

Critical review of contaminant transport time through the Vadose Zone

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Report prepared for Environment Canterbury by
Murray Close
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By

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ESR report number: CSC 10010

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Executive Summary

This report reviews existing knowledge on vadose zone travel processes and their impact on groundwater quality and the information that is available from studies relevant to the Canterbury Plains. There are several different types of information and studies including the response of groundwater nitrate concentrations to major recharge events and land use change, tracing experiments using a range of tracers under varying recharge conditions, and age dating of groundwater.

Measurements on the structure of and associated hydraulic properties of alluvial gravel vadose zones have been carried out in the field but these are currently for a limited number of locations. There are three major facies or material types in the alluvial gravel vadose zone in Canterbury - sandy gravel (matrix) material, open-framework gravels and sand lenses. The sandy gravel matrix constitutes about 90% of the vadose zone material and is about 70% stones. The average bulk density of the sandy gravel material is 2.20 g/cm^3 with an average porosity of 17%. The water content (v/v) of the sandy gravel material ranged from 3.5 to 13.9% with a mean of 7.4%. The average porosity of the open-framework gravels was 34% and these gravels were often coated with iron and/or manganese oxides. The sand lenses had an average porosity (v/v) of 34%.

Various comprehensive tracing studies have shown that rapid transport (within days) of nitrate and microbes through the vadose zone and into shallow groundwater can occur when there are saturated conditions and particularly when flood irrigation (with or without effluent) is practised. Non-equilibrium flow conditions, where there is some rapid transport of water and contaminants followed by a much slower moving, long tail of contaminants, have usually been observed in intensive tracing experiments that have been conducted over longer time periods.

Significant increases in nitrate concentrations in shallow groundwater are often observed in response to major recharge events. Analysis of the response of nitrate concentrations in shallow groundwater to major recharge events over the last 25 years indicates that there is a rapid response with a typical lag of between 1 and 4 months between the recharge occurring and the rise in nitrate concentrations. As these major recharge events would generate very saturated conditions, the rapid response could either result from rapid transport of water and contaminants through the vadose zone (similar to the tracing experiments) or could be due to the water in the vadose zone, with associated nitrate, being displaced or "pushed out" from the bottom of the vadose zone into the groundwater. As the nitrate concentrations would be similar for both recharge mechanisms, these observations of major recharge events do not distinguish between the recharge mechanisms.

There are few examples of groundwater quality response to land use that are suitable for analysis as the land use change needs to be well documented, the surrounding groundwater quality needs to be monitored in wells screened close to the water table over the critical period and the land use change needs to occur over a fairly short time period in order to provide information for response times. Two situations were analysed.

The Ashburton Meat Processing plant made a series of improvements to its effluent management from 2000-2002. These improvements mean that a similar volume of effluent was being applied but the nitrogen concentrations in the effluent were significantly reduced. Down-gradient wells showed a decrease in nitrate concentrations, with most of the response to the land use change taking place within a year. However, with the high volume of effluent being applied, the annual recharge at the site is greater than the amount of water held in the vadose zone so a response within a year would be expected.

The other land use change analysed was the cessation of effluent disposal at the Islington Freezing works in 1988. Unfortunately at this site most of the monitoring wells either have data during the effluent discharge period and were not monitored after discharge ceased or monitoring only commenced after 1988. A well 3 km down-gradient has the best monitoring data and indicates that nitrate concentrations decreased about 7 years after effluent discharge ceased. The water content in the vadose zone at the site is equivalent to about 4 years recharge and indicates that there was a significant additional period of time required to flush the stored nitrate out of the vadose zone.

The age dating measurements that have been carried out for wells down to a depth of about 70 m were examined for consistency with the transport processes described in this report. There were slight positive relationships between the age of water and the depth of vadose zone and depth of water above the well screen, but there was significant variability and the relationships were not as strong as could be expected.

Some shallow wells were identified with relatively old ages that also showed rapid responses to recharge events and were examined more closely. There is the possibility that irrigation with older water, particularly if deeper groundwater is used, could cause the water from a particular well to appear older than it actually is, if the irrigation retained some or much of its age signature. Retention of age signature by the irrigation water could explain some of the groundwater having older ages than expected. It may also provide an explanation for the SF₆ showing the youngest age, followed by CFC-12, then CFC-11 and then tritium, as the more volatile tracers will re-equilibrate fastest and retain less of their age signature. The input of irrigation is significant in Canterbury and could have an important influence on the apparent age of the shallow groundwater, depending on how much the age signature of the irrigation water is retained through the application process. There is no information and no experiments have been carried out to determine how much of the age signature is retained for the different tracers and different irrigation application systems. It is recommended that this research is carried out as it might provide insight to these anomalies.

It should be noted that this review is a summary of our understanding at the present time and active research is being carried out into processes where there is still a lack of knowledge and understanding. Many of the studies, such as the tracer experiments, have been carried out under high recharge, saturated flow conditions and there is a lack of information for situations with lower infiltration rates. The vadose zone is situated in between the soil and the groundwater, and much of our knowledge has been inferred indirectly from groundwater measurements without being able to directly observe the vadose zone processes. The ability to obtain direct observations is being developed, such as the use of the Vadose Zone Sampler and the collection of intact cores of vadose zone material by ESR, and the development of the Spydia facility near Taupo by LVL. However, studies using these methods have just commenced and only preliminary insights are available at this time. We are anticipating further insights into vadose zone transport processes as these studies progress.

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1 Introduction

Environment Canterbury is working collaboratively with the primary industry and other parties who have an interest in water management to develop better ways to manage the cumulative effects of non-point source discharges of nutrients, sediment and pathogens on rivers, lakes, wetlands and groundwater. Environment Canterbury's focus for the period July 2010 to June 2011 is on developing policy options that address the cumulative impacts of nutrients (nitrogen and phosphorus) on groundwater and surface water values. A case study approach is being used to develop the methodology for exploring land use linkages, impacts and options.

One of the areas of uncertainty for the project is the time taken for contaminants to travel through the vadose zone. Observations by Environment Canterbury staff show that there are broad changes in groundwater quality as a result of changing land uses and short-term or seasonal changes in response to specific events. Observations suggest that at least some types of contaminants, eg bacteria and nitrate-N, can move quickly through the vadose zone in response to major precipitation events (heavy rain or snow fall) while work by some authors suggest that contaminants travel relatively slowly through the vadose zone. Various studies have used isotope and/or tracer dating methods to estimate the age of groundwater. There is some uncertainty in the large number of assumptions and modelling used to determine groundwater ages from isotope or tracer results.

Better knowledge of the time taken for contaminants to travel through the vadose zone and the aquifers will assist in the interpretation of groundwater quality monitoring data. It will also assist in monitoring for the effects of land use change in Canterbury.

The purpose of this study is to carry out a 'desktop review' that critically examines research on the transport time of contaminants through the vadose zone, typically alluvial gravel material in Canterbury, and provide explanations for the apparent discrepancy between modelled travel times for key contaminants and observations made in research and groundwater monitoring data for Canterbury. This study will also critically review groundwater age dating methods commonly used in Canterbury and discuss the relevance of groundwater age data.

It should be noted that this review is a summary of our understanding at the present time and active research is being carried out into processes where there is still a lack of knowledge and understanding. Many of the studies, such as the tracer experiments, have been carried out under high recharge, saturated flow conditions and there is a lack of information for situations with lower infiltration rates. The vadose zone is situated in between the soil and the groundwater, and much of our knowledge has been inferred indirectly from groundwater measurements without being able to directly observe the vadose zone processes. The ability to obtain direct observations is being developed, such as the use of the Vadose Zone Sampler and the collection of intact cores of vadose zone material by ESR, and the development of the Spydia facility near Taupo by LVL. However, studies using these methods have just commenced and only preliminary insights are available at this time. We are anticipating further insights into vadose zone transport processes as these studies progress.

2 Vadose zone travel processes

2.1 Overview of unsaturated flow theory

There has been a lot of research into unsaturated flow through soils and the relationships between soil moisture, soil tension or head and hydraulic conductivity. Some relevant concepts are summarised briefly. Water flow through a soil profile depends on both the water content and the texture of the media. The hydraulic conductivity (K) is the flow per unit area for a unit gradient or head difference and is constant for a saturated media. However K is highly dependent on the amount of water in the media and as the soil becomes more saturated, K and the associated water flow rapidly increases. Figures 2-1 and 2-2 show typical curves for the dependence of K on matric potential head and water content, respectively, for two different soil media. Both plots of K are on a log scale and show that as the media becomes saturated the K increases dramatically. Figure 2-1 also shows the effects of the

different size pores on K. At or near saturation, the coarser sandy soil has a higher K than the finer clay soil because it contains larger pores that are filled and conducting water rapidly. However, as the soil dries, these pores drain and are no longer filled, producing a dramatic decrease in K. As the soils continue to dry the K curves cross and the finer clay soil will have a higher K than the sandy soil, because the clay soil retains more water and has a higher number of filled pores.

One conceptual model of unsaturated flow in porous media is to consider a bundle of capillary tubes of different sizes. The number and sizes of the capillary tubes in the bundle are chosen so as to retain water in the same way as the soil they represent. Jury *et al.* (1991) show how this conceptual model can be used to predict the unsaturated K as the soil water content decreases. There are certain assumptions that limit its application to real world situations but other workers such as Brooks and Corey (1966) and Mualem (1976) have developed more generalised forms of these relationships by linking model parameters together. A modification of this model is to consider the effect of flow through films that occur at the surface of particles and this may be an important mechanism for gravelly media that make up most of the Canterbury Plains.

There has been much less research carried out on the flow of water through unsaturated vadose zone material, particularly where the vadose zone contains a high proportion of stones and gravels. Soil researchers usually sieve out the stones above 2 mm before determining soil properties and this fraction is the major component for alluvial gravel vadose zone material. Some workers for example, (Khaleel and Relyea, 1997; Khaleel and Heller, 2003) have looked at methods to adjust for the stone content in stony soils and some of their approaches may be applied to stony vadose zone materials. The structure of soils has been recognised as an important factor in understanding and modelling the flow of water and contaminants through many soils and the structure is also likely to be important in characterising flow through the vadose zone. It is extremely challenging to obtain intact cores of stony vadose zone material. Some of the current research at ESR has involved obtaining several cores of intact vadose zone material and we are currently carrying out experiments on the movement of water and contaminants through those cores at varying saturation and infiltration rates.

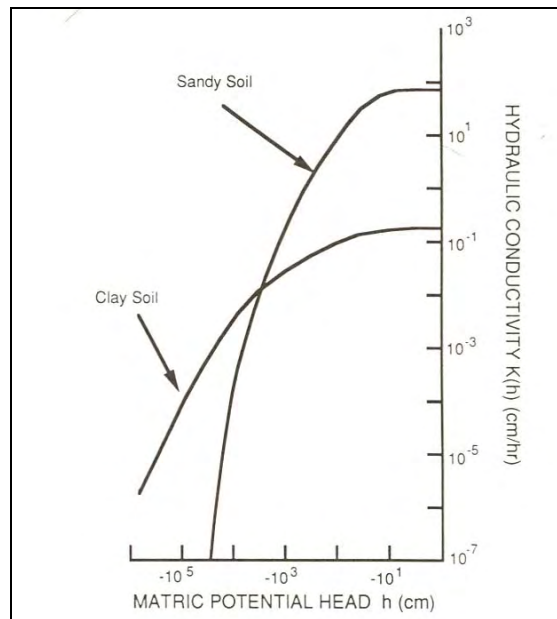


Figure 2-1: Typical hydraulic conductivity – matric potential curves for a sandy and a clayey soil (from Jury *et al.*, 1991)

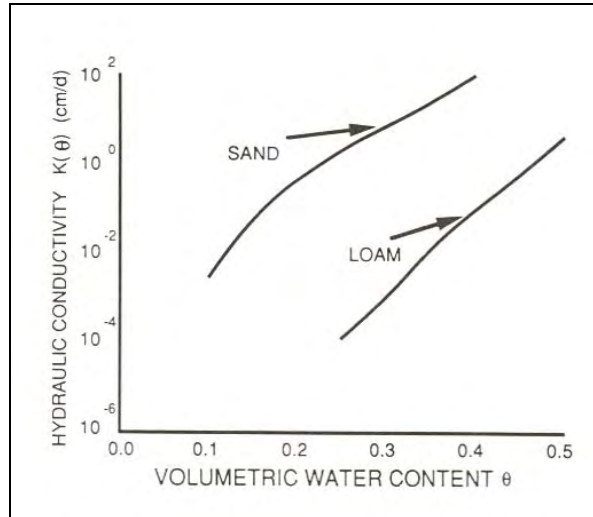


Figure 2-2: Unsaturated hydraulic conductivity – water content function for a sandy and a loamy soil calculated using the capillary bundle model (from Jury *et al*, 1991)

ESR has been studying the structure and associated hydraulic properties of alluvial gravel vadose zones in the field for the past 7 years. Methods and equipment have been developed to access samples and characterise properties such as porosity, particle size distribution and hydraulic conductivity. The first measurements have been reported by Dann *et al.* (2009) and are briefly summarised here. Three major facies or material types in the alluvial gravel vadose zone in Canterbury have been identified and characterised. These are sandy gravel (matrix) material, open-framework gravels and sand lenses (Figure 2-3). Other materials include fine silts, clay, and clay-bound gravel layers. These materials are not as common and have not yet been characterised although they might have an important influence on some transport and transformation processes in the vadose zone.

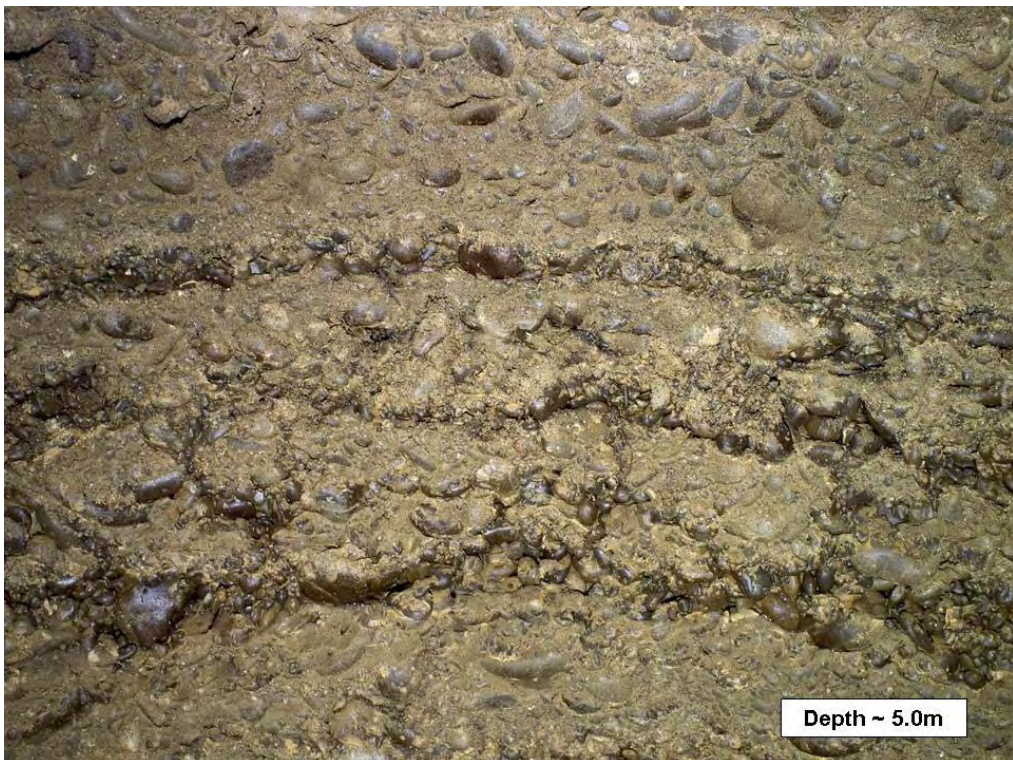


Figure 2-3: Alluvial gravel vadose zone showing a sand lens, open framework gravels and sandy gravel matrix material

The sandy gravel matrix constitutes about 90% of the vadose zone material and is about 70% stones (Dann *et al.*, 2009). The average bulk density of the sandy gravel material is 2.20 g/cm³ with an average porosity of 17%. The water content (v/v) of the sandy gravel material ranged from 3.5 to 13.9% with a mean of 7.4%. The saturated hydraulic conductivity for the sandy gravel material, estimated from the grain size distribution, ranged from 0.25 to 4.85 m/day with a mean of 1.7 m/day. The average porosity of the open-framework gravels was 34% and these gravels were often coated with iron and/or manganese oxides. The sand lenses had an average porosity (v/v) of 34%.

Non-equilibrium flow or flow that has a rapid flow component as well as a slower flow component has often been observed in soil leaching studies. It is also referred to as macropore, bypass, mobile-immobile, dual porosity, or dual permeability flow processes. These types of flow processes can also occur in the vadose zone and can result both in a rapid response to recharge and land use change as well as a more delayed and extended response. The degree of non-equilibrium flow will depend on both the structure of the vadose zone as well as the moisture status and recharge regime. In addition to the non-equilibrium flow processes there can also be sorption of the contaminants to the solid media. This is discussed further in section 3.5.

2.2 Response to major or intense recharge events

Major or intense recharge events occur when large amounts of rainfall or snow occur. The amount of recharge from these events is greater if the soil is already wet because of irrigation or previous rainfall. Major recharge events during the summer are less likely as the soil moisture deficit will provide a buffer which generally fills before significant deeper recharge occurs. However, if the rainfall intensity or irrigation application rate is higher than the soil infiltration rate, then some surface flooding can occur and transport will occur through the larger pores and cracks (macropores). Rapid transport can occur in this situation even though the soil is not fully saturated. In some situations more cracks can occur in dry soils which permit the rapid movement of water through macropores, providing the rainfall or irrigation intensity is sufficiently high.

Significant snowfall can also trigger a major recharge event when it melts. Examples of this type of recharge event happened in Canterbury in August 1992 and June 2006. Significant snowstorms have occurred around Christchurch in 1895, 1896, 1901, 1918, 1945 and 1992, and the depth of snow can be quite variable throughout Canterbury.

A recharge event usually produces a rapid response at the groundwater table as there is a release of water to the groundwater. This can be considered as a pressure response that propagates more rapidly than the actual water velocity, which means that water and solutes present in the vadose zone near the water table will be “pushed out” of the vadose zone into the groundwater in response to water entering the top of the vadose zone. The rise in water table level will also incorporate nitrate held in the vadose zone into the shallow groundwater. The result of these events can be a large increase in nitrate concentrations in the shallow groundwater. Alternatively, it is possible that some of the water that enters the groundwater may come from the recharge event and travel rapidly through the vadose zone.

A key question is whether the solutes that enter the groundwater in response to recharge events come from that recharge event and travel right through the vadose zone, or are already present in the vadose zone and correspond to recharge from a previous time (months or years previously) or a mixture of both. The type of recharge process will depend on the type and intensity of the recharge event and the textural characteristics of the vadose zone material. It is usually difficult to determine this question as there is no way to distinguish between contaminants from different recharge times. Various tracer experiments have been carried out by different research groups which do allow comparisons of these recharge processes and these are described later in the report.

An assessment of the amount of water stored in the vadose zone can be estimated from the thickness of the vadose zone combined with an estimate of the average water content. This can be used, assuming certain flow processes, with the annual recharge estimates, to give an indication of the average travel time for water in the vadose zone. There are significant uncertainties in this approach and this concept is developed further in section 5.3.

2.3 Response to land use change

A land use change may result in a change to the mass loading of a contaminant with no change in recharge, or a change in the volume of recharge with no change in mass loading or a change in both mass loading and recharge. For example, an improvement in process recovery in a meat works could reduce the N content of an effluent without changing the amount of water discharged; using less water for cleaning could result in less recharge with the same mass loading (and higher concentrations); and stopping effluent application would decrease both the recharge amounts and the mass loading. Changes in the method of effluent application, for example, a change from flood irrigation to spray irrigation, would have an impact on the degree of preferential or non-equilibrium flow that would be expected. The response, and the speed of that response, seen at the groundwater table would depend on how the land use changes affected the recharge, mass loading and typical flow regime.

2.4 Age dating of groundwater

During the past 60 years, a number of chemical substances have been released into the atmosphere in sufficient quantities to allow their use as tracers. The substances such as chlorofluorocarbons (CFCs), SF₆, and tritium, dissolve in precipitation and become incorporated in the water cycle (Stewart *et al.*, 2002). Measurement of their concentrations in groundwater enables comparison with the historical levels in the atmosphere and can provide an estimate of how long it has been since the water was in equilibrium with the atmosphere and thus the likely age of the groundwater.

