18.1	23	14	<2	99	38	<1
9800397	Leslie	1998/11/17;00:00	-5.1	-29	57.34	<0.01	0.1	10.3	20.5	0.11	0.01	7.3	<0.01	4.2	0.13	4.5	27	23	18.2						
9800407	Leslie	1998/11/19;00:00																		15	6.7	<2	72	40	<0.5
9900823	Leslie	1999/02/16;08:40	-5.34	-30.6	59.78	<0.01	0.12	10.4	20	0.13	<0.02	7.3	<0.02	4.3	<0.1	4.7	28	23	18.8	8.6	4.7	<2	30	21	<0.5
898/2/4	Bellevue	1998/08/18;09:40	-5.5	-31.8	41	<0.01	0.12	11.6	18.2	0.09	<0.01	6.3	<0.01	4.9	0.11	4.1	22.4	21	21						
9800052	Bellevue	1998/09/16;00:00	-5.18	-27.7	42	0	0.1	11.5	18.5	0.1	<0.01	6	<0.01	4.9	<0.1	4	22.5	24	20.3	9.8	13	<2	160	32	<1
9800275	Bellevue	1998/10/20;14:15	-5.18	-27.1	39.04	0.02	0.11	11.6	18.4	0.11	<0.01	6.1	<0.01	5.1	0.1	4.2	23	20.3	20	14	33	<2	14	27	<1
9800404	Bellevue	1998/11/18;00:00	-5.02	-30	41.48	<0.01	0.1	11.9	19.6	0.11	<0.01	6.4	<0.01	5.62	0.11	4.4	24	22	22						
9900827	Bellevue	1999/02/16;08:50	-5.36	-30	58.56	0.04	0.13	11.3	17.3	0.15	0.09	6.5	<0.02	5.4	0.17	4.7	25	21	23	39	47	5.7	110	82	<0.5
9900828	Bellevue	1999/02/16;10:45																		4.9	9.3	<2	3.8	11	<0.5
9901242	Bellevue	27/04/1999	-5.07	-28.8	42	<0.01	0.11	11.9	15.6	0.1	<0.2	6	<0.02	5.2	<0.1	4.3	24	19.6	18.3	6.6	6.6	<2	29	27	<0.5
9901247	Bellevue	28/04/1999	-5.05	-28.8	43	<0.01	0.11	10.7	15.5	0.11	<0.2	6.2	<0.02	5	<0.1	4.3	24	21	19.2	13	20	<2	11	33	<0.5
9901251	Bellevue	29/04/1999	-5.18	-28.7	45	<0.01	0.12	11.3	16.1	0.11	<0.2	6	<0.02	5.3	0.1	4.2	24	21	20	8.4	15	<2	4.3	17	<0.5
9800053	Plant Barn	1998/09/16;00:00	-5.26	-29.7	61	<0.01	0.1	11.7	16.4	0.2	0	7	<0.01	4.4	<0.1	6.7	25.2	25	24	6.2	<2	<2	1	60	<1
9800276	Plant Barn-D	1998/10/22;16:40	-0.17	2.9	8.54	0.24	0.48	28	127	<0.05	0.28	5.7	<0.01	<0.05	<0.1	4.3	5.2	66	26	78	9.7	<2	32	62	<1
9800405	Plant Barn	1998/11/18;00:00	-5.17	-30.7	73.2	<0.01	0.1	11.5	18.3	0.11	0.01	7	<0.01	4.65	0.06	6.9	26	26	21.7						<1
9900832	Plant Barn	1999/02/18;09:10	-5.41	-30.5	68.32	<0.01	0.11	11.1	18.1	0.16	<0.02	6.7	<0.02	4.2	<0.1	7	28	26	21.1	<2	<2	<2	<1	11	<0.5



**Table 3.** Tritium and CFC measurements from groundwater wells. Recharge temperature of 12.5°C was used for CFC calculations

