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DISSOLVED PHOSPHORUS IN CANTERBURY GROUNDWATER

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Abstract
We reviewed available data to look for factors that could be controlling how phosphorus behaves in groundwater in the Canterbury Region, South Island, New Zealand. We found that geological sources of phosphorus contribute dissolved reactive phosphorus (DRP) to groundwater, especially north of Christchurch and south of Timaru along the coast and below rolling hill country. Rural land uses may also be adding to the DRP in groundwater, but the groundwater redox state is a better predictor of phosphorus mobility in aquifers than the phosphorus retention indices of the overlying soils. Most groundwater below shallow, stony alluvial soils on the Canterbury Plains is well oxygenated and we seldom see high concentrations of DRP in groundwater in this environment.

Introduction
Recent research (Dodd *et al.*, 2014; McDowell *et al.*, 2015) has indicated that there could be more phosphorus leaching to groundwater from agriculture than we have previously thought. This could affect the way we need to manage land use to protect water quality. Phosphorus has not generally been a problem for groundwater abstractors in Canterbury who mostly rely on aquifers for irrigation and drinking-water. But phosphorus-enriched groundwater could cause problems if discharging to surface waterways. Even relatively low concentrations of phosphorus are enough to cause nuisance plant and algal growth in some waterways. The potential leaching of phosphorus to groundwater from agricultural land use and the resultant threat this may pose to surface water quality prompted a review of Environment Canterbury's phosphorus data for groundwater (Scott and Wong, *in prep.*).

Environment Canterbury has collected 1922 records for dissolved reactive phosphorus (DRP) concentrations in groundwater samples from 918 wells across the Region between 1995 and 2014. We analysed the available data to characterise the current state, distribution and trends in DRP concentrations. We also used well construction details, spatial data on soil properties and land use and other groundwater chemistry data to look for factors that could be controlling the patterns we see in the data.

Current state
Canterbury groundwater DRP data are highly skewed with lots of samples having low concentrations and few samples with high DRP concentrations. The distribution of DRP concentrations is similar to published national DRP statistics compiled from regional council groundwater monitoring programmes (Daughney and Randall, 2009), but the proportion of wells with higher DRP concentrations is slightly lower in Canterbury (Table 1).

Figure 1 shows median DRP concentrations for wells that Environment Canterbury has tested for this parameter in the past 20 years.

Table 1: Summary statistics for DRP concentrations in Canterbury groundwater samples compared with data for all of New Zealand groundwater

Statistic	**Canterbury groundwater DRP (mg/L) (1995 - 2014)**	**National groundwater PO_4-P (mg/L) (1995 – 2008)**
25th percentile	0.004	0.01
Median	0.007	0.01
75th percentile	0.014	0.04
95th percentile	0.078	0.24
Maximum	2.5	4.94
Well count	918	705
No. of wells with median > 0.009 mg/L	402 (44%)	383 (54%)*
No. of wells with median > 0.030 mg/L	123 (13%)	200 (28%)

* wells with <0.01 mg/L (national data were only reported to the nearest 10 µg/L).