The basis for using these chemicals to date water and the assumptions associated with this technique have been described by Stewart *et al.* (2002), and are summarised briefly here. Age-dating using tritium is based on radioactive decay of tritium after rainwater penetrates the ground during recharge. The half-life of tritium is 12.3 years. Figure 2-4 shows the history of tritium concentration in rainfall; the peak in tritium concentration in the 1960s and early 1970s is due to nuclear weapons testing. Age-dating using dissolved gases is possible due to the steady increase in atmospheric CFC and SF₆ concentrations since their production began in the 1940s. The measured concentrations in groundwater are used to calculate the corresponding atmospheric concentrations using Henry's Law and the recharge temperature, and the age is determined by comparing these with the atmospheric record (Stewart, 2006).

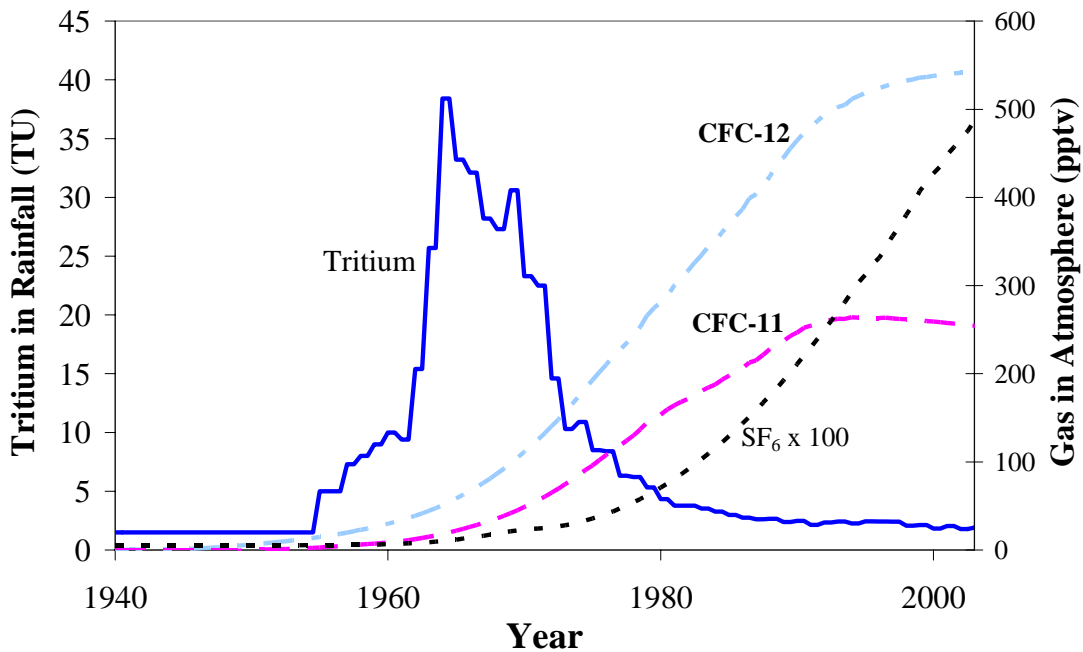


Figure 2-4: Tritium concentration in rainfall at Kaitoke, New Zealand, and SF₆ and CFC concentrations in the Southern Hemisphere atmosphere. (after Stewart, 2006)

There are several assumptions involved in assigning an age of a water sample from the measurements of tracers. The tracer is assumed to be at equilibrium with the atmosphere when entering the soil or subsurface and the age is estimated from that point. There is some opportunity for re-equilibration in the vadose zone but this is assumed to be small. If the water emerges into surface waters such as rivers, then re-equilibration with the atmosphere does not occur immediately but retains most, if not all, of its age signature. This can be seen in the age of river water such as the Waimakiriri River (4 years old; Stewart *et al.*, 2002) and the Wairau River (50% is about 8 years old; (Taylor *et al.*, 1992). If this river recharges a groundwater system or is used for irrigation then the water will appear older than it would have been with full re-equilibration at the time of recharge.

This is particularly relevant for irrigation from groundwater and the implications of this process have not yet been fully considered. The water will retain a measure of its age signature as it moves through the soil, vadose zone and into the groundwater and may appear older than it would have been with full re-equilibration at the time of recharge. The extent to which it retains its age signature will depend on the type of irrigation system and the volatility of the tracer. Border strip (flood) irrigation and drip irrigation encourage less exchange with the atmosphere compared to spray irrigation and, among the spray systems, finer droplets and low application rates will promote more equilibration. With respect to tracer volatility, tritium (water) is by far the least volatile followed by CFC-11, CFC-12 and then SF₆ (Stewart, 2010, pers comm). Tritium is unlikely to be altered by re-equilibration, whereas the others are increasingly likely to be completely reset. Lack of equilibration will have a relatively minor effect (< 5 years) on reported ages for areas where the irrigation water is sourced from surface waters, but may have a more significant effect where irrigation is sourced from deeper older groundwater. It is currently not known how much re-equilibration with atmosphere occurs for the different spray irrigation systems, and therefore the extent that the irrigation water retains its previous age signature. In the IRAP vadose zone tracing experiments the leaching water, which was irrigated using drip irrigation, was found to retain its groundwater tritium age signature (ESR, unpublished data). Lack of equilibration would result in groundwaters that are affected by recharge from irrigation being older than expected. As Canterbury has large areas that are under irrigation, this could be a significant process that needs to be better understood. The possible implications of this process will be further discussed later in the report.

Another assumption relates to the way water moves through an aquifer and the way that water moves into a well screen, particularly for wells with long well screens. The groundwater will comprise mixtures of waters of different ages due to differing travel paths and dispersion processes. The degree of mixing will depend on the type of aquifer, whether it is confined or unconfined, and where the recharge comes from (Stewart *et al.*, 2002). Stewart *et al.* (2005) characterise dispersive mixing in terms of a 'piston-flow' flow of transport with no dispersive mixing, and an 'exponential model' which describes a completely dispersed system. Real aquifers are then described as a combination of the two models in series. Thus a model denoted as E30%PM, indicates an exponential–piston flow model with 30% of dispersive mixing.

Identification of the correct model to use for estimation of the age of a groundwater sample is critical and can result in significant error depending on the choice of model. Stewart (2005) gives examples of estimated ages for several wells using different models and different tracers (Table 2-1). For well L36/1334 there is a difference in age estimated using tritium of 19 years between a 20% and 50% mixing model and a difference in estimated age using CFC-11 of 18 years between a piston flow and 50% mixing model. For well L36/0205 and L36/0666 there is a difference in estimated age using CFC-11 of 13 and 7 years, respectively, between a piston flow and 50% mixing model. The choice of appropriate model is better and more reliable with more samples and multiple tracers analysed but there is significant potential error when analyses from only one sample are available.

Table 2-1: Estimated groundwater age in years for selected wells using different mixing models and different tracers. Data from Stewart (2005). The recommended mean age is bolded

| Well | CFC-11 | | CFC-12 | | SF ₆ | | Tritium | |
|----------|--------|-----------|--------|--------|-----------------|--------|-----------|-----------|
| | PM | E50%PM | PM | E50%PM | PM | E50%PM | E20%PM | E50%PM |
| L36/0317 | 25 | 27 | | | | | 1, 30, 46 | 1, 39 |
| L36/0205 | 35 | 48 | 24 | 26 | 8 | 8 | | |
| L36/0666 | 30 | 37 | 20 | 21 | 6 | 6 | | |
| L36/1334 | 41 | 59 | 35 | 46 | | | 51 | 70 |

There are often differences in estimated age between the various tracers. For the dissolved gases the ages from CFC-11 are usually the oldest, followed by CFC-12 and then SF₆ (see Table 2-1). This is thought to be related to higher volatility and greater penetration into the vadose zone of the SF₆ and CFC-12 (Stewart, 2005), which results in greater equilibrium with present day atmosphere and thus younger ages than is actually the case.

In addition for tritium, because of the shape of the input function (Figure 2-4), certain tritium measurements can correspond to quite different ages. An example of this is seen in Table 2-1 for well L36/0317. In these situations additional information or samples are required to distinguish between the possible ages.

Age estimates using tritium are considered most reliable, followed by CFC-11, then CFC-12 and then SF₆.

2.5 Travel time for different contaminants

The travel time for different contaminants relates to their physical and chemical properties. If a chemical sorbs to the aquifer media then its residence time is increased and it is retarded with respect to water. The contaminants considered in this section are nitrate, phosphorous, and microbes. Nitrate is negatively charged and generally does not sorb to soil and vadose zone media which usually have a negative charge as well. If allophane or similar minerals, which can have variable (sometimes positive) charge, are present in the profile then nitrate can be retarded with respect to water movement. However, these minerals are generally found in association with volcanic soils and are not found in Canterbury. In Canterbury, nitrate can be expected to move with the transporting water, although it can still diffuse with the water into zones of immobile water and exhibit non-equilibrium transport behaviour. If nitrogen is applied to the surface as urea in urine via grazing animals, or as ammonia fertiliser, then transformation from urea to ammonia to nitrate needs to occur before leaching of nitrate takes place.

Phosphorous (P) is strongly sorbed to clay minerals and therefore is usually retarded. There is evidence (de Jonge *et al.*, 2004) that P can also sorb to colloidal sized particles and be transported via macropores. Recent research indicates discharge of P to groundwater may be more important than previously thought (Abraham and Hanson, 2009; Holman *et al.*, 2008). Some NZ soils have very low P-retention and significant P loss can occur through soil macropores (McDowell *et al.*, 2008), predominately co-transported with mobile colloids. If significant P transport occurs through the vadose zone, it is likely to be associated with sorption to colloids and will occur via macropores under saturated flow conditions. Under these conditions P transport could be rapid. Otherwise P transport times will be large (probably decades).

Irrigation and intensive rainfall can promote the transport of faecal microbes down through the vadose zone via bypass flow. If macropore or bypass flow occurs then microbial transport times can be short (hours or days). If transport occurs through the matrix material then the rate will be much slower, but more importantly, most of the microbes will be filtered out or die-off during the extended time associated with the slower transport mode. Because of their greater size, bacteria are 'filtered' more effectively in soil and the vadose zone than are viruses. Many factors and processes affect microbial removal rates in subsurface media, including the physical-chemical nature of the media, physical

filtration, preferential flow paths, source/carrier characteristics of the microbial contaminants and management practices (Pang, 2009).

2.6 Seasonal changes in groundwater quality

Observations of seasonal changes in groundwater quality seem to be related to recharge inputs derived from rainfall and irrigation. A good example of this is shown in Figure 2-5 for well M35/1003. The variability is greatest for shallow wells, with the seasonal variability being dampened with depth. Shallow wells will better reflect the land use in the immediate vicinity and recharge from that land use more closely whereas deeper wells will have recharge sources that may be many kilometres up-gradient and will reflect recharge from that source. In Canterbury many deep wells reflect the recharge from the major alpine rivers which have water of high quality and low variability. Figure 2-5 shows the comparison between nitrate concentrations in well M35/1003 at a depth of 40 m (depth to water table = 28 m) compared to those in well M36/3071 at a depth of 163 m (depth to water table = 16 m), with a distance of about 7 km between the wells. There is a large difference in the depth below the water table at which these wells are screened and a large difference in the observed variability of nitrate concentrations.

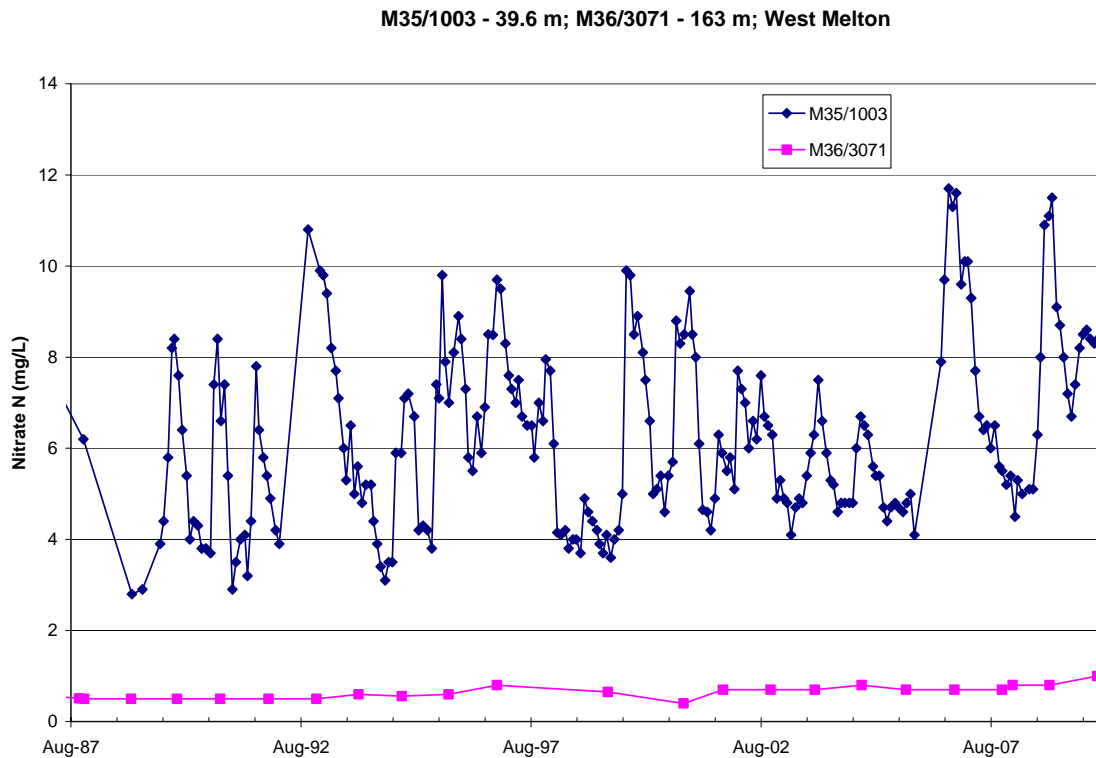


Figure 2-5: Variation in nitrate-N concentrations with time for wells M35/1003 (well depth = 40 m; depth to water table = 28 m) and M36/3071 (well depth = 163 m; depth to water table = 16 m)

3 Key Canterbury and New Zealand studies

3.1 IRAP tracing experiments

Extensive tracing experiments through the vadose zone have been carried out at two sites in the Canterbury Plains as part of the Integrated Research for Aquifer Protection (IRAP) research programme. The modelling of the transport of a tracer, bromide, through the vadose zones at the Lincoln and Dunsandel sites has been reported by Dann *et al.* (2010). A description of both experiments and the key results from the observed leaching of the tracer and the model simulations are given here.

The Lincoln site is located on a slightly undulating silt loam soil with a thickness of approximately 1 m. The site has most recently been used for cropping and prior to this, dryland sheep grazing. The gravel vadose zone at Lincoln generally consists of coarse alluvial sandy gravel interspersed with lenses of pure sand and open-frameworks gravels. The groundwater level was approximately 9 m below ground level at the time of the study. The Dunsandel site is located on a working dairy farm, on slightly undulating land with a silt loam soil to about 1.4 m. The gravel vadose zone is similar to Lincoln though a perched water table was encountered at about 4.5-5 m. Both sites were instrumented with ceramic suction cup samplers at depths ranging between 1 and 7 m (total of 12 at Lincoln and 24 at Dunsandel), neutron probe access tubes (3 at Lincoln and 4 at Dunsandel), time-domain reflectometry (TDR) probes, gas samplers (for an associated study) and groundwater wells. A schematic of the subsurface installation at both sites is presented in Figure 3-1. At Lincoln the suction cups were installed in triplicate (in 3 rows with suction cups installed approximately 4 m apart along the row) at depths of 1, 3, 5 and 7 m on a 20° angle from vertical, to enable sampling of undisturbed flow and transport from the surface to the suction cups. The annulus around each access tube was sealed with bentonite to prevent by-pass flow down along the suction cups.

At Lincoln, 200 kg/ha of bromide and 400 kg/ha of nitrogen (N) (applied as calcium ammonium nitrate, CAN) were applied in October 2004 to a 400 m² area sown with potatoes. The potato crop was harvested on 14 April 2005, and ryegrass was sown on the site on 22 April 2005. There was a second application of bromide (200 kg Br/ha) and N (400 kg N/ha, applied as CAN) in November 2006. The Dunsandel dairy experimental site was fenced off from the dairy cows for approximately 6 months prior to the application of bromide and urea in April 2007 to minimize the spatial variability due to urine patches. The site was split into two equal size plots (400 m²) and bromide was applied at a rate of 400 kg Br/ha to both plots.

Bromide concentrations in the Lincoln vadose zone suction cup samples indicated physical non-equilibrium transport processes with rapid initial macropore flow through the profile to the 7 m suction cups, reflected in an early peak, followed by long tailing before a second application of bromide which results in a similar early peak before the sampling was stopped (Figure 3-2). A smaller secondary peak in May 2005 occurred after the potatoes were harvested and the site cultivated. It appears that the physical disturbance of the soil released some bromide from the immobile fraction into the mobile fraction of the silt loam soil, or bromide may have been released from mineralization of the disturbed soil or plant organic matter into the mobile fraction of the soil zone. The low peak at 7 m after the second bromide application was due to the water table rising to 7 m at this time (i.e. concentrations are much lower and reflect groundwater chemistry affected by leaching, not the vadose zone). These observed values were not used in the modelling. Concentrations obtained from the suction cups at the same depth were more variable after application than later in the experiment where concentrations were more even and lower. Bromide is also plotted against cumulative drainage (Figure 3-3), which permits a better assessment of the appropriate model, along with the non-equilibrium model fit.

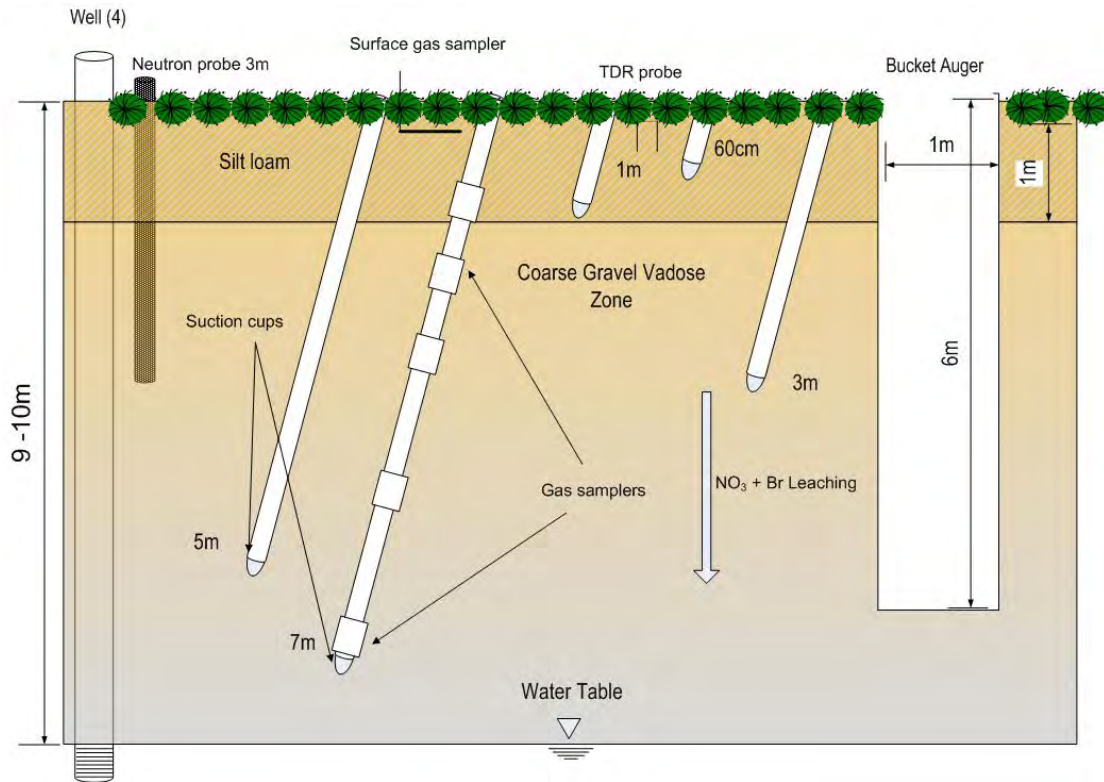


Figure 3-1: Schematic of sampling equipment including suction cups at each of the sites. (after Dann *et al.*, 2010)

The shape of the breakthrough curves at the Dunsandel site (Figure 3-4), also indicated physical non-equilibrium transport with a rapid response to the application of bromide though with lower concentrations (and mass) in the initial peak, and a more pronounced later pulse of bromide. Significant variability is observed during the early stages of drainage within the three suction cups in the non-urine plot. Less variability is represented on the urine plot as there were only 2 suction cups located at 3 m and 1 functioning suction cup at 4 m. Bromide concentrations were approximately twice the concentrations at Lincoln, reflecting the factor of two in the applied mass. Bromide is also plotted against cumulative drainage (Figure 3-5), which permits a better assessment of the appropriate model, along with the non-equilibrium model fit.