Well	Sample	Sampling Date	Tritium Ratio	Tritium Recharge Year	Calculated Atmospheric Partial Pressure in pptv		Model CFC Recharge Dates		Recommended CFC Recharge Year
					CFC-11	CFC-12	CFC-11	CFC-12	
Golf Course	3	17 Nov 98	0.260	47 ±2	8.0	187.5	1959.5	1974.5	Early 1970s?
	4	17 Nov 98	± 0.019		7.4	153.8	1959	1972.5	
Selkirk	1	18 Nov 98	2.02	1 +2	387.9	12955.4	Hi Cont.	Hi Cont.	Excess CFCs. Modern?
	2	18 Nov 98	± 0.06	-1	404.2	13171.2	Hi Cont.	Hi Cont.	
Volcanic	2	18 Nov 98	1.95	1 +2	176.8	527.4	1982.5	1997	Modern
	1	18 Nov 98	± 0.06	-1	176.5	545.8	1982.5	Modern	
Bellevue	4	18 Nov 98	2.17	1 +0.5	410.7	666.0	Hi Cont.	Hi Cont.	Excess CFCs. Modern?
	5	18 Nov 98	± 0.06	-1	438.9	653.8	Hi Cont.	Hi Cont.	
Plant Barn	3	18 Nov 98	-	-	361.4	7261.5	Hi Cont.	Hi Cont.	Excess CFCs
	1	18 Nov 98			367.1	7298.9	Hi Cont.	Hi Cont.	
Rocky Nook	4	19 Nov 98	-	-	385.3	767.3	Hi Cont.	Hi Cont.	Excess CFCs
	2	19 Nov 98			409.5	824.1	Hi Cont.	Hi Cont.	
Leslie	3	17 Nov 98	-	-	435.9	904.6	Hi Cont.	Hi Cont.	Excess CFCs
	4	17 Nov 98			434.4	850.0	Hi Cont.	Hi Cont.	
Watson Ave	4	17 Nov 98	2.02	1 +2	220.4	993.7	1987.5	Hi Cont.	Late 1980s? Most likely modern
	2	17 Nov 98	± 0.06	-1	227.2	1053.5	1988	Hi Cont.	
Meola	1	18 Nov 98	-	-	78.5	4365.4	1973	Hi Cont.	Excess CFC-12. CFC-11 likely to be degraded

**Table 4.** PAH results for samples collected from 17/8/98 to 19/8/98 (Groundwater samples)

Sample Name Units	#2 Morvern (g.m <sup>-3</sup> )	#3 Marsden (g.m <sup>-3</sup> )	#4 Volcanic (g.m <sup>-3</sup> )	#5 Bellevue (g.m <sup>-3</sup> )	#7 Watson... av. 1 (g.m <sup>-3</sup> )	#8 Golf Course (g.m <sup>-3</sup> )	#9 Selkirk (g.m <sup>-3</sup> )	#10 Rocky Nook (g.m <sup>-3</sup> )	#11 Rocky Nook (g.m <sup>-3</sup> )	#12 Meola (g.m <sup>-3</sup> )	#13 Leslie (g.m <sup>-3</sup> )
Naphthalene	0.000233	< 0.00001	< 0.00001	< 0.00001	< 0.00001	0.00025	< 0.00001	< 0.00001	< 0.00001	0.00428	0.000022
Acenaphthylene	0.000014	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000007	< 0.000005	< 0.000005	< 0.000005	0.00023	< 0.000005
Acenaphthene	< 0.000005	< 0.00003	< 0.00003	< 0.00003	< 0.00003	< 0.000005	< 0.00003	< 0.00003	< 0.00003	0.000807	< 0.00003
Fluorene	0.000013	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000006	< 0.000005	< 0.000005	< 0.000005	0.00036	< 0.000005
Phenanthrene	0.000131	0.000012	< 0.00001	< 0.00001	0.000012	0.00011	< 0.00001	< 0.00001	< 0.00001	0.00101	< 0.00001
Anthracene	0.000013	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000005	< 0.000005	< 0.000005	< 0.000005	0.000069	< 0.000005
Fluoranthene	0.000184	0.000018	< 0.000005	< 0.000005	0.000008	0.000115	< 0.000005	< 0.000005	0.000011	0.000096	0.000007
Pyrene	0.000227	0.000022	< 0.000005	< 0.000005	0.000006	0.000095	< 0.000005	< 0.000005	0.000019	0.000073	0.000006
Benzo [a] anthracene	0.000203	0.00002	< 0.00002	< 0.00002	< 0.00002	0.00012	< 0.00002	< 0.00002	< 0.00002	0.000039	< 0.00002
Chrysene	0.000033	0.000006	< 0.000005	< 0.000005	< 0.000005	0.000027	< 0.000005	< 0.000005	< 0.000005	0.00001	< 0.000005
Benzo [b] fluoranthene	0.000135	0.00003	< 0.00002	< 0.00002	< 0.00002	0.000086	< 0.00002	< 0.00002	0.00002	0.000009	< 0.00002
Benzo [k] fluoranthene	0.000028	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000015	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Benzo [a] pyrene	0.000052	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000027	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Indeno (1,2,3-c,d) pyrene	0.000045	0.000008	< 0.000005	< 0.000005	< 0.000005	0.00029	< 0.000005	< 0.000005	0.000006	< 0.000005	< 0.000005
Dibenzo [a,h] anthracene	0.000009	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Benzo [g,h,i] perylene	0.000042	0.000007	< 0.000005	< 0.000005	< 0.000005	0.000023	< 0.000005	< 0.000005	0.000005	< 0.000005	< 0.000005
Total PAH	0.00136	0.00012	< 0.00015	< 0.00015	0.00003	0.00118	< 0.00015	< 0.00015	0.00006	0.00698	0.00004



**Table 5.** PAH results for the groundwater samples taken from 14/9/98 to 17/9/98

Sample Name	#1 Morvern (g.m <sup>-3</sup> )	#2 Volcanic (g.m <sup>-3</sup> )	#3 Selkirk (g.m <sup>-3</sup> )	#4 Rocky Nook (g.m <sup>-3</sup> )	#5 Golf Course (g.m <sup>-3</sup> )	#6 Watson (g.m <sup>-3</sup> )	#7 Field Blank (g.m <sup>-3</sup> )	#8 Leslie (g.m <sup>-3</sup> )	#9 Bellevue (g.m <sup>-3</sup> )
Units									
Naphthalene	< 0.00003	< 0.00003	< 0.00003	< 0.00003	< 0.00003	< 0.00003	< 0.00003	0.00003	< 0.00003
Acenaphthylene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000006	< 0.000005
Acenaphthene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Fluorene	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001
Phenanthrene	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001
Anthracene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Fluoranthene	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001
Pyrene	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001
Benzo [a] anthracene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Chrysene	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001
Benzo [b] fluoranthene	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001
Benzo [k] fluoranthene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Benzo [a] pyrene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000008	< 0.000005
Indeno (1,2,3-c,d) pyrene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000009	< 0.000005
Dibenzo [a,h] anthracene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000006	< 0.000005
Benzo [g,h,i] perylene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Total PAH	< 0.00014	< 0.00014	< 0.00014	< 0.00014	< 0.00014	< 0.00014	< 0.00014	0.000068	< 0.00014

**Table 6.** PAH results for the groundwater samples collected in February 1999

SAMPLE NAME Units	#1 Selkirk (g.m <sup>-3</sup> )	#3 Field Blank (g.m <sup>-3</sup> )	#4 Leslie (g.m <sup>-3</sup> )	#5 Morvern (g.m <sup>-3</sup> )	#6 Volcanic (g.m <sup>-3</sup> )	#7 Meola Unfiltered	#7 Meola Filtered	#8 Bellevue Unfiltered	#8 Bellevue Filtered	#10 Watson av 1 (g.m <sup>-3</sup> )	#11 Golf Course (g.m <sup>-3</sup> )	#13 Rocky Nook (g.m <sup>-3</sup> )	#14 Plant Barn (g.m <sup>-3</sup> )	#15 Rocky Nook (g.m <sup>-3</sup> )
Naphthalene	0.00005	< 0.00002	< 0.00002	< 0.00002	< 0.00002	< 0.00003	< 0.00003	0.00022	< 0.00003	0.00007	< 0.00002	< 0.00003	< 0.00002	< 0.00002
Acenaphthylene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000008	0.000008	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000005	0.000005	< 0.000005
Acenaphthene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000005	0.000005	< 0.000005
Fluorene	< 0.000001	< 0.000001	< 0.000001	< 0.000001	< 0.000001	< 0.000001	< 0.000001	0.000008	0.000008	< 0.000001	< 0.000001	0.000005	0.000005	< 0.000001
Phenanthrene	< 0.000001	< 0.000001	< 0.000001	< 0.000001	< 0.000001	0.000005	0.000005	0.000005	0.000005	< 0.000001	< 0.000001	0.000005	< 0.000001	< 0.000001
Anthracene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000031	0.000031	0.000009	0.000009	< 0.000005	< 0.000005	0.000005	0.000005	< 0.000005
Fluoranthene	0.000007	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000019	0.000019	0.000015	< 0.00001	< 0.000005	0.000005	0.000011	0.000005	< 0.000005
Pyrene	0.000005	< 0.000005	< 0.000005	0.000002	< 0.000005	0.000054	0.000054	0.000022	< 0.00001	< 0.000005	0.000005	0.000012	0.000005	< 0.000005
Benzo [a] anthracene	< 0.000005	< 0.000005	< 0.000005	0.000008	< 0.000005	0.000128	0.000128	0.000034	0.000011	< 0.000005	< 0.000005	0.000035	< 0.000005	< 0.000005
Chrysene	< 0.000005	< 0.000005	< 0.000005	0.000007	< 0.000005	0.000058	0.000058	0.000068	0.000017	< 0.000005	< 0.000005	0.000034	< 0.000005	< 0.000005
Benzo [b] fluoranthene	0.000005	< 0.000005	< 0.000005	0.000012	< 0.000005	0.000067	0.000067	0.00009	0.000021	< 0.000005	0.000005	0.000064	0.000005	< 0.000005
Benzo [k] fluoranthene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000026	0.000026	0.000016	0.000012	< 0.000005	0.000005	0.000034	< 0.000005	< 0.000005
Benzo [a] pyrene	0.000005	< 0.000005	< 0.000005	0.000012	< 0.000005	0.000037	0.000037	0.000067	0.000014	< 0.000005	0.000005	0.000063	0.000005	< 0.000005
Indeno (1,2,3-c,d) pyrene	< 0.000005	< 0.000005	< 0.000005	0.000008	< 0.000005	0.000007	0.000007	0.000011	< 0.000005	< 0.000005	0.000005	0.000009	0.000005	< 0.000005
Dibenzo [a,h] anthracene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000005	< 0.000005	0.000005	< 0.000005
Benzo [g,h,i] perylene	< 0.000005	< 0.000005	< 0.000005	0.000001	< 0.000005	0.000009	0.000009	0.000017	< 0.000005	< 0.000005	0.000005	0.000012	0.000005	< 0.000005
Total PAH	0.000067	< 0.0001	< 0.0001	0.000094	< 0.0001	0.000395	0.000465	0.000629	0.000098	0.00007	< 0.0001	0.000279	< 0.0001	< 0.0001