At the Lincoln site drip irrigation was applied to the potato crop at a higher than normal rate to move the tracers from the soils into the vadose zone below the root zone, which was the zone of interest. Irrigation commenced in December 2004 at a rate of about 40 mm/week and this was combined with a period of heavy rainfall of 131 mm in December 2004. The observed breakthrough curves (BTCs) for bromide (Figure 3-2) indicate very rapid leaching of the bromide down to a depth of 7m. The leaching was much quicker than expected and the peaks of the BTCs were not well defined. In order to get better definition of the BTC and hence the parameters associated with the tracer transport, it was decided to flush out the bromide from the vadose zone using spray irrigation and to repeat the experiment with better definition of the BTC. The cumulative drainage curve (Figure 3-2) indicates the large amount of drainage (approximately 1 m) needed to reduce the bromide concentrations in the vadose zone. A second application of bromide and nitrogen fertiliser was applied in November 2006. Irrigation was applied at 35 – 45 mm/week but the rainfall amounts were less than for the first application, with 64 mm, 89 mm and 43 mm falling in November 2006, December 2006, and January 2007, respectively. The bromide BTC following the second application showed a similar pattern to the first application (Figure 3-2) but with better definition of the peak.

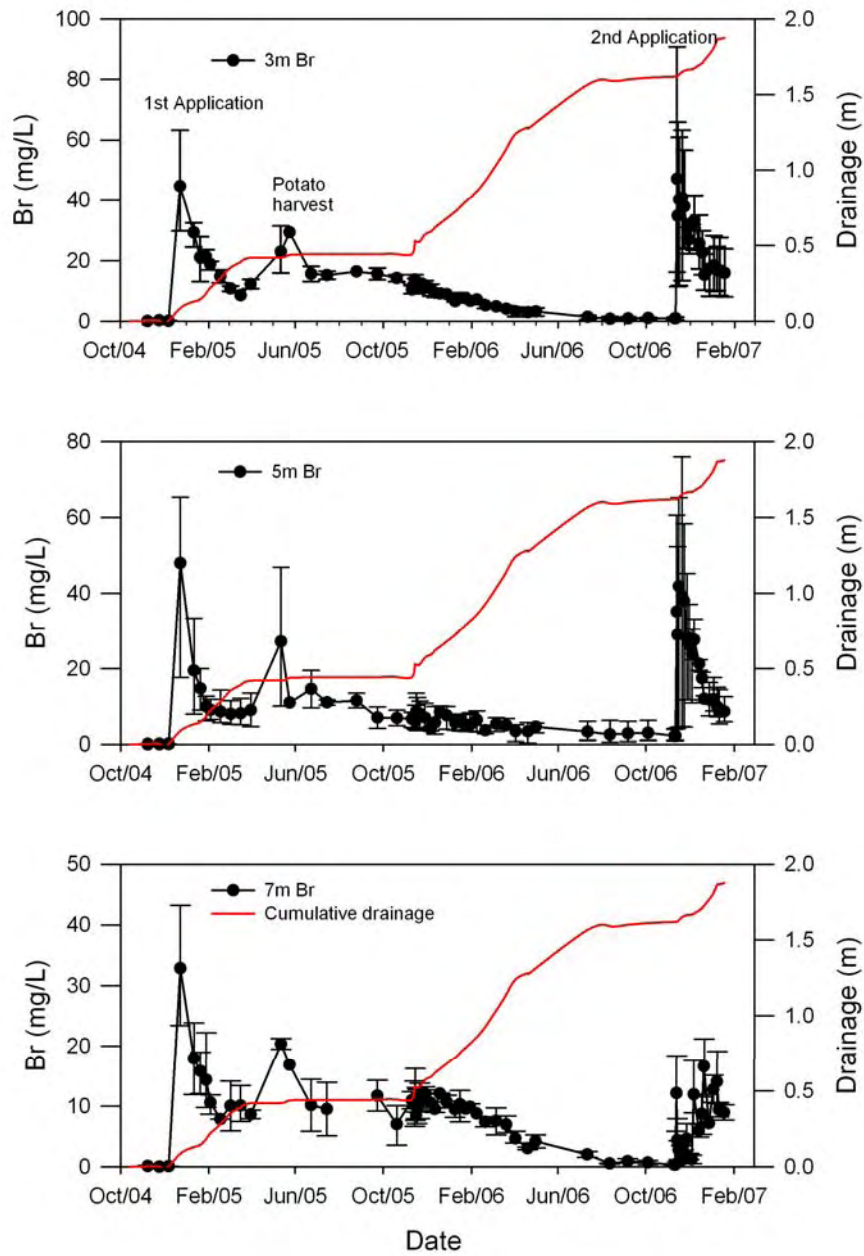


Figure 3-2: Observed bromide concentration data (dots with max-min range) and calculated cumulative drainage (red line) at Lincoln (after Dann *et al.*, 2010)

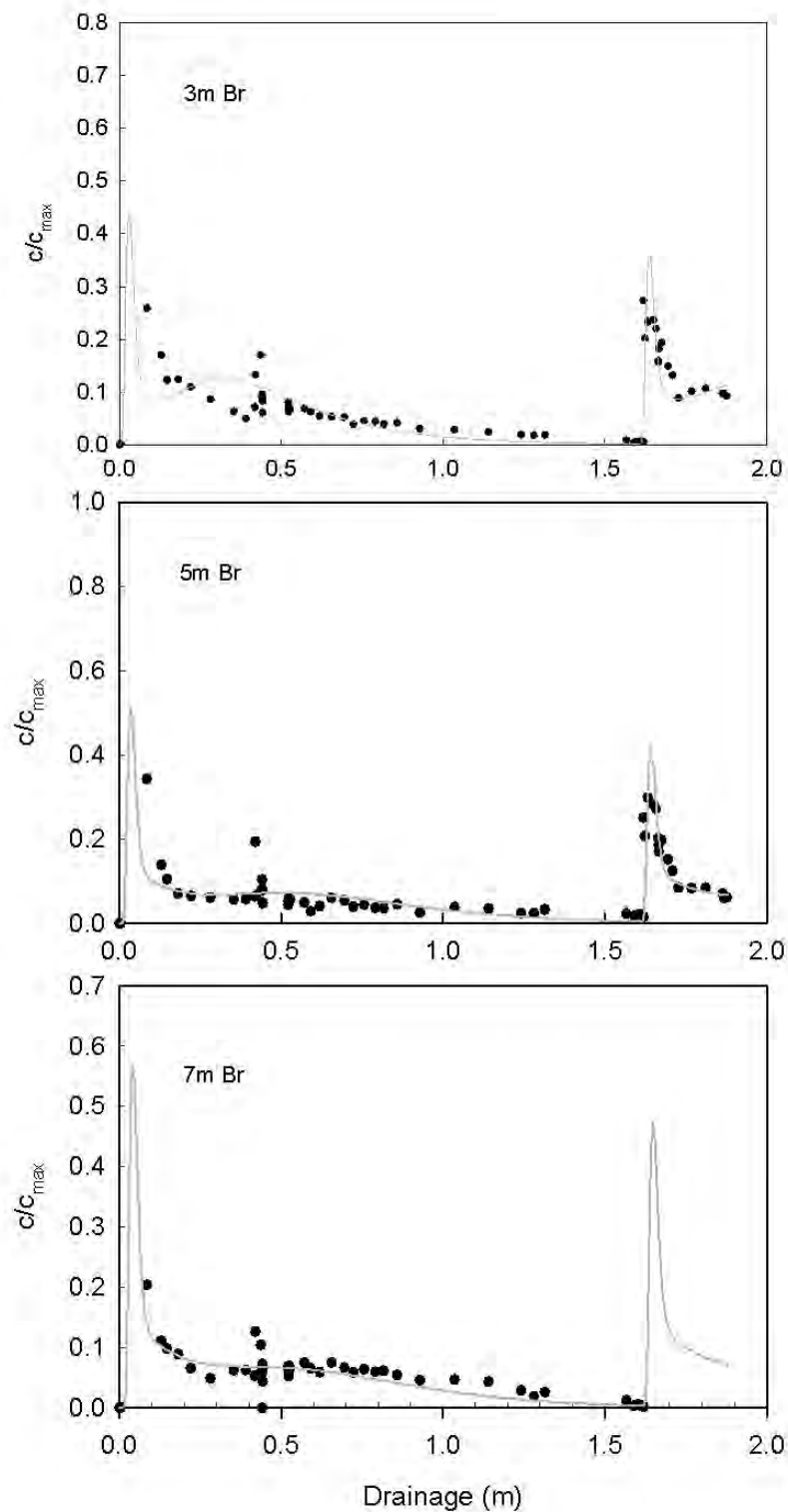


Figure 3-3: Observed Br versus cumulative drainage for the Lincoln site. Gray line is the non-equilibrium mixing cell model simulations (after Dann *et al.*, 2010)

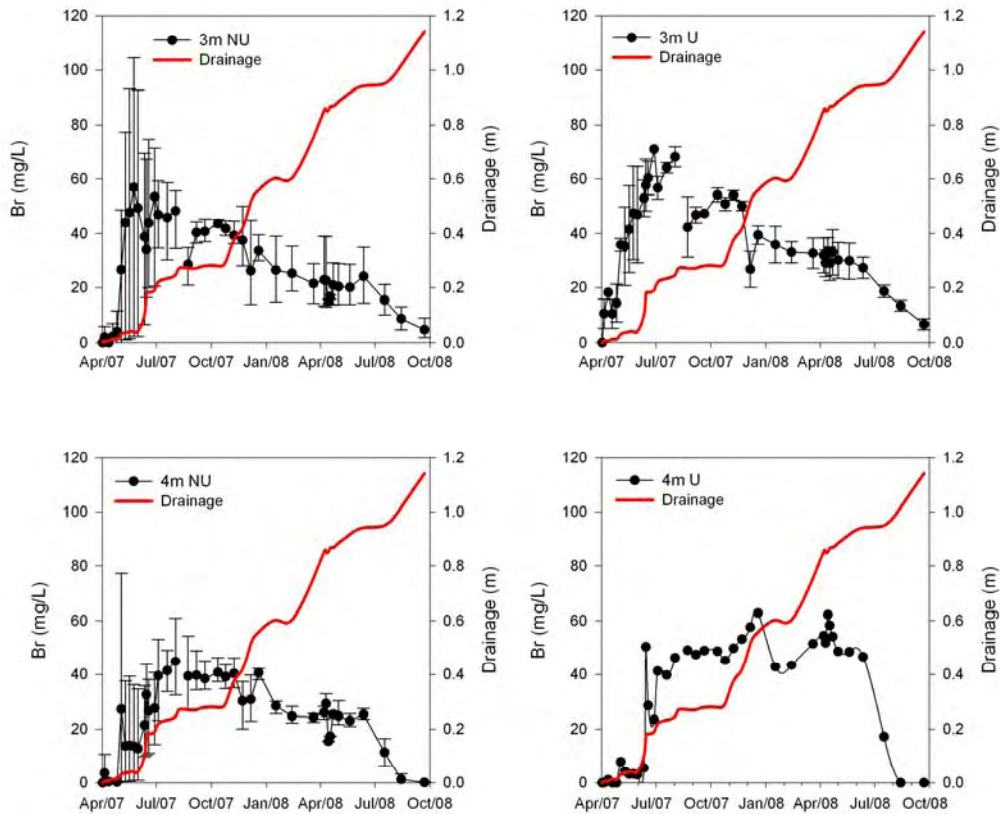


Figure 3-4: Observed bromide concentration data at 3 and 4 m depths for urine (U) and non urine (NU) plots (dots with max-min range) and calculated cumulative drainage (red line) at Dunsandel. No error bars for 4 m U due to data from only one suction cup (after Dann *et al.*, 2010)

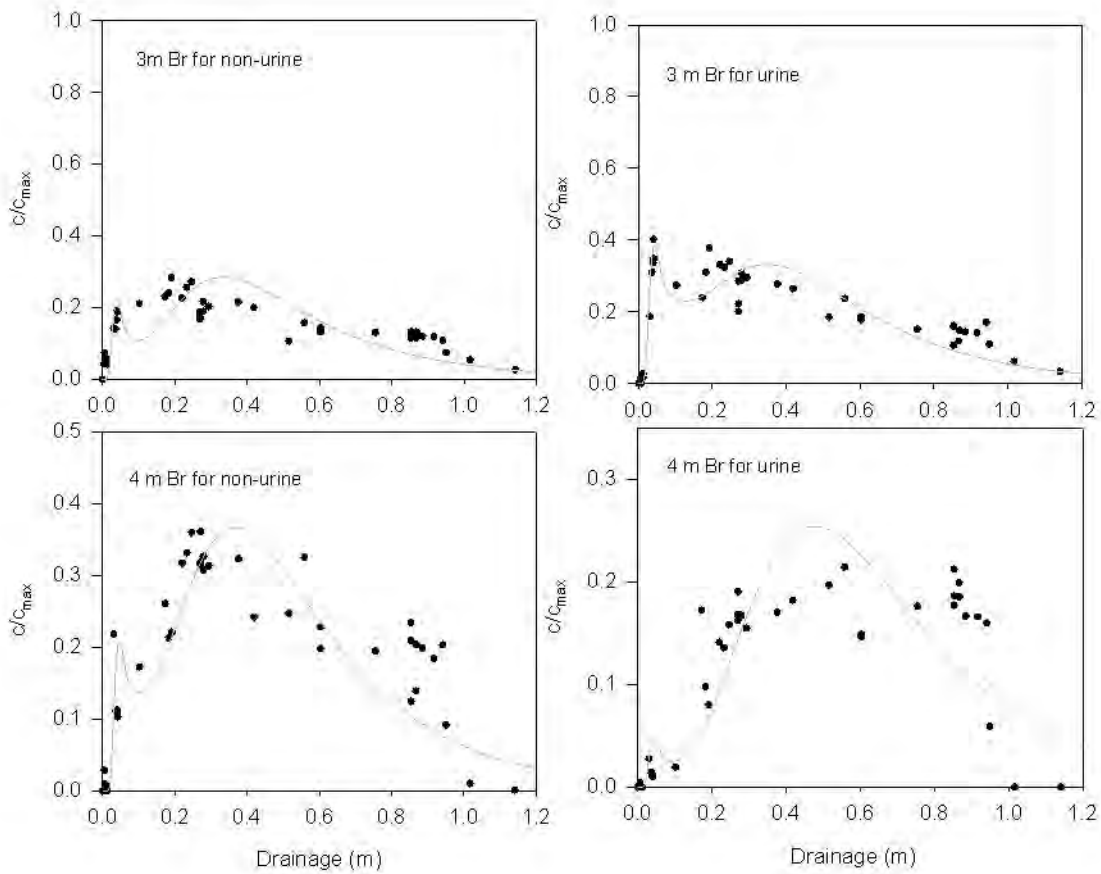


Figure 3-5: Observed Br versus cumulative drainage for the Lincoln site. Gray line is the non-equilibrium mixing cell model simulations (after Dann *et al.*, 2010)

At the Dunsandel site irrigation was applied using spray irrigation. The irrigation regime was different to the Lincoln cropping site because of the differences in nitrogen application. At Dunsandel the nitrogen was applied as synthetic urine. As we wanted the bromide tracer to move at a similar rate so that the bromide:nitrate ratio could be compared, there needed to be a period of time (approximately a month) to allow the urea to be transformed to ammonia and then nitrate. Thus there was only a small amount of irrigation in the few weeks after urea application and then irrigation (175 mm in June 2007) was applied to move the tracer and nitrate through the soil layer and into the vadose zone. There were small amounts (38 and 35 mm) of rainfall in April and May 2007, respectively. There was some leaching of the bromide in April and May down to 2m depth (results not shown) with leaching to greater depths in May and June 2007. There was a more gradual movement down the profile at Dunsandel compared to almost immediate transport of tracer to 7 m in the first application and 5 m in the second application for the Lincoln site. This probably reflects the more intense water application at the Lincoln site.

At both sites there was rapid transport of the tracer to depths of 5 and 7 m under fairly wet conditions, followed by a long tail. Complete removal of the tracer from the vadose zone required a large amount of drainage. An estimate of the “pore volume” of the vadose zone profile at Lincoln from 1 to 7 m is 444 mm (6 m times 74 mm/m), suggesting that a further 2.5 pore volumes was required to flush the tracer from the vadose zone after the initial peak had leached through the profile.

The results were simulated using a mixing cell model which partitioned the transporting water and tracer mass into a macropore domain and a matrix domain (Dann *et al.*, 2010). The simulation results

indicated that about 40-60% and 5-40% of the mass was transported by macropores at the Lincoln and Dunsandel sites, respectively. At Dunsandel the lower macropore mass fraction, compared to Lincoln, is represented by a smaller early peak, with more mass (61-95% modelled) moved through the matrix domain, represented by a larger, broader second peak. The initial peak reflects a rapid transport component through the profile. The simulated transporting water contents for Dunsandel matrix domain (range 0.105 - 0.176 v/v) were similar to the Lincoln site (range 0.096-0.164). These values are also similar to water content values derived from bucket auger samples at the Dunsandel site (range 0.08 - 0.139 v/v). Total modelled solute transporting water contents (combined matrix and macropore domains) for Lincoln were 9.3%, 7% and 4.1% for 3, 5 and 7 m depths respectively. At Dunsandel, total transporting water contents ranged from ~8 to 12%. The greater values at Dunsandel are a reflection of the greater proportion of mass transport through the matrix domain.

Eight samples were collected from the suction cups at the Lincoln site on 11 February 2005 and analysed for tritium content to give the age of water down the profile. All the samples had much less tritium than would be expected and it was evident that the water used for irrigation, which came from a 41 m deep well, had percolated through the vadose zone profile by the time the samples had been collected. Nearby wells screened at similar depth had zero tritium content indicating old water, consistent with groundwater up-welling from depth in this area. If the old irrigation water is assumed to have a value of zero and the recent rain is assumed to have a value of 2.4 tritium units (TU), then the vadose zone samples had proportions of old water ranging between 26 and 75%. There was slightly more "old" irrigation water near the top of the profile as would be expected but there was lots of variability and the deepest sample still had 49% of "old" irrigation water. These samples were taken 2 months after irrigation commenced at this site and the detection of irrigation water throughout the profile is consistent with the observed nitrate and bromide concentrations.

3.2 Flood irrigation of effluent spiked with tracers at Templeton

Martin & Noonan (1977) and Sinton & Close (1983) carried out a series of microbial tracing experiments at the Templeton sewage treatment plant. Domestic effluent was applied to land using border strip (flood) irrigation following treatment in oxidation ponds. They showed that microbial contamination of the shallow groundwater down-gradient of the effluent application area was occurring and that microbes could be detected in wells about 400 m down-gradient.

Sinton *et al.* (1997) describe an experiment where the movement of bacteria and bacteriophage in the effluent at Templeton was monitored in down-gradient wells following flood irrigation of particular border strips. One well was 60 m down-gradient and the other was 445 m down-gradient of the centre of the border strips. The depth of vadose zone was 13 m at the time of the experiment and the estimated velocities through the vadose ranged from 1.2 – 8.1 m/hr, depending on where along the border strip percolation was assumed to occur. This analysis assumed that the bacteria detected in the wells had originated from the effluent irrigated during the experiment. Because bacteria and phage can survive for weeks or months in the vadose zone (Close *et al.*, 2010), it was possible that some of the microbes may have originated from a previous irrigation event and thus travelled a shorter distance at a slower velocity.

Sinton *et al.* (2005) tested that assumption by the addition of tracer bacteria and bacteriophage into the effluent being applied. The depth of vadose zone at the time of the experiment was 16.8 m and the distance to the down-gradient monitoring well ranged from 114 to 192 m, corresponding to the bottom and the top of the border strip, respectively. The tracer microbes were detected in the well from 15 hours after the start of irrigation and decreased after about 20 hours (Figure 3-6). Analysis of the travel times through the groundwater compared to the total travel times indicated percolation velocities through the vadose zone of greater than 15.7 m/hr. Analysis was also carried on the chloride data, which is at higher concentrations in the effluent compared to the groundwater and had very differently shaped breakthrough curves compared to the microbes (Figure 3-6), with a similar increase in concentration but remaining at a high plateau for more than 100 hours. This indicated that the chloride and the microbes reach the groundwater table via two pathways – both undergo rapid transport to the groundwater through macropores, but chloride also undergoes far slower transport through the media matrix as well.

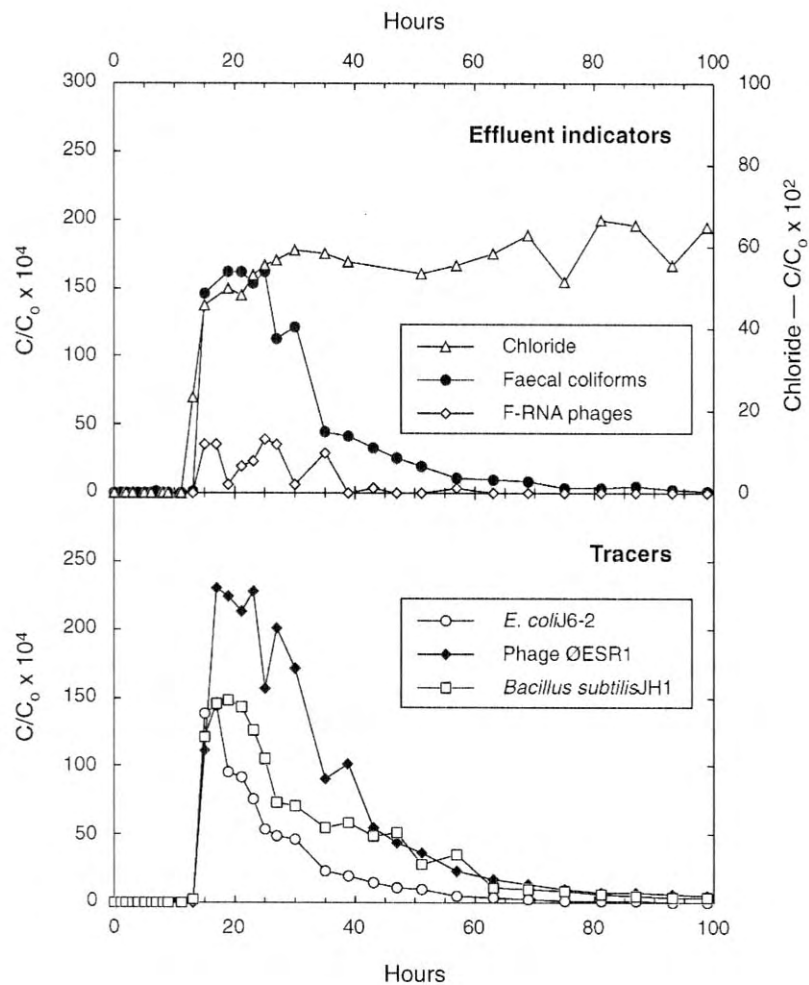


Figure 3-6: Concentrations of the waste stabilisation pond indicators, chloride, faecal coliforms, and F-RNA phages, and the tracers *E. coli* J6-2, phage Φ ESR1, and *B. subtilis* JH1 endospores, in bore 9, following tracer seeding of an irrigation of strip 32, at the Templeton effluent irrigation area. The chloride data have been adjusted to remove the background concentrations in the groundwater (after Sinton *et al.* 1997, Figure 3)

These experiments confirmed that the microbes can travel rapidly through a 13-16 m vadose zone within a day under flood irrigation conditions and that solutes can move both rapidly through macropores and much more slowly through the media matrix.

3.3 Other vadose zone tracing experiments

3.3.1 Heretaunga vertical tracing experiments

Thorpe *et al.* (1982) carried out a series of experiments on the movement of contaminants through the vadose zone of the Heretaunga Plains aquifer in Hawkes Bay. This aquifer consists of alluvial gravel material very similar to aquifers in the Canterbury Plains. The contaminants used in the vertical transport experiments were NaCl, NO₃, *E. coli* and petrol. The experiment was set up to simulate a leaky sewer pipe and thus continuous injection conditions were used. The vadose zone was pre-wet with water over 24 hours and then the tracer solution was injected over a period of 6.5 – 7.5 hours,

followed by a post-injection flushing for 24 to 30 hours. Both the nitrate and bacterial tracers were detected in shallow wells immediately down-gradient of the injection within a few hours of the injection. The water table was about 6 m bgl at the time of the experiments and the rate of movement of the tracers in the vadose zone was between 20 and 60 m/day. This rate is extremely rapid and is likely to be a maximum rate as the experimental conditions are saturated conditions with continuous injection of the tracers into the gravels. The rate of movement of nitrate and bacteria was similar, with greater removal of the bacteria compared to the nitrate as would be expected.

3.3.2 Fairton vertical tracing experiment

An experiment to determine the maximum rate of vertical transport in alluvial gravel vadose zone material was carried out in the late 1970's at the Fairton meatworks near Ashburton (Keeley and Quin, 1979). Levels of chloride (140 mg/L), sodium (115 mg/L) and nitrate-N (28 mg/L) were high in the shallow groundwater under the effluent disposal area and river water, with much lower levels of these compounds, was used as a tracer. The levels of chloride, sodium, and NO₃-N in the river water were 4 mg/L, 6 mg/l and 0.8 mg/L, respectively. In addition, a tracer bacteria, H₂S +ve E. coli, was added to the infiltrating water. The river water was flooded continuously into a shallow excavation 20m in diameter adjacent to a shallow monitoring well. The infiltration rate was 17 mm/hr.

The results (Figure 3-7) showed that the drainage took 22 hours to be observed and travel the 21 m to the water table. This gives a transport rate of about 1 m/hr. However, there was a long tail and the shape of the breakthrough curve indicated that in excess of 100 hours were required for a concentration plateau to be reached, which implies that a long time is required to flush all of a contaminant from the vadose zone profile.

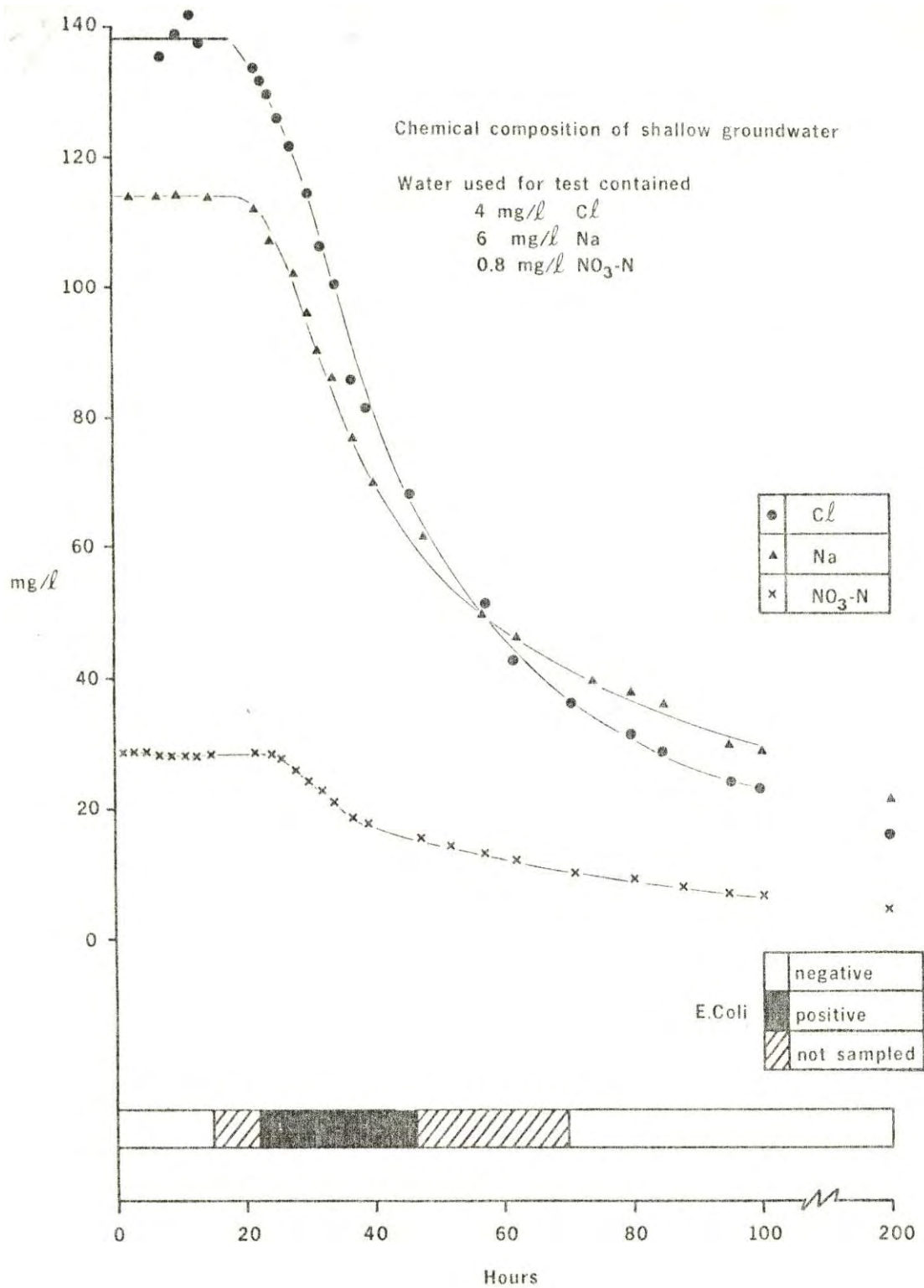


Figure 3-7: Breakthrough curves for CL, Na and NO₃-N from “inverse” tracing experiment at Fairton meatworks site (after Keeley & Quin, 1979)

3.4 Flood irrigation with dairying in Waikakahi catchment, South Canterbury

The effects of intensive dairying and border-strip irrigation on the leaching of *E. coli* and *Campylobacter* to shallow groundwater were assessed over a three-year period in the Waikakahi catchment in South Canterbury (Close *et al.*, 2008). This catchment was chosen as previous surveys by Environment Canterbury had shown high levels of bacterial contamination in shallow wells and an inspection of selected wells (Close, 2002) had indicated that, although some of the contamination was likely to be issues with wellhead protection and contamination by septic tank effluent, contamination by the land use was likely in the shallow groundwater.

Well selection excluded other sources of contamination so that the effect of dairying with border-strip irrigation could be assessed. Groundwater samples (135) were collected, mostly during the irrigation season, with *E. coli* being detected in 75% of samples. *Campylobacter* was identified in 16 samples (12%). *Campylobacter* has a rapid die-off in the vadose zone and the groundwater, with a >4 log removal over 7-14 days for *Campylobacter* in unsaturated alluvial gravel media, typical of vadose zone material in Canterbury (Close *et al.*, 2010). This is equivalent to a T_{90} (time for 90% removal) of 2.1 to 3.6 days. Sinton *et al.* (2007) found similar die-off rates in river and seawater in dark conditions equivalent to groundwater with T_{90} values for *Campylobacter* between 1.5 and 3.4 days. The high levels of microbial contamination in the shallow wells in the Waikakahi catchment, particularly for *Campylobacter*, indicate that the contamination is fairly recent and the water, with the accompanying microbes, has rapidly travelled to the groundwater, probably within a month.

The Waikakahi study is consistent with the flood irrigation experiments with domestic effluent reported by Sinton and colleagues (section 4.2). The significant difference is that these results were obtained for dairying with border strip irrigation, which is a much more widespread land use activity compared to land application of domestic effluent. Both studies demonstrate that rapid transport through the vadose zone of water and microbes will occur under flood irrigation conditions.

4 Environment Canterbury groundwater monitoring data for nitrate-N

4.1 Response to recharge events

Rapid responses of nitrate concentrations in wells to major recharge events have been observed in Canterbury (see section 3.2). An analysis was carried out of the major recharge events at a range of sites in Canterbury. The response of nitrate concentrations in selected wells was compared to the timing of recharge events. Recharge amounts were calculated by Environment Canterbury (David Scott, Nicola Wilson) for 7 locations in Canterbury (Figure 4-1) ranging from Ikawai in South Canterbury to Swannanoa in North Canterbury from January 1960 to May 2010. Climate data from the NIWA (virtual) climate stations were used and profile available water (PAW) were taken for each site from regional soil map information. The locations and parameters for each site are given in Table 4-1. Potential evapotranspiration (PET) data were only available from 1972 onwards so average monthly PET values for each site were used from 1960 to 1971. The recharge depths were estimated for both a dryland situation and an irrigated situation whereby irrigation was applied during the irrigation season when the soil was below 50% of the PAW. The irrigation was applied to restore the soil to field capacity with an 80% irrigation efficiency (N. Wilson, Environment Canterbury, pers comm. June 2010). The recharge estimates were calculated using a daily water balance approach and summed to give monthly totals. An initial analysis of the irrigated data indicated that major recharge events tended to occur during the winter months and, while irrigation increased the amounts of recharge because the soil was wetter, irrigation did not alter the pattern of major recharge events to a large extent (Figure 4-2). Thus only the dryland recharge estimates have been analysed in this report and all recharge estimates are for a dryland situation.

Table 4-1: Locations and profile available water (PAW) values for recharge estimates

| Site | Easting | Northing | nearest NIWA climate site | PAW average (mm) |
|-------------|---------|----------|---------------------------|------------------|
| Ikawai | 2347000 | 5590900 | P099055 | 80 |
| Pareora | 2367000 | 5634400 | P105063 | 150 |
| Temuka | 2380000 | 5665000 | P108068 | 150 |
| Mayfield | 2390000 | 5710000 | P111076 | 75 |
| Pendarves | 2430000 | 5701000 | P121075 | 95 |
| West Melton | 2460000 | 5740000 | P128082 | 65 |
| Swannanoa | 2470000 | 5760000 | P131085 | 85 |

The recharge estimates were analysed as monthly and annual totals. The variation in annual recharge totals is shown in Table 4-2 for 1960 to 2009. There is a wide range in mean annual recharge from 93 mm at Pareora to 319 mm at Mayfield. More significantly, there is a lot of variability in the recharge patterns between the sites, with some major recharge events at some sites not being evident at other sites. In general the 3 most southerly sites, Ikawai, Pareora and Temuka had similar patterns and the 4 other sites had similar patterns. However there were also exceptions, such as Mayfield in 2000 having much more recharge than previous years, which was similar to the 3 southerly sites but different to the 2 most northerly sites.

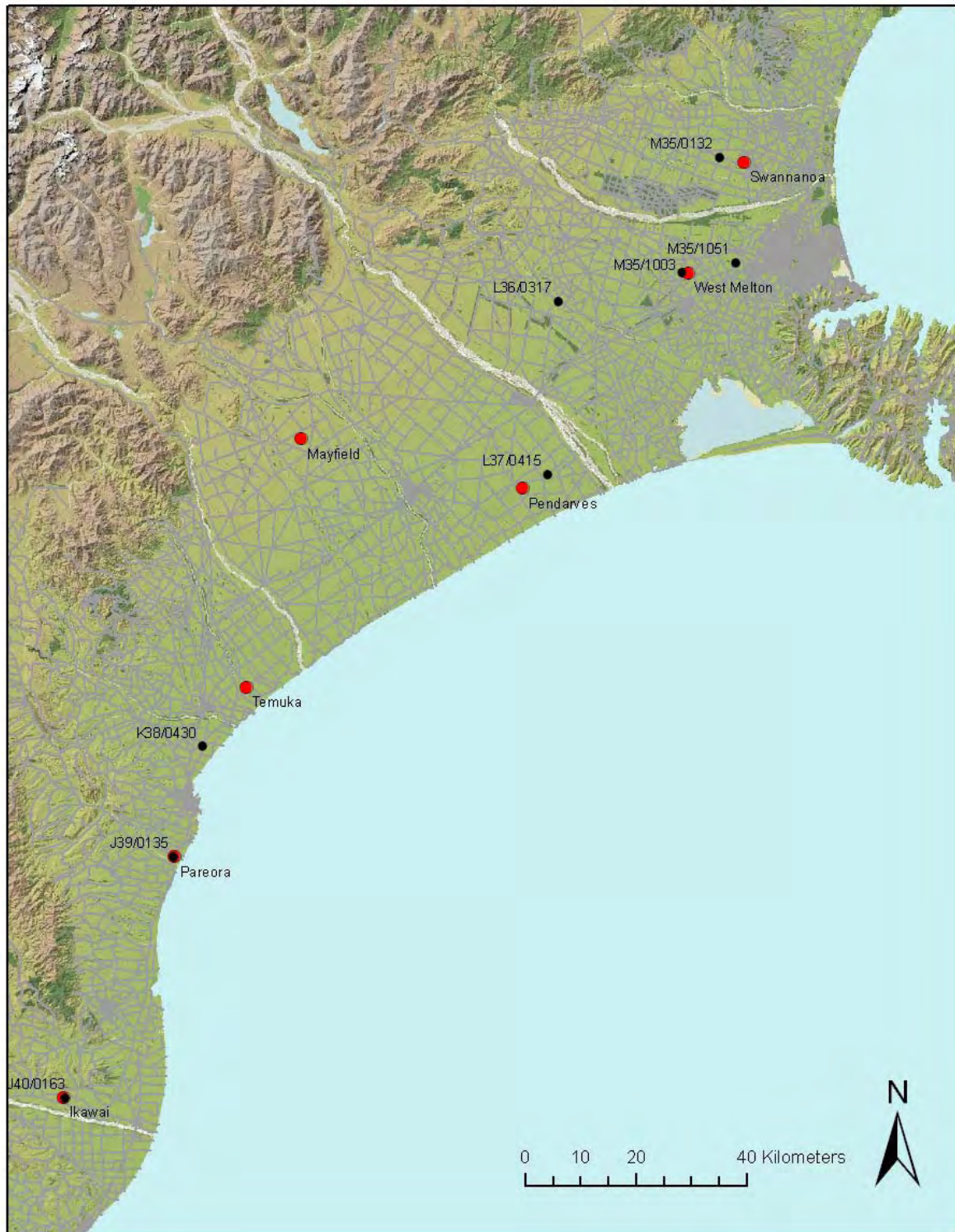


Figure 4-1: Location of recharge sites (red) and wells (black) selected for nitrate response analysis in Canterbury

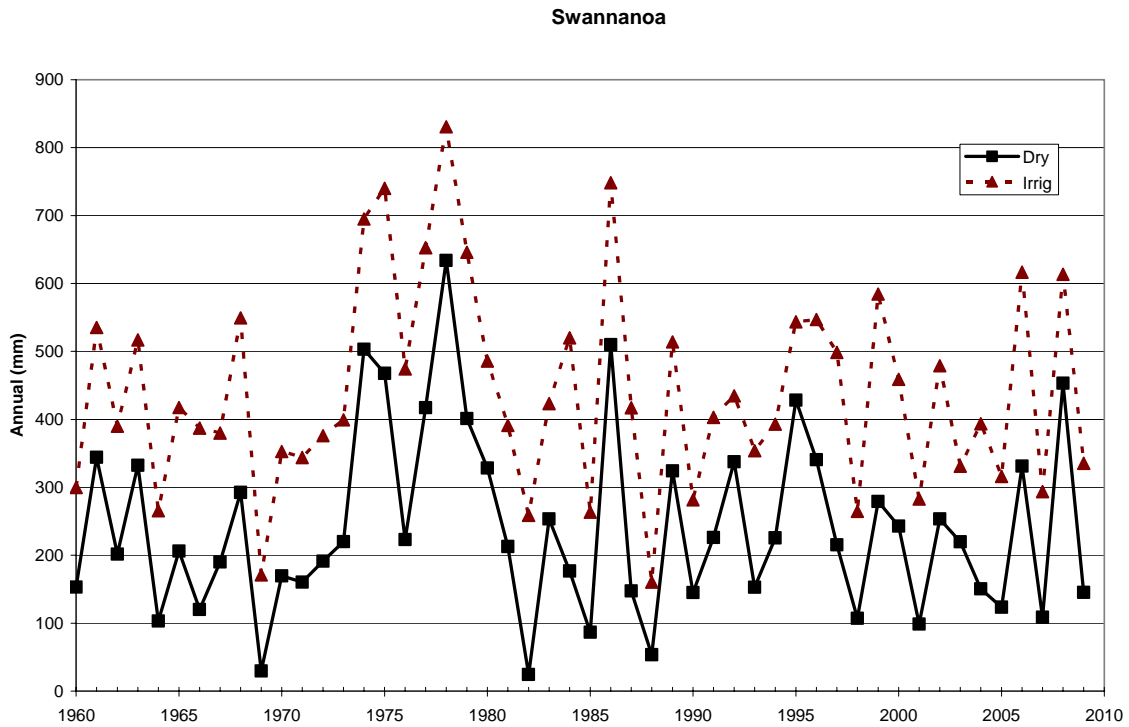


Figure 4-2: Annual estimates of recharge for dryland and irrigated conditions at Swannanoa

An interesting aspect of Table 4-2 is the relatively low levels of recharge that have occurred in Canterbury in the past 20 years, compared to recharge in the previous 30 years. In particular the 1970's were much wetter and other wet years prior to 1990 were 1963, 1968 and 1986. This implies some limitations for the analysis able to be carried out in this project as most of the continuous groundwater nitrate concentration data are from 1990 onwards.