**Table 7.** PAH results for the samples collected from 21/10/98 to 23/10/98 over a rainfall event

Sample Name Units	Volcanic 21/10 (g.m <sup>-3</sup> )	Volcanic 22/10 (g.m <sup>-3</sup> )	Volcanic 23/10 (g.m <sup>-3</sup> )	Watson 21/10 (g.m <sup>-3</sup> )	Watson_av_1 23/10 (g.m <sup>-3</sup> )	Watson_av_1 D 22/10 (g.m <sup>-3</sup> )
Naphthalene	< 0.00002	0.00005	0.00012	0.00003	0.00004	0.0001
Acenaphthylene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Acenaphthene	< 0.000005	< 0.000005	< 0.000005	0.000027	< 0.000005	< 0.000005
Fluorene	< 0.00001	< 0.00001	< 0.00001	0.000025	< 0.00001	< 0.00001
Phenanthrene	< 0.00001	< 0.00001	< 0.00001	0.000067	< 0.00001	0.000046
Anthracene	< 0.000005	< 0.000005	< 0.000005	0.000008	< 0.000005	0.000006
Fluoranthene	< 0.000005	< 0.000005	< 0.000005	0.000012	< 0.000005	0.000156
Pyrene	0.000006	0.000005	< 0.000005	0.000008	< 0.000005	0.000243
Benzo [a] anthracene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.00005
Chrysene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000105
Benzo [b] fluoranthene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000134
Benzo [k] fluoranthene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000048
Benzo [a] pyrene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000085
Indeno (1,2,3-c,d) pyrene	0.000006	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000078
Dibenzo [a,h] anthracene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000027
Benzo [g,h,i] perylene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.00017
Total PAH	0.00001	0.00006	0.00012	0.00018	0.00004	0.00125