The key implication of the variability of recharge patterns within Canterbury is that a single recharge time series is not sufficient for determining the effect of recharge on nitrate concentrations. As a corollary groundwater patterns of nitrate concentrations in different parts of Canterbury should not be expected to be similar even if they are responding to recharge in the same way.

Table 4-2: Annual estimates of dryland recharge (mm) from 7 Canterbury sites. High recharge totals are highlighted with 300-400mm being blue; 400-500mm being yellow; 500-600mm being green and >600mm being pink

| Year | Ikawai | Pareora | Temuka | Mayfield | Pendarves | West Melton | Swannanoa |
|-------------|------------|------------|------------|------------|------------|-------------|------------|
| 1960 | 45 | 2 | 47 | 202 | 197 | 197 | 153 |
| 1961 | 203 | 157 | 216 | 523 | 333 | 351 | 344 |
| 1962 | 105 | 60 | 81 | 336 | 190 | 226 | 202 |
| 1963 | 310 | 261 | 331 | 559 | 378 | 336 | 332 |
| 1964 | 24 | 0 | 29 | 157 | 78 | 117 | 103 |
| 1965 | 77 | 54 | 56 | 347 | 198 | 232 | 206 |
| 1966 | 50 | 27 | 73 | 255 | 95 | 112 | 120 |
| 1967 | 43 | 28 | 66 | 242 | 102 | 175 | 190 |
| 1968 | 417 | 309 | 285 | 430 | 330 | 311 | 292 |
| 1969 | 1 | 0 | 0 | 121 | 28 | 52 | 30 |
| 1970 | 71 | 26 | 61 | 230 | 152 | 213 | 169 |
| 1971 | 166 | 58 | 73 | 206 | 109 | 152 | 160 |
| 1972 | 152 | 56 | 62 | 240 | 103 | 198 | 191 |
| 1973 | 128 | 71 | 109 | 284 | 255 | 255 | 220 |
| 1974 | 279 | 146 | 207 | 478 | 490 | 527 | 503 |
| 1975 | 148 | 156 | 168 | 521 | 411 | 504 | 468 |
| 1976 | 82 | 0 | 25 | 287 | 174 | 231 | 223 |
| 1977 | 147 | 74 | 121 | 330 | 408 | 440 | 417 |
| 1978 | 525 | 334 | 419 | 712 | 621 | 643 | 634 |
| 1979 | 173 | 155 | 181 | 497 | 403 | 369 | 401 |
| 1980 | 302 | 253 | 236 | 407 | 256 | 279 | 328 |
| 1981 | 209 | 109 | 104 | 256 | 272 | 244 | 213 |
| 1982 | 8 | 2 | 0 | 158 | 90 | 58 | 25 |
| 1983 | 196 | 163 | 171 | 422 | 350 | 298 | 253 |
| 1984 | 97 | 0 | 0 | 165 | 172 | 176 | 177 |
| 1985 | 29 | 0 | 49 | 248 | 196 | 85 | 87 |
| 1986 | 537 | 397 | 461 | 692 | 539 | 470 | 510 |
| 1987 | 305 | 153 | 217 | 441 | 260 | 213 | 148 |
| 1988 | 26 | 0 | 0 | 98 | 30 | 55 | 53 |
| 1989 | 105 | 70 | 112 | 295 | 264 | 327 | 324 |
| 1990 | 228 | 52 | 42 | 265 | 162 | 195 | 145 |
| 1991 | 198 | 99 | 113 | 227 | 173 | 227 | 226 |
| 1992 | 296 | 135 | 204 | 345 | 315 | 342 | 337 |
| 1993 | 139 | 0 | 85 | 315 | 228 | 252 | 153 |
| 1994 | 310 | 75 | 97 | 333 | 219 | 274 | 225 |
| 1995 | 192 | 144 | 244 | 393 | 356 | 359 | 429 |
| 1996 | 142 | 101 | 250 | 386 | 352 | 315 | 341 |
| 1997 | 63 | 0 | 0 | 283 | 180 | 257 | 215 |
| 1998 | 52 | 9 | 38 | 198 | 114 | 137 | 107 |
| 1999 | 108 | 104 | 129 | 290 | 198 | 283 | 279 |
| 2000 | 325 | 260 | 328 | 522 | 304 | 228 | 243 |
| 2001 | 96 | 17 | 34 | 178 | 73 | 129 | 99 |
| 2002 | 165 | 51 | 55 | 231 | 159 | 237 | 253 |
| 2003 | 16 | 8 | 62 | 262 | 202 | 166 | 220 |
| 2004 | 56 | 32 | 75 | 249 | 88 | 167 | 151 |
| 2005 | 17 | 37 | 8 | 87 | 0 | 69 | 123 |
| 2006 | 169 | 93 | 154 | 309 | 309 | 406 | 331 |
| 2007 | 107 | 56 | 61 | 131 | 59 | 112 | 109 |
| 2008 | 162 | 137 | 162 | 478 | 375 | 450 | 453 |
| 2009 | 198 | 141 | 124 | 351 | 133 | 196 | 145 |
| Mean | 160 | 93 | 124 | 319 | 230 | 253 | 241 |
| Max | 537 | 397 | 461 | 712 | 621 | 643 | 634 |

Eight wells located from Ikawai to Swannanoa with sufficient record and variability in nitrate concentration were selected and analysed in detail for their response to recharge. The location of these wells is shown in Figure 4-1. The time series for nitrate was visually compared to the nearest monthly recharge time series and the graphs are shown in Figure 4-3 to 4-11. The information from the comparison between recharge and nitrate concentration is summarised in Table 4-3. The events with greatest responses (1 to 4 events) in nitrate concentration were classed as major responses, with smaller responses being classed as minor to provide some discrimination between events. The recharge in the previous 2 months was also recorded in Table 4-3 to assist in the interpretation. The recharge for the dryland situation was used for this comparison and there were some events during the summer or autumn period that would have been affected by irrigation. The lag between the recharge event and the nitrate response was estimated to the nearest month where possible.

The lag times generally ranged from zero lag to 5 months lag, with most lags being 1 to 3 months. Many of the recharge inputs were complex and often occurred over a period of 2-3 months and the responses in nitrate concentration were also often complex. There was very little relationship between the lag and the depth to the water table. This may imply that the recharge mechanism is displacement of water with nitrate from the bottom of the vadose zone into the groundwater. However, as these major recharge events would often create saturated flow conditions, a rapid non-equilibrium response similar to that observed in the tracer studies could also be the explanation and these recharge – nitrate response relationships do not clearly distinguish between the two processes.

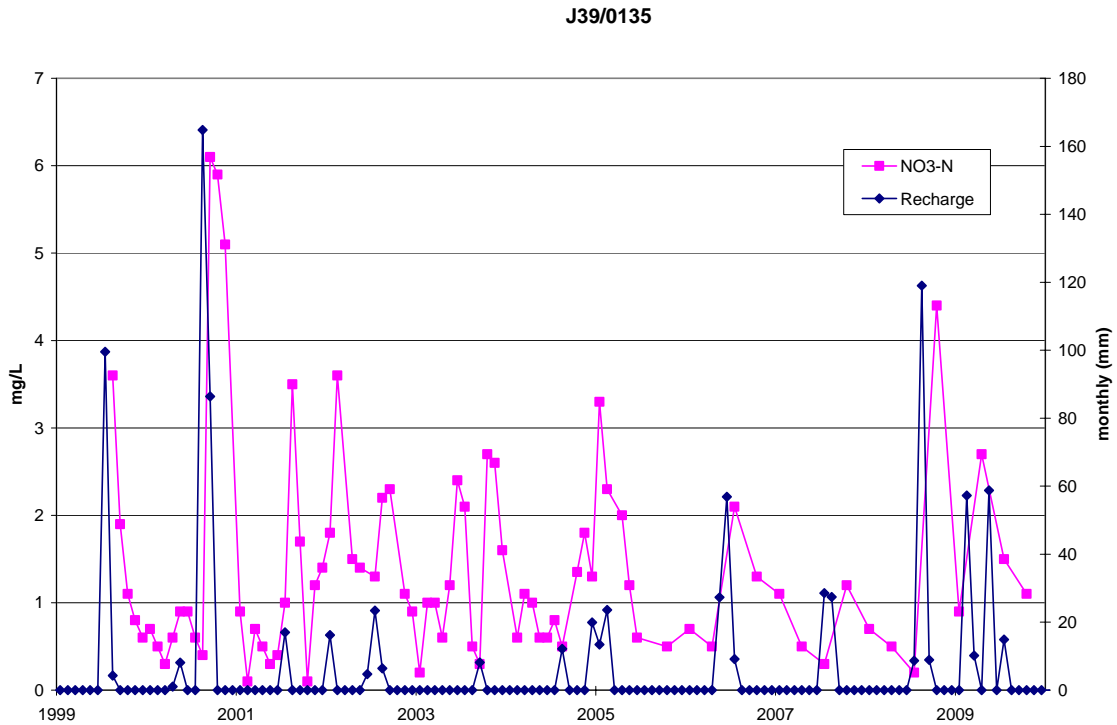


Figure 4-3: Comparison between monthly recharge amounts from Pareora and nitrate-N concentrations for well J39/0135, located near Pareora

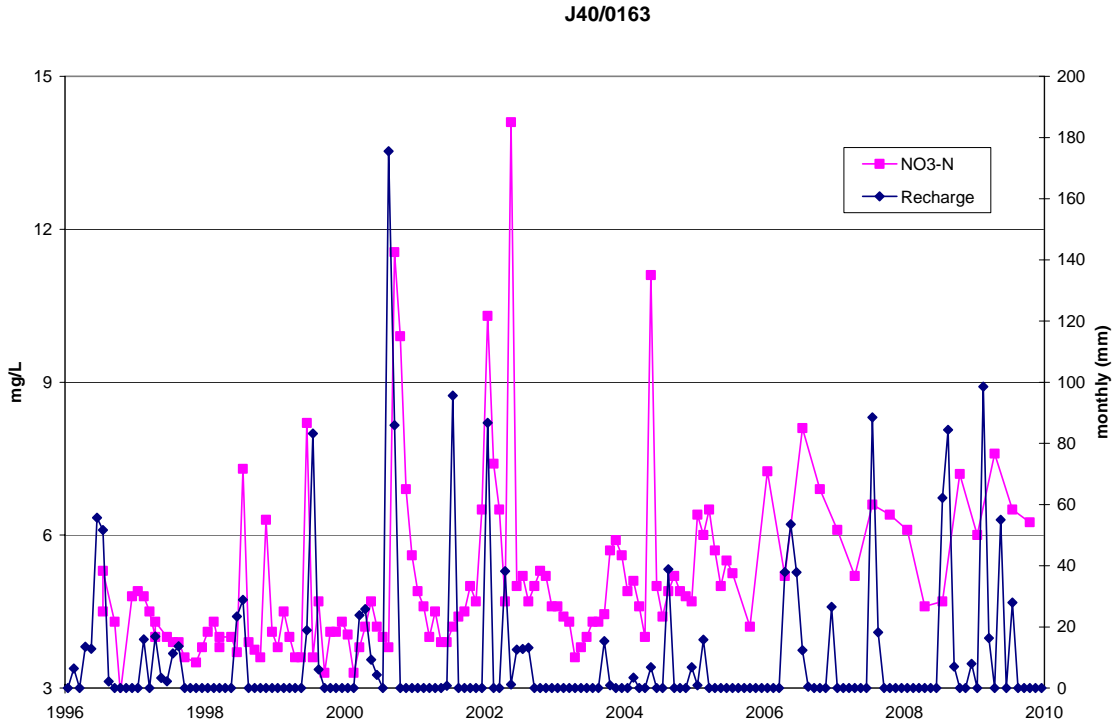


Figure 4-4: Comparison between monthly recharge amounts from Ikawai and nitrate-N concentrations for well J40/0163, located near Ikawai

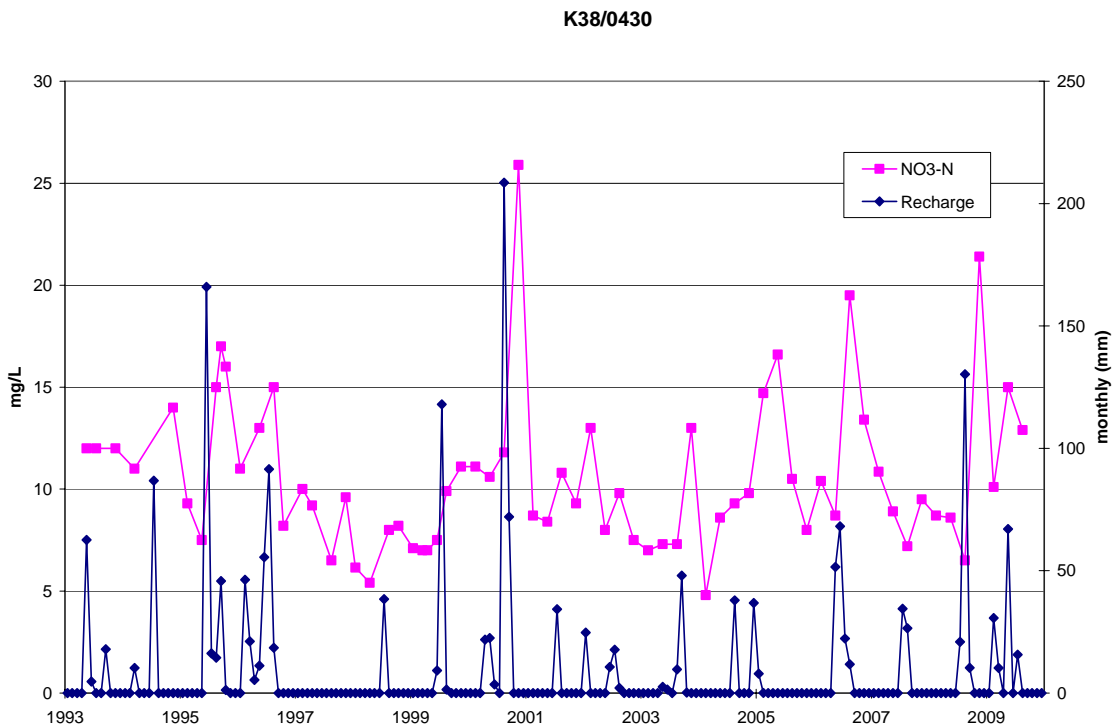


Figure 4-5: Comparison between monthly recharge amounts from Temuka and nitrate-N concentrations for well K38/0430, located near Seadown

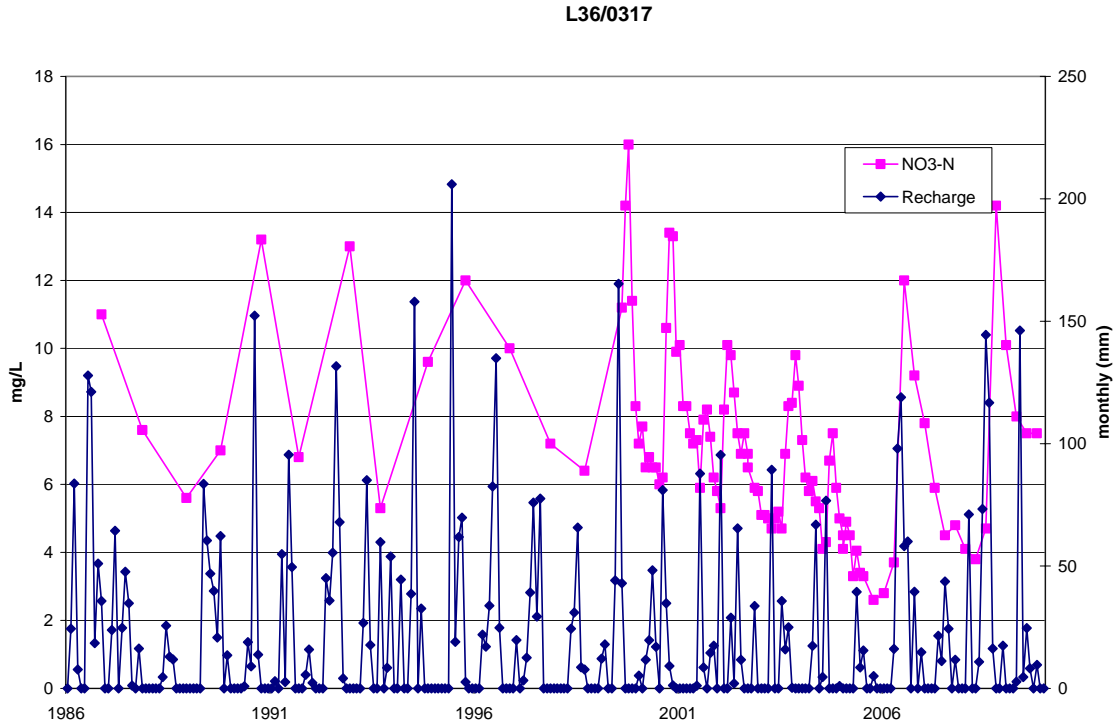


Figure 4-6: Comparison between monthly recharge amounts from West Melton and nitrate-N concentrations for well L36/0317, located near Greendale

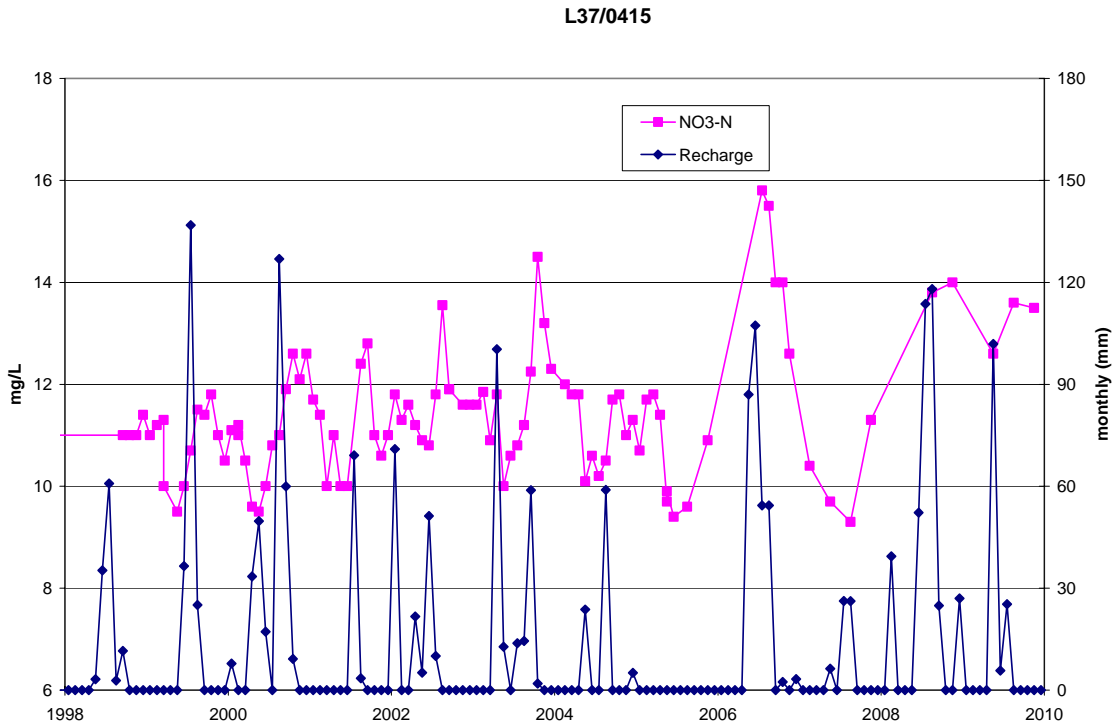


Figure 4-7: Comparison between monthly recharge amounts from Pendarves and nitrate-N concentrations for well L37/0415, located near Dorie

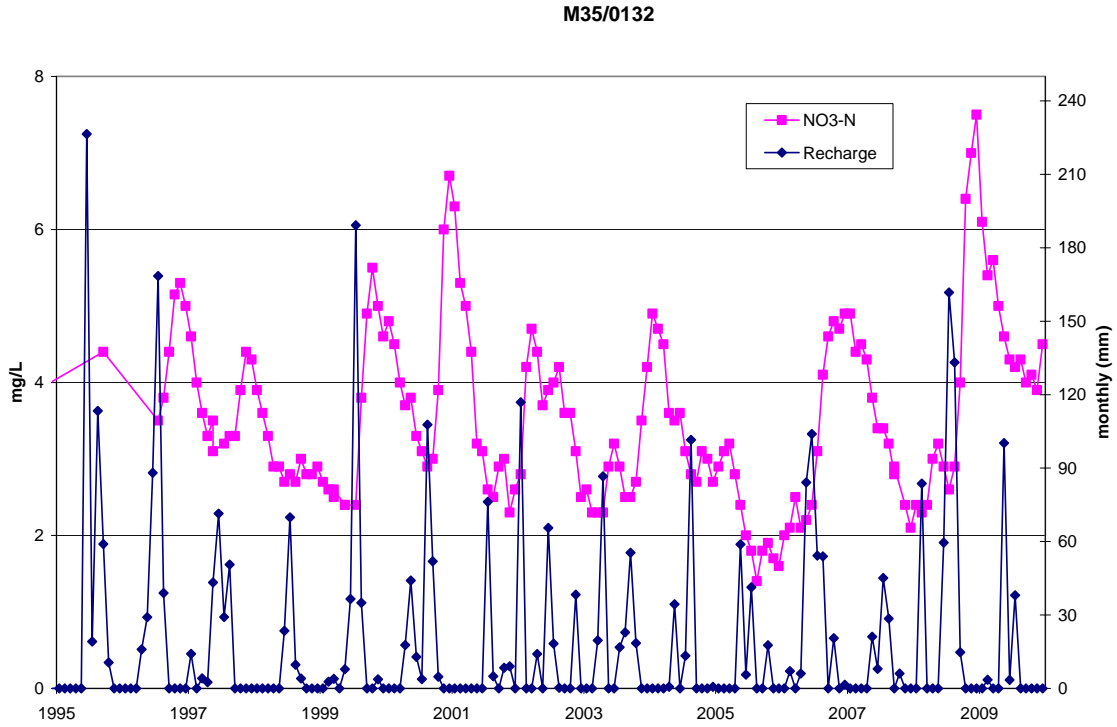


Figure 4-8: Comparison between monthly recharge amounts from Swannanoa and nitrate-N concentrations for well M35/0132, located near Swannanoa

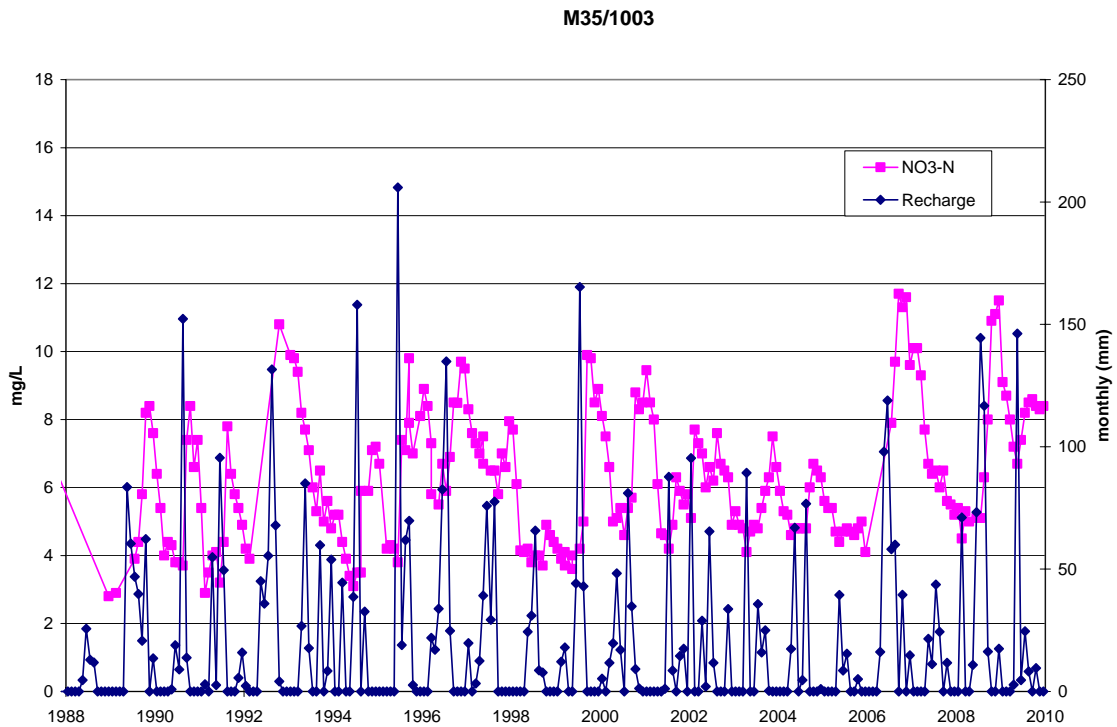


Figure 4-9: Comparison between monthly recharge amounts from West Melton and nitrate-N concentrations for well M35/1003, located near West Melton

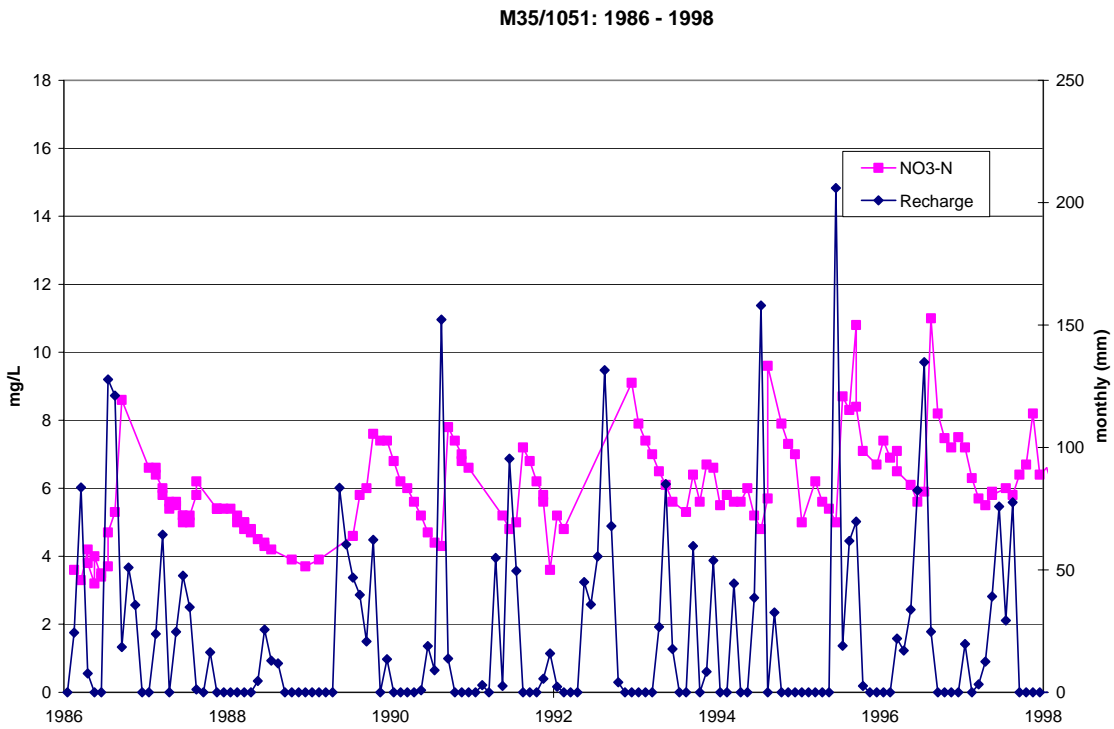


Figure 4-10: Comparison between monthly recharge amounts from West Melton and nitrate-N concentrations for well M35/1051, located near Yaldhurst, for period 1986 to 1998

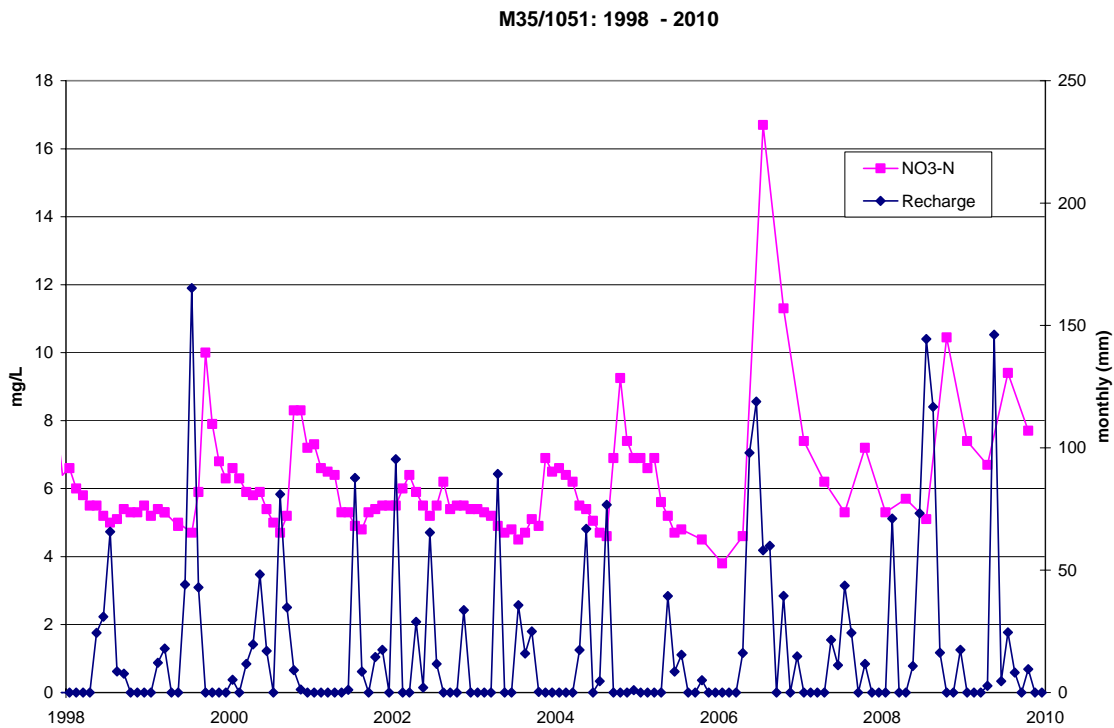


Figure 4-11: Comparison between monthly recharge amounts from West Melton and nitrate-N concentrations for well M35/1051, located near Yaldhurst, for period 1998 to 2010

Table 4-3: Comparison between recharge and nitrate-N response for selected wells

| Recharge Date | Response | Lag (months) | Monthly dryland recharge (mm) | Previous recharge in 2 months (mm) |
|--|----------|--------------|-------------------------------|------------------------------------|
| Well J39/0135; Pareora; well depth = 11m; Depth to water table = 4m.* | | | | |
| May 2000 | Minor | 1 | 8 | 1 |
| August 2000 | Major | 1-2 | 165 | 0 |
| July 2001 | Minor | 1 | 17 | 0 |
| Jan 2002 | Minor | 1-2 | 16 | 0 |
| July 2002 | Minor | 1 | 23 | 5 |
| Sept 2003 | Minor | 1 | 8 | 0 |
| Aug 2004 | Minor | 1-2 | 12 | 0 |
| Dec 04 – Feb 05 | Minor | 1 | 20, 13, 24 | NA |
| June 2006 | Minor | 1 | 57 | 27 |
| July 2007 | Minor | ~2 | 29 | 0 |
| Aug 2008 | Major | 1 | 119 | 9 |
| Feb 2009 | Minor | 1-3# | 57 | 0 |
| Well J40/0163; Ikawai; well depth = 4.6m; Depth to water table = 2m | | | | |
| June 1996 | Minor | 1 | 56 | 26 |
| June 1998 | Minor | 1 | 23 | 0 |
| July 1999 | Minor | 0 | 83 | 19 |
| Aug 2000 | Major | 1 | 176 | 4 |
| July 2001 | No peak | | 96 | 1 |
| Jan 2002 | Major | 0 | 87 | 0 |
| Apr 2002 | Major | 1 | 38 | 0 |
| May 2006 | Minor | 1 – 2# | 53 | 38 |
| July 2007 | Minor | 1 | 88 | 0 |
| Aug 2008 | Minor | 1 – 3# | 84 | 62 |
| Feb 2009 | Minor | 1 – 3# | 99 | 8 |
| Well K38/0430; Seadown; well depth = 3.6m; Depth to water table = 3m | | | | |
| June 1995 | Minor | 2 | 166 | 0 |
| July 1999 | Minor | 2 | 118 | 9 |
| Aug 2000 | Major | 2 | 209 | 4 |
| Sept 2003 | Minor | 1 | 48 | 10 |
| June 2006 | Minor | 2-3# | 68 | 52 |
| Aug 2008 | Major | 2 | 130 | 21 |
| Well L36/0317; Greendale; well depth = 24m; Depth to water table = 11m | | | | |
| July 1999 | Major | 2 | 165 | 44 |
| Aug 2000 | Major | 2 | 81 | 17 |
| July 2001 | Minor | 2 | 88 | 1 |
| Jan 2002 | Minor | 2 - 3 | 95 | 18 |
| Apr 2003 | Minor | 3 | 89 | 0 |
| Aug 2004 | Minor | 2 | 77 | 5 |
| June 2006 | Major | 1 - 2 | 119 | 114 |
| Jul 2008 | Major | 2 | 144 | 84 |

* there were some NO₃-N peaks in this well that may have corresponded to recharge from irrigated pasture.

Nitrate data are quarterly for this period so not possible to be more precise.

Critical review of contaminant transport time through the Vadose Zone

Table 4-3 continued.

| Recharge Date | Response | Lag (months) | Monthly dryland recharge (mm) | Previous recharge in 2 months (mm) |
|--|----------|--------------|-------------------------------|------------------------------------|
| Well L37/0415; Dorie; well depth = 30m; Depth to water table = 25m. | | | | |
| July 1999 | Minor | 0 | 137 | 37 |
| May 2000 | Minor | 1 - 2 | 50 | 33 |
| Aug 2000 | Minor | 1 - 2 | 127 | 17 |
| July 2001 | Minor | 1 - 2 | 69 | 0 |
| Jan 2002 | Minor | 1 | 71 | 0 |
| June 2002 | Minor | 2 | 51 | 27 |
| Jul – Sept 2003 | Major | 4@ | 100; 59 | |
| May – June 2006 | Major | 1 - 2 | 87; 107 | 0 |
| Well M35/0132; Swannanoa; well depth = 20.4m; depth to water table = 5m | | | | |
| July 1996 | Minor | 3 | 168 | 117 |
| July 1999 | Major | 3 | 189 | 44 |
| Aug 2000 | Major | 4 | 108 | 16 |
| Jan 2002 | Minor | 2 | 117 | 9 |
| Sept 2003 | Minor | 4 | 55 | 39 |
| May – June 2006 | Major | 5 | 84; 104 | 6 |
| Jul – Aug 2008 | Major | 3 - 4 | 162; 133 | 66 |
| Well M35/1003; West Melton; well depth = 39.6m; depth to water table = 28m | | | | |
| May 1989 | Minor | 3 | 84 | 0 |
| Aug 1990 | Minor | 2 | 152 | 28 |
| June 1991 | Minor | 2 | 95 | 57 |
| Aug 1992 | Major | 1-3# | 132 | 91 |
| Jul 1994 | Minor | 4 | 158 | 39 |
| June 1995 | Minor | 3@ | 206 | 0 |
| July 1996 | Minor | 4 | 135 | 115 |
| July 1999 | Minor | 3 | 165 | 44 |
| Aug 2000 | Minor | 3 – 4 | 81 | 17 |
| June 2006 | Major | 4 | 119 | 114 |
| Jul 2008 | Major | 4 – 5 | 144 | 84 |
| Well M35/1051; Yaldhurst; well depth = 32.6m; depth to water table = 17m | | | | |
| July 1986 | Minor | 2 | 128 | 0 |
| May 1989 | Minor | 4 | 84 | 0 |
| Aug 1990 | Minor | 1 | 152 | 28 |
| June 1991 | Minor | 2 | 95 | 57 |
| Aug 1992 | Minor | 1 – 4# | 132 | 91 |
| Jul 1994 | Minor | 1 | 158 | 39 |
| June 1995 | Minor | 1 – 3 | 206 | 0 |
| July 1996 | Minor | 1 | 135 | 115 |
| July 1999 | Minor | 2 | 165 | 44 |
| Aug 2000 | Minor | 2 | 81 | 17 |
| June 2006 | Major | 1 – 2 | 119 | 114 |
| Jul 2008 | Minor | 2 | 144 | 84 |

@ complex recharge pattern

Nitrate data are quarterly for this period so not possible to be more precise.

4.2 Response to land use changes

4.2.1 Change in effluent disposal practices at Ashburton Meat Processing Plant

The Ashburton Meat Processing Plant has discharged effluent from the plant onto land since about 1912. The area for effluent application is 24.6 ha and the actual maximum average weekly effluent volume was 1647 m³ (Hayward and Hanson, 2004). This gave a weekly application depth of about 7 mm. If this was applied for the consent period (280 days per year) then the annual recharge could be as much as 280 mm from the effluent application and an annual total of about 520 mm when combined with the mean recharge for Pendarves (Table 4-2).

In 2000 a series of improvements were made to the management of the effluent which were implemented over a 2 year period. The area for effluent application has remained the same and the volume of effluent applied has remained reasonably constant, but has decreased by about 20% in the 2008-2010 period due to a decreasing kill (Brad Cook, site manager, June 2010, pers comm.). A cut and carry operation started in 2000 instead of grazing and has continued to the present time. A significant amount of the blood has been removed from the effluent and is recycled as blood meal and the yard washing now go through two settlement tanks before land application, which would reduce the concentration of various contaminants. The amount of effluent would not be affected by these improvements which implies that the improvements are not recharge-related but are related to a reduction in the mass loadings of contaminants in the applied effluent. For this type of land use change you would expect a more gradual response compared to a recharge-related change.

Nitrate-N concentrations in up-gradient and down-gradient wells are shown in Figure 4-12. These wells are screened in shallow groundwater (14-20 m bgl) and should show a reasonably rapid response to land use changes. The groundwater table is approximately 6 m bgl at this site. The up-gradient well (L37/0914) shows a steady increase over this period from about 3 mg/L around 1994 to around 7 mg/L in 2007. In contrast, the down-gradient well (L37/0918) showed a large degree of variability with a mean nitrate-N level around 19 mg/L prior to 2001, followed by a slightly lower degree of variability with a mean nitrate-N level of around 12 mg/L. The response due to the land use change seems to taken place within a year. It is difficult to be more precise than this due to lack of knowledge concerning the exact timing of the improvements.