**Table 8.** PAH results for samples collected 27/04/99 to 29/04/99 after rainfall event

	Volcanic 27/04/1999 (g.m <sup>-3</sup> )	Volcanic 28/04/1999 (g.m <sup>-3</sup> )	Volcanic 29/04/1999 (g.m <sup>-3</sup> )	Selkirk 27/04/1999 (g.m <sup>-3</sup> )	Selkirk 28/04/1999 (g.m <sup>-3</sup> )	Selkirk 29/04/1999 (g.m <sup>-3</sup> )	Plant Barn 27/04/1999 (g.m <sup>-3</sup> )	Plant Barn 28/04/1999 (g.m <sup>-3</sup> )	Plant Barn 29/04/1999 (g.m <sup>-3</sup> )	Bellevue 27/04/1999 (g.m <sup>-3</sup> )	Bellevue 28/04/1999 (g.m <sup>-3</sup> )	Bellevue 29/04/1999 (g.m <sup>-3</sup> )	Field Blank 27/04/1999 (g.m <sup>-3</sup> )
Naphthalene	0.00004	0.00003	< 0.00002	< 0.00002	< 0.00002	< 0.00002	< 0.00002	< 0.00002	< 0.00002	0.00002	< 0.00002	0.00003	< 0.00002
Acenaphthylene	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001
Acenaphthene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Fluorene	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001
Phenanthrene	0.000013	< 0.00001	< 0.00001	< 0.00001	0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001	< 0.00001
Anthracene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Fluoranthene	0.000011	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Pyrene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Benzo(a)anthracene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Chrysene	0.000005	< 0.000005	< 0.000005	< 0.000005	0.000006	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Benzo(b)fluoranthene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	0.000006	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Benzo(k)fluoranthene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Benzo(a)pyrene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Indeno(1,2,3-c,d)pyrene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Dibenzo(a,h)anthracene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Benzo(g,h,i)perylene	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005	< 0.000005
Total	0.000069	0.00003	< 0.0001	< 0.0001	0.000022	< 0.0001	< 0.0001	0.000005	< 0.0001	0.00002	< 0.0001	0.00003	< 0.0001



## **APPENDIX 2**

### **CHEMICAL ANALYSES OF STORM WATER DRAIN SEDIMENT**

**Table 1.** PAH results for sediments collected from the Bellevue drain (Site Bellevue\_D)

Depth from top of core (cm) Sample Name Units	0-5 1 (mg/kg)	15-20 4 (mg/kg)	30-35 7 (mg/kg)	45-50 10 (mg/kg)	65-70 14 (mg/kg)	85-90 18 (mg/kg)
Naphthalene	0.138	0.028	0.021	0.027	0.048	0.075
Acenaphthylene	0.356	0.2	0.155	0.115	0.311	0.219
Acenaphthene	0.177	0.045	0.052	0.01	0.055	0.103
Fluorene	0.259	0.093	0.041	0.021	0.062	0.103
Phenanthrene	2.51	1.15	1.04	0.315	1.05	1.5
Anthracene	0.733	0.263	0.298	0.091	0.25	0.3
Fluoranthene	5.08	1.97	2.57	0.37	2.35	2.82
Pyrene	5.05	2.14	2.94	0.465	2.52	2.91
Benzo [a] anthracene	1.59	0.68	1.2	0.223	1.04	0.88
Chrysene	1.57	0.69	1.13	0.218	1.06	0.89
Benzo [b] fluoranthene	2.49	0.94	1.61	1.58	1.4	1.39
Benzo [k] fluoranthene	1	0.32	0.54	0.36	0.49	0.33
Benzo [a] pyrene	2.09	0.82	1.4	1.78	1.29	1.04
Indeno (1,2,3-c,d) pyrene	1.42	0.55	0.89	0.673	0.85	0.73
Dibenzo [a,h] anthracene	0.41	0.15	0.3	0.33	0.24	0.2
Benzo [g,h,i] perylene	2.03	0.76	1.22	1.52	1.21	1.12
Total PAH	26.903	10.799	15.407	8.098	14.226	14.61

**Table 2.** PAH results for sediment samples from Plant Barn and two reference soils

Site Depth DSS's identifier Lab No Sample Name Units	Plant Barn-D 0-6cm UAP-1 env98/332/UAP-1 6/11 #1 (mg/kg)	Plant Barn-D 17-22 cm UAP-4 env98/333/UAP-4 6/11 #4 (mg/kg)	Plant Barn-D 32-37 cm UAP-7 env98/333/UAP-7 6/11 #7 (mg/kg)	Plant Barn-D 47-52 cm UAP-10 env98/333/UAP-10 6/11 #10 (mg/kg)	Plant Barn_D Soil Reference env98/334 ENV98-334 (mg/kg)	Watson_av_1_D Soil Reference env98/335 ENV98-335 (mg/kg)
Naphthalene	0.068	0.046	0.04	0.063	0.237	0.018
Acenaphthylene	0.04	0.116	0.163	0.019	0.33	0.018
Acenaphthene	0.007	0.02	0.021	0.003	0.106	0.002
Fluorene	0.012	0.027	0.031	0.008	0.22	0.003
Phenanthrene	0.162	0.492	0.588	0.078	2.29	0.052
Anthracene	0.033	0.15	0.196	0.016	0.5	0.011
Fluoranthene	0.548	1.07	1.52	0.188	5.89	0.192
Pyrene	0.717	1.16	1.61	0.218	6.26	0.21
Benzo [a] anthracene	0.253	0.41	0.6	0.131	3.28	0.114
Chrysene	0.426	0.4	0.56	0.145	3.08	0.123
Benzo [b] fluoranthene	0.149	0.44	0.68	0.109	3.11	0.201
Benzo [k] fluoranthene	0.56	0.18	0.32	0.187	1	0.081
Benzo [a] pyrene	0.412	0.47	0.64	0.149	2.53	0.193
Indeno (1,2,3-c,d) pyrene	0.268	0.33	0.42	0.147	1.64	0.118
Dibenzo [a,h] anthracene	0.088	0.1	0.12	0.056	0.44	0.033
Benzo [g,h,i] perylene	0.616	0.54	0.64	0.263	2.16	0.152
Total PAH	4.36	5.95	8.15	1.78	33.1	1.52