Table 4-4 Nitrate-N concentrations (mg/L) in up-gradient and down-gradient wells around the Ashburton Meat Processors effluent disposal area

| Time period | Up-gradient L37/0914 | Down-gradient L37/0918 |
|--------------------------------|-----------------------------|-------------------------------|
| 1993 – 2001 (pre-improvement) | 3.61 | 18.79 |
| 2002 – 2009 (post-improvement) | 6.86 | 12.24 |

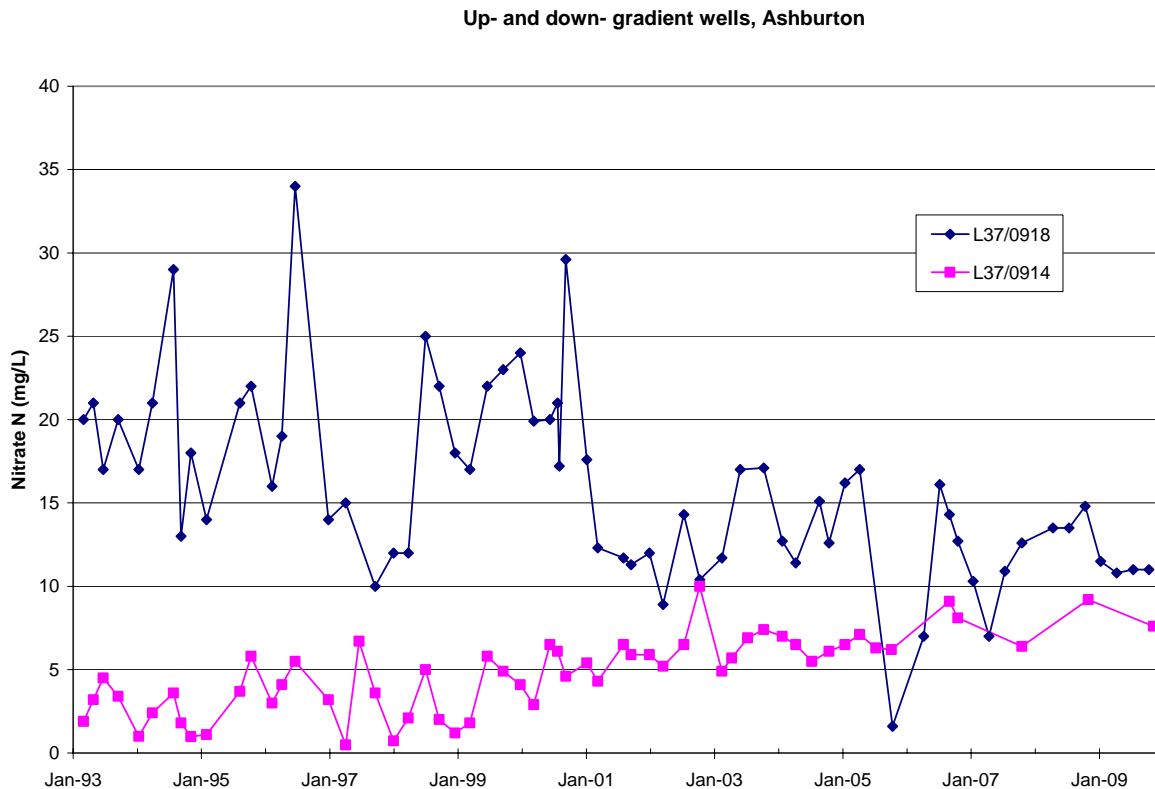


Figure 4-12: Nitrate-N concentrations in wells up-gradient (L37/0914, 20 m deep) and down-gradient (L37/0918, 14 m deep) of Ashburton Meat Processor effluent application area. Improvements to effluent management occurred between 2001 and 2003 and are ongoing

For a groundwater table about 6 m bgl, if we assume a PAW of 95 mm for the top metre of soil (Table 4-1) and a soil water content for the underlying gravels of 7.4% v/v (Dann *et al.*, 2009), then the profile water content (pore volume) could be estimated as $95 + 5 \text{ times } 74 = 465 \text{ mm}$. The annual recharge at the site is greater than this amount so the change due to effluent improvement would be expected within a year, providing it is a uniform or equilibrium recharge process. This is consistent with the response seen in Figure 4-12 which seems to be less than one year. For a site with a lower recharge rate, the response is likely to be slower.

4.2.2 Cessation of effluent disposal from Islington Freezing Works in 1988

The freezing works commenced operation at Islington in 1880 and land disposal of effluent took place from that time until 1988 when the freezing works were sold. The effluent disposal is described in Curtis (1981) and is briefly summarised here. In the early 1980's effluent was disposed at three separate sites around Islington (Figure 4-13). Effluent was disposed onto the main disposal area by wild flooding and ponding until about 1945 when a program of more controlled irrigation using border strips was implemented. The area of land was increased between 1960 and 1980 and totalled 93.4 ha in 1981. In 1975 a sedimentation tank was added to remove settled solids and floatable grease. The oxidation pond disposal area totalled 23 ha in 1981 and received oxidation pond effluent via border strip irrigation. Before 1974 the effluent was discharged straight into soakage pits. The pelt effluent disposal area received effluent from the chemical treatment of pelts which used lime, sodium sulphide, ammonium sulphate, sulphuric acid and sodium chloride. The continued application of this effluent had resulted in decreased flows through the top soil so the top soil was removed and the effluent applied directly into the gravels. Analyses of the main works and pelt effluents indicated that these had high levels of chemical oxygen demand (2500 – 3100 mg/L), nitrogen (130 and 350 mg N/L for the main works and pelt effluents, respectively) and the pelt effluent was very alkaline (pH = 11.8) and had high levels of chloride and sulphide (Curtis, 1981). The mean flow of the main works effluent was 88,860

m³/month and the flow of the pelt effluent was 7,524 m³/month with the works operating between November and June each year.

The groundwater table at the site was described as varying from 13 to 17 m bgl, (Curtis, 1981). If we assume a PAW of 65 mm for the top metre of soil (Table 4-1) and a mean soil water content for the underlying gravels of 7.4% v/v (Dann *et al.*, 2009), then the profile water content (pore volume) could be estimated as 65 + 14 times 74 = 1100 mm, for a water table at 15 m bgl. The annual recharge totals, as estimated from West Melton data (Table 4-2), since 1988 are 327mm, 195mm, 227mm, 342 mm, and 252 mm for 1989 to 1993, respectively. The cumulative recharge total since 1988 reaches 1091 mm (approximately the profile water storage) after 1992, or a period of 4 years. After this period plus the travel time in the groundwater system, you would expect to see changes in water quality if there was predominately uniform flow. If there was significant bypass or rapid flow then you would expect to see some changes more rapidly but the total change in water quality would take longer to observe. The recharge responsible for flushing the nitrate from the vadose zone would be from dryland environment and would thus be less likely to produce very saturated recharge conditions.

Down-gradient wells showed elevated levels of nitrate and wells down-gradient of the pelt wastes disposal area also showed elevated levels of chloride and sulphate (Curtis, 1981). Well M35/1101, situated immediately down-gradient of the effluent disposal area (Figure 4-13), was monitored intermittently between 1979 and 1983 and had nitrate-N levels ranging between 7 and 33 mg/L (median = 12 mg/L). This compares to well M35/1100 (24 m deep) sited immediately up-gradient of the main disposal area (Figure 4-13), which had nitrate-N levels ranging between 2.8 and 5.5 mg/l from 1979 to 1983 (median = 3.7 mg/L). Well M35/1839 (25 m deep), situated 600 m down-gradient from the main effluent disposal area, had nitrate-N levels ranging between 3 and 27 mg/L with a median value of 13.6 mg/L. Unfortunately these two wells and others immediately down-gradient of the effluent disposal areas were not monitored after the plant was sold in 1988 and effluent disposal ceased.

The nearest down-gradient well with more recent nitrate data is well M35/1883 (29 m deep) and is about 3 km down-gradient of the main effluent disposal area (Figure 4-13). This well has been sampled annually since July 1989. Nitrate-N concentrations were around 10 mg/L (ranged between 7.7 and 13 mg/L) from 1989 to 1996 and then decreased to around 6 mg/L from 1997 to 2007 (Figure 4-14). This indicates a period of around 7 years after effluent discharge ceased before nitrate concentrations decreased in this well. The continuing slow decline in nitrate concentrations indicates that there was probably significant non-equilibrium transport at this site with a long tail of high nitrate inputs over a period of years. The distance of the well down-gradient and the natural variability of the nitrate concentrations limits more precise interpretation of the non-equilibrium nature of leaching.

Graphs showing the time series of nitrate-N concentrations in well further down-gradient from the effluent disposal area are shown in Figure 4-15 – 4-17. There are decreases in nitrate-N concentrations with time in each of the wells which may possibly be linked to the cessation of effluent disposal. The nitrate concentrations in well M36/1059 are quite variable and, although they decrease from 1989 to 1993, they increase and decline from 1995 to 2003 and then increase again from 2005 to 2009. This implies that this well is responding to several sources and is not a good indicator of the land use change at Islington. Well M36/0974 has higher levels of nitrate from 1987 (start of data record) to 1993 and then levels decrease from 1994 onwards. This would correspond to a lag of about 6 years. Well M36/1057 has nitrate-N concentrations between 5 and 6 mg/L for the period 1987 to 2001, which then decrease to between 4 and 5 mg/L from 2002 onwards. If this decrease is associated with the land use change at Islington then this would correspond to a lag of about 13 years. However the decreases in nitrate-N levels are only slight for these last two wells and the further down-gradient the well is, the less confident is the link between the change in water quality and the up-gradient land use change.

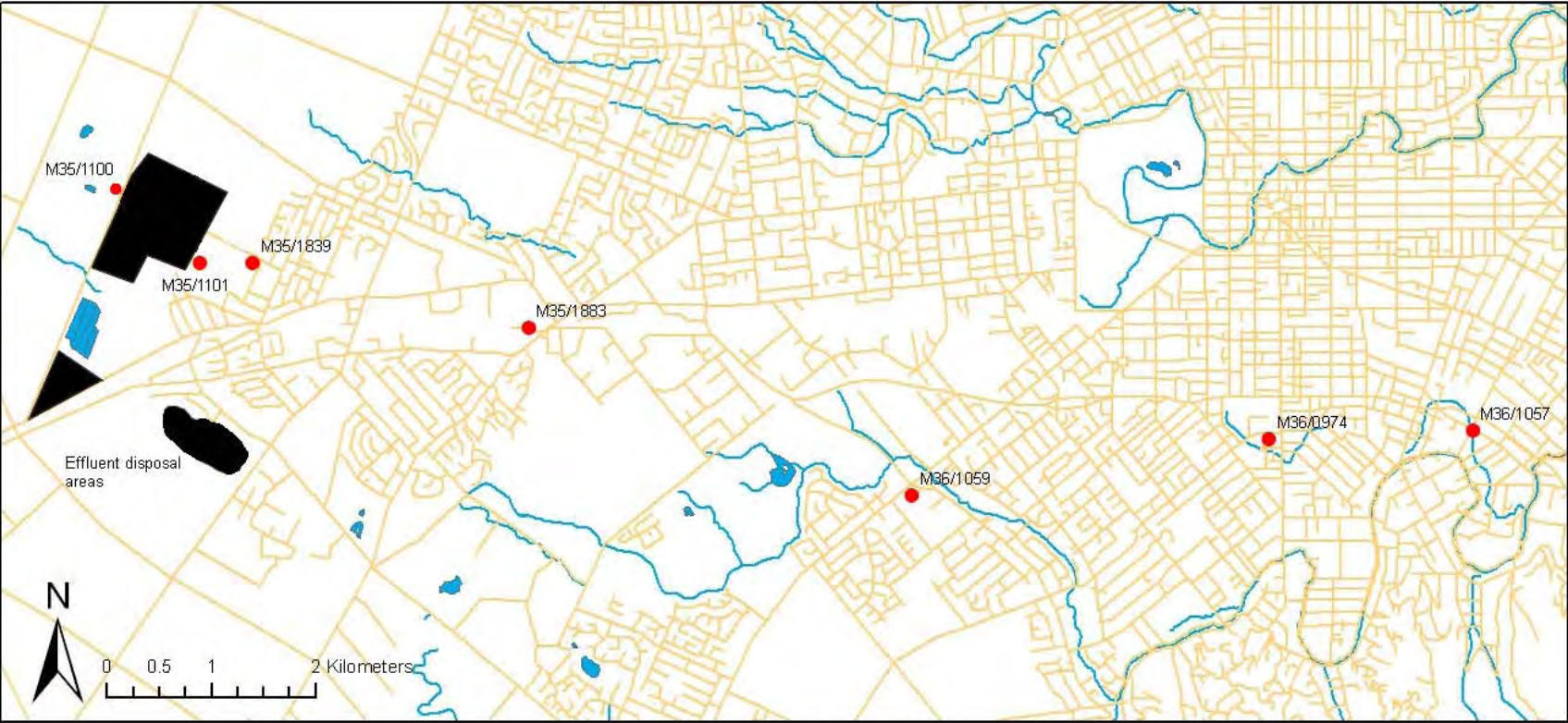


Figure 4-13: Location of effluent disposal areas around Islington and key monitoring wells

For the most reliable down-gradient monitoring well, M35/1883, the pattern of nitrate decrease in the down-gradient monitoring wells shows a decrease in nitrate concentrations since 1988, with a plateau period after 1988 of about 7 years followed by a decrease over a period of 2-3 years. This is consistent with a mostly uniform leaching process, with some of the nitrate in the vadose zone taking longer to leaching than expected from a totally equilibrium process.

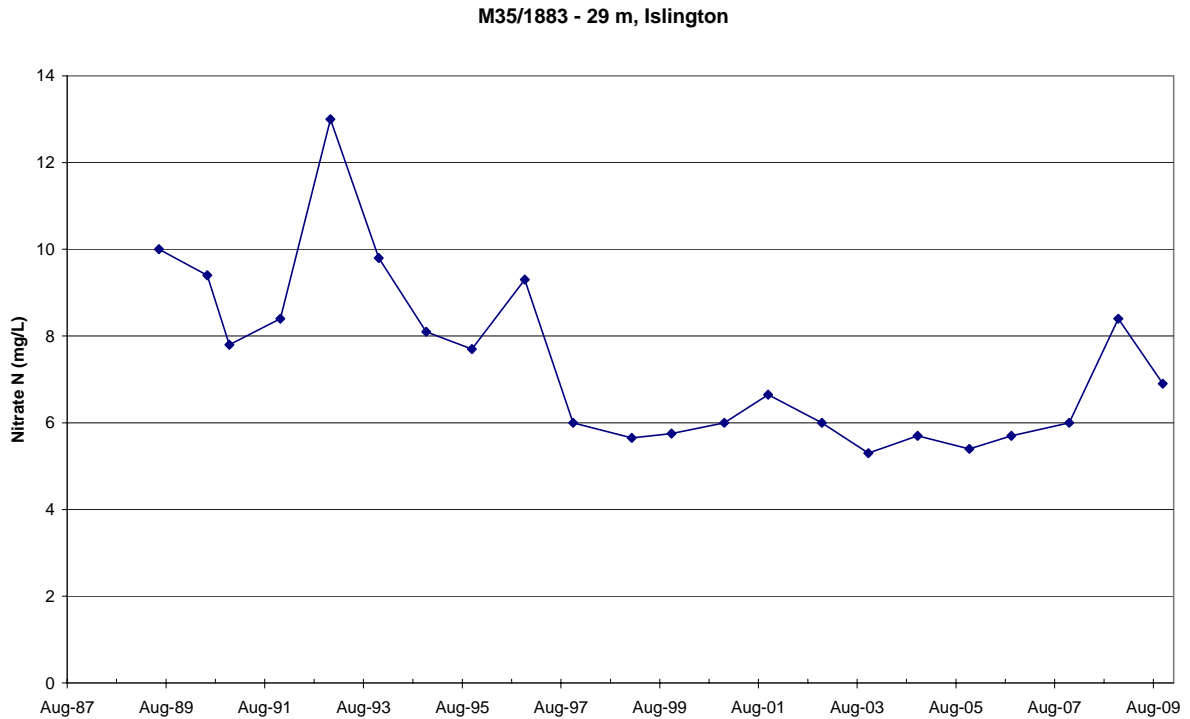


Figure 4-14: Nitrate-N concentrations in well M35/1883 located 3 km down-gradient from Islington effluent disposal area

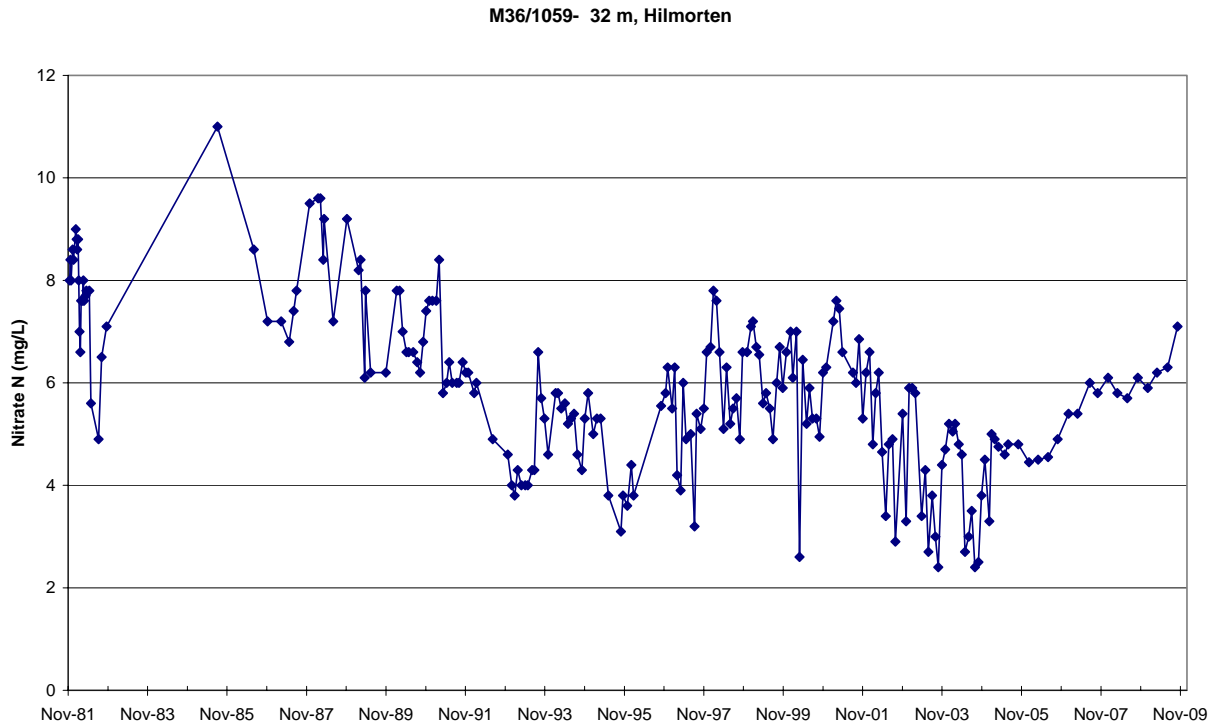


Figure 4-15: Nitrate-N concentrations in well M36/1059 located 7 km down-gradient from Islington effluent disposal area

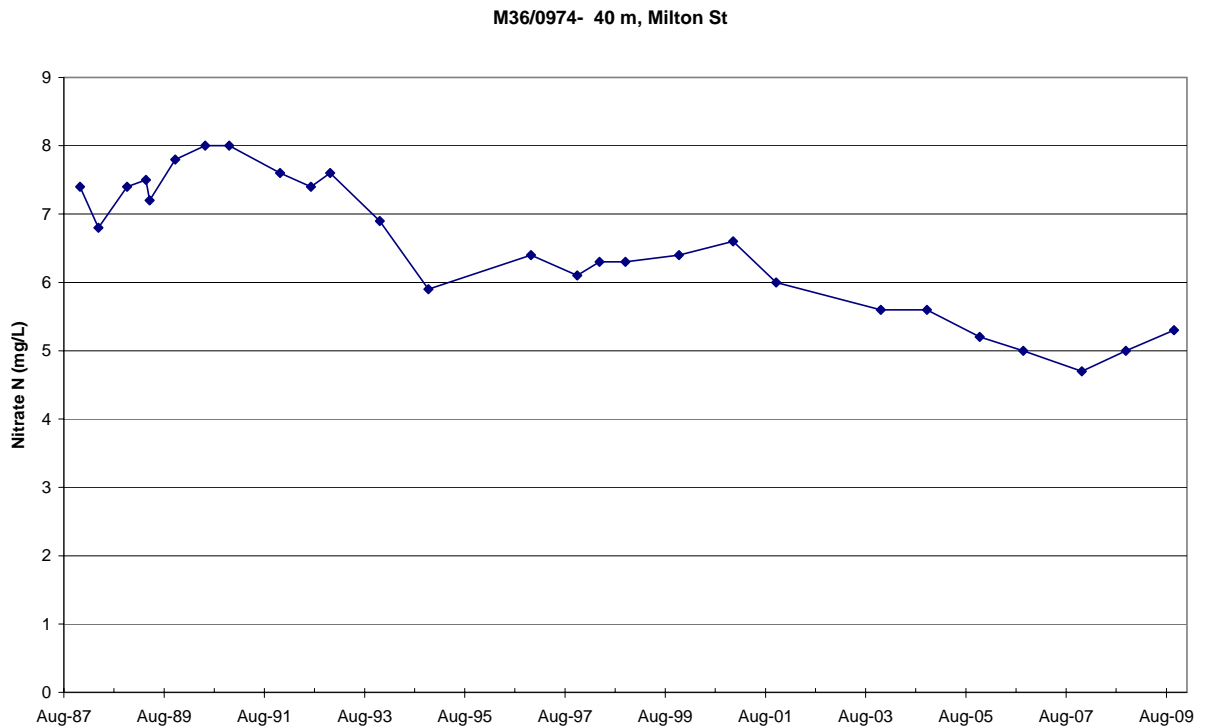


Figure 4-16: Nitrate-N concentrations in well M36/0974 located 10 km approximately down-gradient from Islington effluent disposal area