**Table 3.** Chemical analyses of sediment collected in drains from all sites

Sample Location	Date collected	ENV Lab Identifier	Depth cm	Moisture %	Coarse (>2mm) wt %	pH	Conductivity $\mu\text{S/cm}$	C %	N %	Fe2O3 %	MnO %	TiO2 %	CaO %	K2O %	P2O5 %	SiO2 %
Bellvue-D	24-Aug-98	98/323	0 - 5	28	4	5.9	52.0	6.86	0.26	8.94	0.12	1.56	5.61	0.89	0.43	48.19
		UAB-1														
		UAB-2	5 - 10	23	15	6.3	31.0	4.78	0.11	9.35	0.15	2.08	7.28	1.15	0.39	48.35
		UAB-3	10 - 15	19	12	6.2	36.0	1.86	0.05	9.77	0.15	2.24	7.36	1.1	0.38	49.99
		UAB-4	15 - 20	17	10	6.1	33.0	3.55	0.10	10.07	0.15	2.19	7.85	1.13	0.42	48.71
		UAB-5	20 - 25	23	15	5.9	31.0	4.21	0.10	8.77	0.13	1.75	6.79	1.02	0.39	49.84
		UAB-6	25 - 30	24	11	6.4	32.7	4.06	0.12	9.58	0.13	1.99	7.3	1.07	0.44	49.11
		UAB-7	30 - 35	14	14	6.5	27.3	3.00	0.07	10.3	0.15	2	7.3	1.07	0.47	49.43
		UAB-8	35 - 40	19	18	6.3	39.4	3.87	0.09	9.04	0.13	1.68	6.98	1.03	0.37	49.71
		UAB-9	40 - 45	26	12	5.7	36.3	3.25	0.11	8.91	0.14	1.62	6.5	0.97	0.35	50.76
		UAB-10	45 - 50	11	64	6.6	39.9	6.67	0.14	10.72	0.14	1.9	7.75	1.04	0.45	44.42
		UAB-11	50 - 55	4	41	6.7	12.4	2.60	0.04	9.8	0.14	1.69	7.24	1.06	0.34	52.67
		UAB-12	55 - 60	4	20	6.6	17.8	1.32	0.03	6.12	0.11	0.98	5.89	1.06	0.23	60.21
		UAB-13	60 - 65	11	18	6.3	22.0	2.59	0.06	9.24	0.14	1.64	6.9	1.09	0.34	51.47
		UAB-14	65 - 70	19	14	6.2	22.9	3.47	0.10	9.59	0.15	1.81	7.09	1.07	0.38	48.82
		UAB-15	70 - 75	11	13	6.8	29.8	2.83	0.07	9.37	0.15	1.83	7.77	1	0.37	51.17
		UAB-16	75 - 80	12	25	6.5	14.1	2.58	0.07	9.95	0.16	1.89	7.53	1.03	0.38	50.48
		UAB-17	80 - 85	16	13	6.3	23.7	3.88	0.11	10.28	0.16	1.76	6.91	1.01	0.36	48.81
		UAB-18	85 - 90	19	11	6.1	17.6	4.83	0.15	9.85	0.16	1.69	6.59	0.98	0.36	49.31
Morven-D	24-Aug-98	98/326	top 5 - 10	15	5	6.8	38.6	3.17	0.12	9.22	0.21	1.83	6.14	1.06	0.4	53.07
Plant Barn	17-Oct-98	98/332														
		UAP1	0 - 6	19	50	7.1	69.3	2.22	0.10	11.12	0.16	2.03	8.00	1.10	0.44	48.10
		UAP2	6 - 12	14	55	7.5	64.1	1.87	0.07	12.07	0.17	2.10	8.23	1.08	0.48	48.20
		98/333	12 - 17	26	5	6.8	38.9	2.48	0.09	9.76	0.15	1.62	5.95	0.95	0.37	52.85
		UAP3														
		UAP4	17 - 22	36	5	6.6	38.6	3.70	0.15	8.47	0.13	1.48	5.21	0.89	0.39	52.08
		UAP5	22 - 27	34	6	6.6	38.2	3.89	0.14	8.82	0.13	1.58	5.22	0.87	0.36	52.06
		UAP6	27 - 32	38	4	6.5	57.8	4.90	0.19	8.53	0.12	1.58	4.87	0.80	0.37	51.93
		UAP7	32 - 37	35	8	6.7	26.4	4.18	0.15	7.70	0.11	1.45	4.44	0.82	0.32	53.99
		UAP8	37 - 42	37	6	6.6	31.7	4.26	0.16	7.93	0.12	1.43	4.94	0.86	0.32	54.59
Carmen-D sample 12	17-Feb-99	UAP9	42 - 47	37	21	6.5	31.9	5.94	0.20	6.36	0.10	1.42	4.17	0.82	0.29	52.47
		UAP10	47 - 52	40	13	6.0	75.1	6.54	0.24	5.88	0.08	1.43	3.71	0.74	0.32	50.09
		99/46-1	Surface material	28	85	7.1	116.0	ns	ns	7.88	0.14	1.41	7.01	1.08	0.31	48.18
		-2	5 - 10	33	62	6.9	100.4	10.66	0.46	7.94	0.14	1.54	6.69	1.05	0.35	48.14
CONTROLS	20-Oct-98	-3	10 - 15	33	60	7.0	72.4	8.66	0.41	7.95	0.14	1.50	6.51	1.04	0.37	46.54
		-4	15 - 20	29	56	6.6	30.7	8.44	0.37	8.35	0.14	1.58	6.23	1.02	0.41	48.68
		-5	20 - 25	37	43	6.1	37.0	6.22	0.30	8.37	0.15	2.26	6.27	0.99	0.45	47.31
Plant Barn-D	20-Oct-98	98/334		28	30	6.5	53.2	6.32	0.41	6.40	0.11	1.62	2.09	0.57	0.34	52.61
Watson Ave	20-Oct-98	98/335		31	28	6.4	31.4	4.81	0.44	10.03	0.18	1.90	2.31	0.64	0.37	48.10

ns - insufficient sample

Table 3. (cont.)

Sample Location	Date collected	ENV Lab Identifier	Depth cm	Moisture %	Coarse (>2mm) wt %	pH	Conductivity $\mu\text{S}/\text{cm}$	Al <sub>2</sub> O <sub>3</sub> %	MgO %	Na <sub>2</sub> O %	LOI %	SUM %	As mg/kg	Cd mg/kg	Cr mg/kg	Cu mg/kg	Hg mg/kg	Ni mg/kg	Pb mg/kg	Zn mg/kg
Bellvue-D	24-Aug-98	98/323	0 - 5	28	4	5.9	52.0	11.17	5.56	2.4	14.41	99.28	55	1.00	202	488	0.22	114	1946	666
		UAB-1	5 - 10	23	15	6.3	31.0	12.02	7.21	2.98	8.99	99.95	42	0.30	305	268	<0.08	116	939	387
		UAB-2	10 - 15	19	12	6.2	36.0	11.81	7.7	3	6.11	99.61	22	0.23	277	214	<0.08	129	548	324
		UAB-3	15 - 20	17	10	6.1	33.0	11.97	7.85	3.01	6.3	99.65	24	0.19	265	147	<0.08	135	486	291
		UAB-4	20 - 25	23	15	5.9	31.0	11.35	6.66	3.12	9.85	99.67	27	0.28	249	331	0.12	111	652	364
		UAB-5	25 - 30	24	11	6.4	32.7	11.59	6.85	2.97	8.93	99.96	22	0.35	255	334	0.1	132	739	482
		UAB-6	30 - 35	14	14	6.5	27.3	11.6	7.56	3	7.47	99.35	23	0.42	261	307	0.14	139	628	445
		UAB-7	35 - 40	19	18	6.3	39.4	12.15	6.95	3.16	8.25	99.45	34	0.30	248	182	0.1	123	611	421
		UAB-8	40 - 45	26	12	5.7	36.3	11.68	6.77	3.09	9.14	99.93	33	0.41	244	268	0.12	120	486	421
		UAB-9	45 - 50	64	66	6.6	39.9	11.37	8.9	2.96	10.04	99.69	27	0.29	244	235	0.09	156	493	421
		UAB-10	50 - 55	41	6.7	12.4	12.12	6.98	4.12	4.33	3.21	99.92	17	0.10	211	114	0.09	115	320	179
		UAB-11	55 - 60	4	20	6.6	17.8	13.68	4.12	4.33	3.21	99.94	10	0.10	127	77	<0.08	65	239	143
		UAB-12	60 - 65	11	18	6.3	22.0	12.09	6.67	3.38	6.32	99.28	22	0.20	217	178	<0.08	118	530	255
		UAB-13	65 - 70	19	14	6.2	22.9	11.67	7.19	3.05	8.81	99.63	27	0.22	217	212	0.09	130	490	346
		UAB-14	70 - 75	11	13	6.8	29.8	10.54	7.58	4.33	5.43	99.54	11	0.17	215	167	<0.08	136	241	242
		UAB-15	75 - 80	12	25	6.5	14.1	10.8	7.64	3.91	5.65	99.42	15	0.18	222	191	<0.08	141	329	321
		UAB-16	80 - 85	13	13	6.3	23.7	11.43	7.71	3.17	7.62	99.22	23	0.33	235	229	<0.08	154	598	387