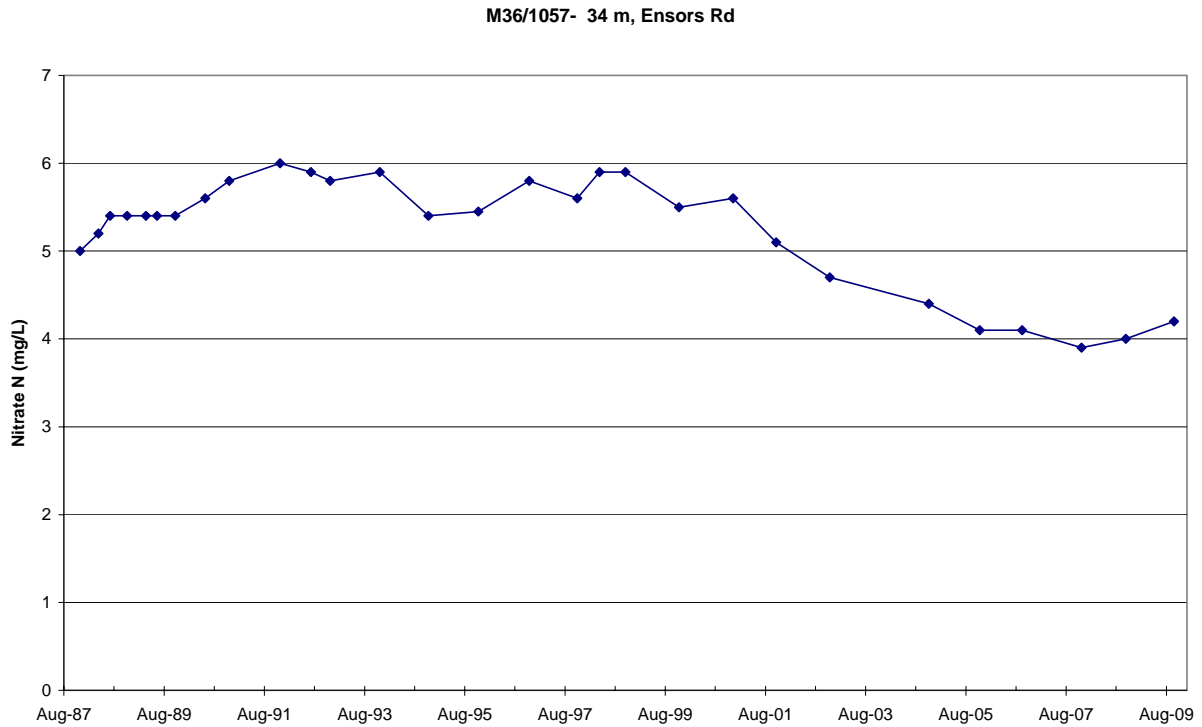


Figure 4-17: Nitrate-N concentrations in well M36/1057 located 12 km approximately down-gradient from Islington effluent disposal area

4.3 Variability of vadose zone profile water content

Two important vadose zone properties related to the hydrological water balance are the total amount of the water held in the vadose zone and the estimated annual flux. Although there is good evidence from tracer studies that non-equilibrium transport often occurs in wet or saturated flow conditions with more rapid transport followed by a long slower moving tail, the movement of the centre of mass for the tracer will not vary as much as the rapid initial front or the long tail and may give useful information about the average movement of tracer. The modelling results from the IRAP tracing experiments (Dann *et al* 2010) discussed in section 4.1 also indicate that the total transporting water contents (combined for both the macropore and matrix domains) were similar to the observed water contents of the profiles. In this section the total amount of water held in the vadose is calculated using limited observations of water content in the vadose zone and combined with estimated annual recharge flux to estimate an average time for water to reach the water table.

Environment Canterbury has estimated the depth to the water table and hence the depth of water above the well screen for a number of the wells in their monitoring network. This information was combined with the soil profile available water for the upper 1 m for the area (based on regional soils database) and the annual dryland recharge totals. The average time that water and associated contaminants would take to reach the water table was estimated from this information assuming uniform equilibrium processes and using the average water content of 7.4% (or 74 mm/m) for vadose zone sandy gravel material from Dann *et al.* (2009). The travel time was calculated as follows:

$$\text{VZ total profile water content (mm)} = \text{PAW for top 1 m} + (\text{VZ depth} - 1) * 74$$

$$\text{Average VZ travel time} = \text{VZ total profile water content} / \text{mean annual recharge}$$

It should be noted that there is a lot of uncertainty in the mean water content value as it is only based on samples from a few locations but it serves to give an estimate of likely travel times throughout

Canterbury for non-irrigated recharge. It is also assumed that the vadose zone is comprised mainly of sandy gravel media. This is a good assumption for most of the Canterbury Plains area but may not be so applicable for some areas, such as around Pareora. The purpose of these calculations was not to provide accurate information for a particular location but to provide an approximate estimate of the travel times and likely range.

The vadose travel time was estimated for each well in the Canterbury Plains area for which a vadose zone depth had been estimated by Environment Canterbury. Each well was matched with the nearest recharge series (section 5.1) to provide the PAW and mean annual recharge. Table 4-4 gives a summary for each of the recharge series locations. The number of wells for each location varied from 15 to 61, and the mean travel times varied from 1.7 to 7.6 years. The minimum travel time was 0.2 years and the maximum travel time was 33 years. These travel times are for average dryland conditions and would be lower for irrigated situations. Further analysis of these vadose zone travel times is beyond the scope of this report and beyond the accuracy and availability of existing data on vadose zone water contents and structure.

Table 4-5: Summary of estimated vadose zone travel times for selected locations assuming equilibrium discharge. Note that the average water content for the sandy gravel vadose zone media of 7.4% v/v is derived from a limited number of sites in central Canterbury

| Recharge series | Mean annual recharge (mm) | Profile available water (mm) | Vadose zone travel time (years) | | | | |
|-----------------|------------------------------|---------------------------------|---------------------------------|------|--------|---------|---------|
| | | | n | mean | median | minimum | maximum |
| Ikawai | 160 | 80 | 21 | 2.4 | 2.4 | 0.5 | 5.6 |
| Pareora | 93 | 150 | 15 | 3.9 | 3.2 | 1.6 | 17.5 |
| Temuka | 124 | 150 | 30 | 3.2 | 2.7 | 1.2 | 9.6 |
| Mayfield | 319 | 75 | 24 | 4.3 | 1.6 | 0.2 | 27.8 |
| Pendarves | 230 | 95 | 44 | 7.6 | 3.3 | 0.4 | 32.9 |
| West Melton | 253 | 65 | 61 | 6.6 | 3.8 | 0.3 | 27.8 |
| Swannanoa | 241 | 85 | 23 | 1.7 | 1.6 | 0.4 | 6.8 |

5 Age dating of groundwater

In this section the age dating measurements that have been carried out for wells in Canterbury are examined with respect to consistency with the transport processes described in this report and for additional information and insights contained in the age dating dataset. The focus was on age data for shallow and moderately shallow wells (down to about 70 m). These data are contained in reports by Stewart *et al.* (2002), Stewart, (2005, 2006), and van der Raaij (2007). Environment Canterbury have estimated the depth to the water table and hence the depth of water above the well screen for a number of the wells in their monitoring network. This information was merged with the age dating information. There were 38 wells with both age data and vadose zone information that were screened such that the well screen was less than 35 m below the water table. This selection criterion was used so that it was possible that water from the vadose zone and vadose zone travel processes could influence the estimated age of the water.

Another factor in explaining groundwater having older ages than expected could be the location of the well. If the well is in a discharge area (say near the coast where the direction of groundwater flow is upwards) then older water could come to shallow levels. Likewise younger water would be expected in a recharge area where the groundwater flow tends to be downwards. For the selected wells in Table 5-1, most are not located in a groundwater discharge area, with one well (M36/0698) probably located in a groundwater discharge area.

There was a positive slope for the trend line between the age of the water and the depth of the vadose zone (Figure 5-1: Age = 0.3 * Vadose Zone depth + 23; $r^2 = 0.12$) but the relationship was much poorer than expected. There was also a slight positive relationship between the age of the water and the depth of water above the well screen (Figure 5-1: Age = 0.36 * Depth water above screen + 24; $r^2 = 0.02$) but the r^2 value was near zero. It should be noted that the depth of water above the well screen was restricted to depths < 35 m to look at wells that were screened relatively close to the water table, which would have affected the observed relationship.

Some shallow wells were identified with relatively old ages that also showed rapid responses to recharge events and were examined more closely (Table 5-1). The possibility of irrigation with older water, particularly if deeper groundwater is used, causing the water from a particular well to appear older than it actually is, has been discussed in Section 3.4. The presence and type of irrigation up-gradient from each well in Table 5-1 was roughly assessed using Google Maps. All of these wells had some possibility of irrigation influencing the composition of the water, which is not surprising given the widespread occurrence of irrigation on the Canterbury Plains. If the irrigation water is retaining its age signature during the irrigation and recharge process then this could explain some of the groundwater having older ages than expected. It may also provide an explanation for the SF₆ showing the youngest age, followed by CFC-12, then CFC-11 and then tritium, as the more volatile tracers will re-equilibrate fastest and retain less of their age signature. The amount of irrigation water applied varies from season to season and also with the application method, crop and soil. Environment Canterbury have calculated the irrigation demand, which could be used as an estimate of irrigation application, for various locations in Canterbury (see section 5.1). This can be used to give an estimate of the amount of irrigation relative to the rainfall input at a particular location. For the seven locations used in section 5.1, the amount of irrigation ranged from 48 – 86% of the rainfall input calculated from 1960 to 2009. The drier locations had higher inputs of irrigation as would be expected. This rough estimate indicates that the input of irrigation is significant and could have an important influence on the apparent age of the shallow groundwater, depending on how much the age signature of the irrigation water is retained through the application process.

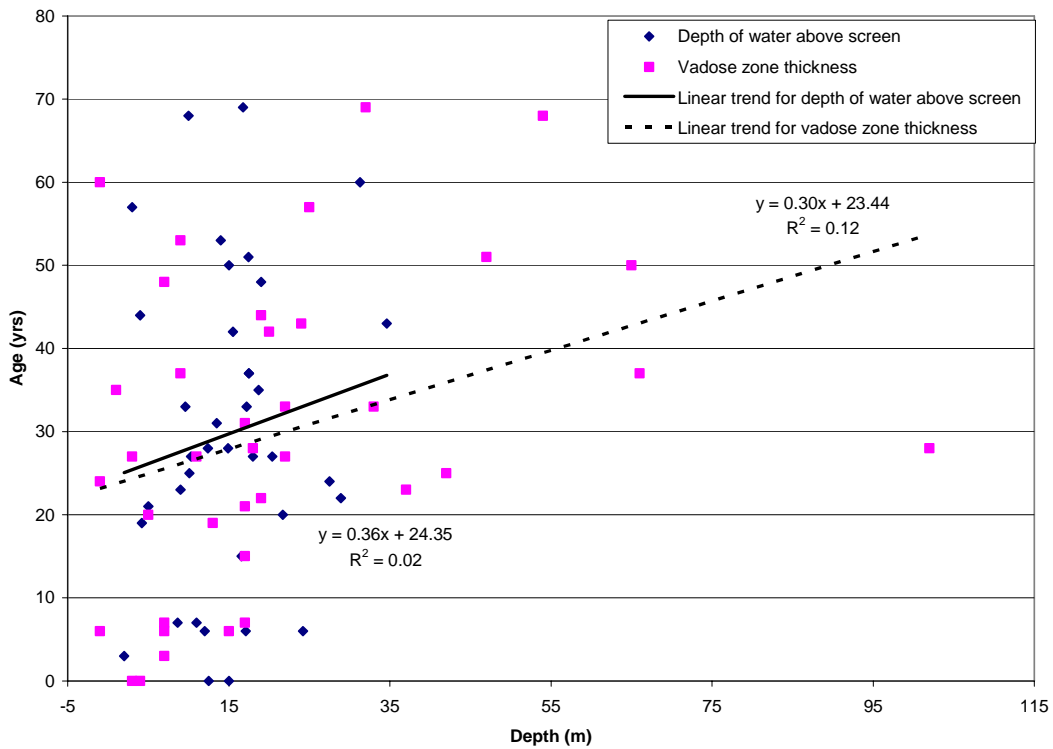


Figure 5-1: Plot of Age of groundwater with vadose zone thickness and depth of water above the well screen. The depth of water above the well screen was truncated at 35 m

At this stage there have been no experiments carried out to determine how much of the age signature is retained for the different tracers and different irrigation application systems. It is recommended that this research is carried out as it might provide insight to these anomalies.

Table 5-1: Wells with elevated age in relation to well and vadose zone depth

| Well | Location | Depth | VZ depth | Water above screen | Recommended Age | Tritium age | CFC-11 age | CFC-12 age | SF6 age | Irrigation type | Recharge response | NO ₃ -N range |
|----------|------------|-------|----------|--------------------|-----------------|--------------|------------|------------|---------|-------------------------------|-------------------|--------------------------|
| L35/0205 | Selwyn | 28 | 7 | 19 | 48 | | | 48 | 26 | Spray | Yes | 2.4 - 6.4 |
| L36/0317 | Greendale | 24.4 | 11 | 10.3 | 27 | 1,30,46 | 1,-39 | 27 | C | Spray | Yes | 2.6 - 16 |
| L37/0297 | Ash-Rakaia | 25 | 19 | 4 | 44 | 9, 28, 47 | 41 | C | 22 | Spray with border up-gradient | Some | 15 - 21.6 |
| L37/0349 | Ash-Rakaia | 66 | 54 | 10 | 68 | 61 | 75 | 58 | 43 | Spray with border up-gradient | Some | 10 - 13.3 |
| L37/0403 | Ash-Rakaia | 37.79 | 9 | 17.5 | 37# | 4, ~40 | 35 | C | 11 | Spray with border up-gradient | No | 4.8 - 6.9 |
| L37/0415 | Dorie | 30 | 25 | 3 | 57@ | 60 | 54 | 37 | 18 | Spray with border up-gradient | Yes | 8.2 - 15.8 |
| L37/1182 | Ash-Rakaia | 25 | 9 | 14 | 53 | 11-15, 50-53 | 53 | 37 | 20 | Spray with border up-gradient | Yes | 10.3 - 13.5 |
| M35/0225 | Waimak-Ash | 22.7 | 1 | 18.7 | 35 | | | | | Spray | * | <.025 |
| M36/0698 | Waimak-Rak | 25 | 3 | 18 | 27 | | | | | Spray | Some | 1.5 - 4.2 |

Note: # Stewart et al. (2002) has an age of 28 years for this well
 @ Stewart et al. (2002) has an age of 35 years for this well
 * only one sample

6 Summary and conclusions

Several different types of information and studies concerning recharge processes and impacts on groundwater quality have been reviewed. These include the response of groundwater nitrate concentrations to major recharge events and land use change, tracing experiments using a range of tracers under varying recharge conditions, and age dating of groundwater.

Measurements on the structure of and associated hydraulic properties of alluvial gravel vadose zones have been carried out in the field but these are currently for a limited number of locations. There are three major facies or material types in the alluvial gravel vadose zone in Canterbury - sandy gravel (matrix) material, open-framework gravels and sand lenses. The sandy gravel matrix constitutes about 90% of the vadose zone material and is about 70% stones. The average bulk density of the sandy gravel material is 2.20 g/cm^3 with an average porosity of 17%. The water content (v/v) of the sandy gravel material ranged from 3.5 to 13.9% with a mean of 7.4%. The average porosity of the open-framework gravels was 34% and these gravels were often coated with iron and/or manganese oxides. The sand lenses had an average porosity (v/v) of 34%.

Various comprehensive tracing studies have shown that rapid transport of nitrate and microbes through the vadose zone and into shallow groundwater can occur when there are saturated conditions and particularly when flood irrigation (with or without effluent) is practised. Non-equilibrium flow conditions in the vadose zone, where there is some rapid transport of water and contaminants followed by a much slower moving, long tail of contaminants, have usually been observed in intensive tracing experiments that have been conducted over longer time periods.

Significant increases in nitrate concentrations in shallow groundwater are often observed in response to major recharge events. Analysis of the response of nitrate concentrations in shallow groundwater to major recharge events over the last 25 years indicates that there is a rapid response with a typical lag of between 1 and 4 months between the recharge occurring and the rise in nitrate concentrations. As these major recharge events would generate very saturated conditions, the rapid response could either result from rapid transport of water and contaminants through the vadose zone (similar to the tracing experiments) or could be due to the water in the vadose zone, with associated nitrate, being displaced or "pushed out" from the bottom of the vadose zone into the groundwater.

There are few examples of groundwater quality response to land use that are suitable for analysis as the land use change needs to be well documented, the surrounding groundwater quality needs to be monitored near the water table over the critical period and the land use change needs to occur over a fairly short time period in order to provide information for response times. Two situations were analysed.

The Ashburton Meat Processing plant made a series of improvements to its effluent management from 2000-2002. These improvements mean that a similar volume of effluent was being applied but the nitrogen concentrations in the effluent were significantly reduced. Down-gradient wells showed a decrease in nitrate concentrations, with most of the response to the land use change taking place within a year. However, with the high volume of effluent being applied, the annual recharge at the site is greater than the amount of water held in the vadose zone so a response within a year would be expected even if there was no rapid non-equilibrium transport occurring at the site. This means that this site does not clearly distinguish between the different recharge mechanisms.

The other land use change analysed was the cessation of effluent disposal at the Islington Freezing works in 1988. Unfortunately at this site most of the monitoring wells either have data during the effluent discharge period and were not monitored after discharge ceased or monitoring only commenced after 1988. A well 3 km down-gradient has the best monitoring data and indicates that nitrate concentrations decreased about 7 years after effluent discharge ceased. The water content in the vadose zone at the site is equivalent to about 4 years recharge and indicates that there was a significant additional period of time required to flush the stored nitrate out of the vadose zone. This could be consistent with normal non-preferential flow.

The vadose travel time was estimated for a selection of wells for which a vadose zone depth had been estimated by Environment Canterbury. Each well was matched with the nearest recharge series to provide the profile available water and mean annual recharge. The mean travel times for each sub-

region varied from 1.7 to 7.6 years, with a minimum travel time of 0.2 years and a maximum travel time of 33 years. These travel times are for average dryland conditions and would be lower for irrigated situations.

The age dating measurements that have been carried out for wells down to a depth of about 70 m were examined for consistency with the transport processes described in this report. There were slight positive relationships between the age of water and the depth of vadose zone and depth of water above the well screen, as would be expected, but there was significant variability.

Some shallow wells were identified with relatively old ages that also showed rapid responses to recharge events and were examined more closely. There is the possibility that irrigation with older water, particularly if deeper groundwater is used, could cause the water from a particular well to appear older than it actually is, if the irrigation retained some or much of its age signature. A retention of age signature by the irrigation water could explain some of the groundwater having older ages than expected. It may also provide an explanation for the SF₆ showing the youngest age, followed by CFC-12, then CFC-11 and then tritium, as the more volatile tracers will re-equilibrate fastest and retain less of their age signature. The input of irrigation is significant in Canterbury and could have an important influence on the apparent age of the shallow groundwater, depending on how much the age signature of the irrigation water is retained through the application process.

Some of the management implications of this report include:

- Promoting the replacement of flood irrigation with spray irrigation, as flood irrigation promotes rapid transport of microbes and contamination of shallow groundwater, whereas good spray irrigation practice results in minimal transport of microbes to groundwater.
- An improved understanding of travel times through the vadose zone will assist in correct interpretation of groundwater quality data and correct assessment of trends. It will also give realistic estimates of when changes in land use might be expected to cause changes in groundwater quality data.

Recommendations

- There is no information and no experiments have been carried out to determine how much of the age signature is retained for the different tracers and different irrigation application systems. It is recommended that this research is carried out as it might provide insight to these anomalies.
- In areas where land use changes are occurring, the land use change should be documented and appropriately sited wells should continue to be monitored for at least 10 years after the land use change has occurred.

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