		UAB-17	85 - 90	19	11	6.1	17.6	11.25	7.77	3.26	8.77	99.99	20	0.25	232	210	0.09	146	624	390
Morven-D	24-Aug-98	98/326 UAM	top 5 - 10	15	5	6.8	38.6	10.72	6.35	2.47	7.6	99.07	41	0.13	184	61	<0.08	129	98	225
Plant Barn	17-Oct-98	98/332	0 - 6	19	50	7.1	69.3	11.97	8.35	2.88	5.38	99.53	23	0.25	311	193	0.1	174	392	309
		UAP1	6 - 12	14	55	7.5	64.1	11.91	9.30	2.90	3.19	99.63	6	0.090	331	137	<0.08	210	289	222
		98/333	12 - 17	26	5	6.8	38.9	11.97	6.31	2.33	6.81	99.07	23	0.34	248	435	<0.08	135	1240	363
		UAP3	17 - 22	36	5	6.6	38.6	11.98	5.12	1.99	11.36	99.10	33	0.51	198	527	<0.08	107	1365	431
		UAP4	22 - 27	34	6	6.6	38.2	12.12	5.32	2.23	10.65	99.36	35	0.53	217	454	0.10	114	1566	462
		UAP5	27 - 32	38	4	6.5	57.8	12.03	4.69	1.68	12.29	98.89	28	0.56	199	435	0.11	100	1615	493
		UAP6	32 - 37	35	8	6.7	26.4	12.77	4.18	1.83	11.65	99.26	30	0.56	175	430	0.12	90	1451	458
		UAP7	37 - 42	37	6	6.6	31.7	11.88	4.65	1.92	10.31	98.95	43	0.45	182	454	0.098	95	1297	399
		UAP8	42 - 47	37	21	6.5	31.9	13.85	3.57	1.67	14.06	98.78	33	0.68	144	306	0.12	70	1172	456
		UAP9	47 - 52	40	13	6.0	75.1	14.41	3.15	1.43	17.54	98.78	62	0.89	165	305	0.23	65	1373	544
Carmen-D	??	99/46-1	Surface material	28	85	7.1	116.0	10.71	5.67	2.64	14.91	99.94	7	0.31	120	85	0.23	98	318	282
sample 12		-2	5 - 10	33	62	6.9	100.4	10.73	5.61	2.62	15.16	99.97	7	0.35	97	103	0.32	101	246	305
		-3	10 - 15	33	60	7.0	72.4	10.77	5.51	2.54	17.09	99.96	8	0.41	89	108	0.61	99	243	328
		-4	15 - 20	29	56	6.6	30.7	11.37	5.78	2.74	13.69	99.99	9	0.63	79	116	0.94	99	306	330
		-5	20 - 25	37	43	6.1	37.0	11.48	5.78	2.48	14.37	99.91	10	0.78	115	147	1.17	118	368	358
CONTROLS																				
Plant Barn-D	20-Oct-98	98/334		28	30	6.5	53.2	15.18	1.98	0.52	16.96	98.38	10	0.60	216	78	0.36	66	144	214
Watson Ave	20-Oct-98	98/335		31	28	6.4	31.4	15.21	3.75	0.70	16.13	99.32	9	0.27	251	51	0.17	138	95	136

ns - insufficient sample