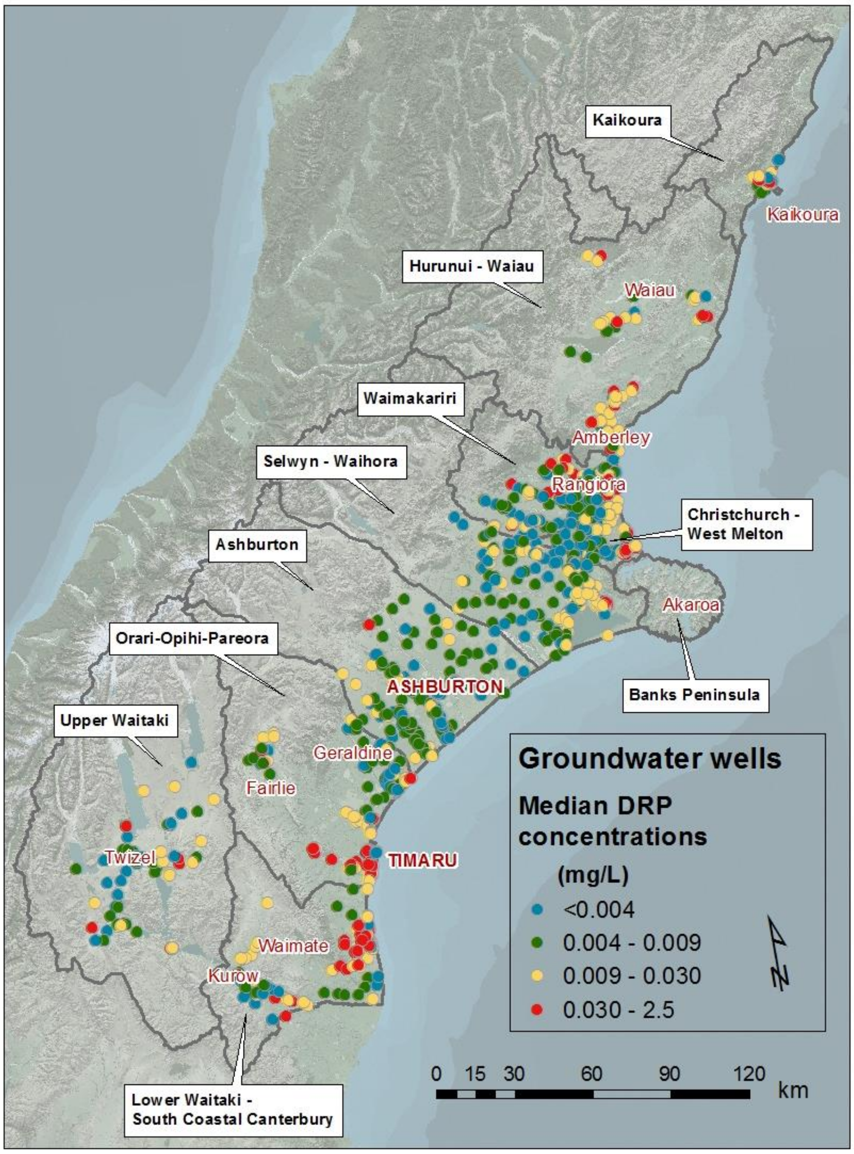

Figure 1: Median DRP concentrations measured at 918 wells across the Canterbury Region

There are no groundwater standards for phosphorus, so we classed the data by surface water quality thresholds. For Canterbury streams and rivers, Stevenson *et al.* (2010) classed concentrations above 0.009 mg/L phosphorus as 'enriched' and concentrations greater than 0.030 mg/L as 'excessive', based on Ministry for the Environment guidelines for recreational uses. However, the coloured symbols in Figure 1 are only meant to display the range of values encountered. They should not be interpreted as having any particular environmental effect. The wells cover a range of depths and not all of the groundwater represented here would be discharging to surface water bodies.

Lower concentrations of DRP in occur in wells on the central Canterbury Plains. Clusters of wells with higher DRP are found in rolling hill country south of Timaru near the coast and also in North Canterbury from north of Christchurch to Kaikoura. The areas of higher DRP correspond to areas with features such as older geological formations, slowly permeable soils, a high proportion of lateral flow or seasonal reducing conditions.

Trends

Because DRP has not been regularly monitored, our long-term data for detecting phosphorus trends in Canterbury groundwater are limited. There are nine wells across the Canterbury Region where we have regular long-term records (more than 10 years) for phosphorus concentrations. We analysed these data using a Mann-Kendall trend test on annual samples collected in the spring. Concentrations were relatively stable year to year and all of the nine wells showed no significant increasing or decreasing trends in the concentration of phosphorus in groundwater over a 10-year period.

We also conducted a survey in 2014 which included DRP analyses from 292 wells with existing older records of DRP (mostly from 2007 and 2008). Most wells had very similar DRP concentrations on repeat sampling. Only five of the wells showed a notable increase (more than 40% increase) in DRP concentration from 2008 to 2014. Two of these were very shallow wells (5 to 6 m deep) that may have been affected by land use changes or surface water infiltration near the wellhead. The other three were deeper wells where the DRP is likely coming from geological sources, including two coastal wells in Christchurch possibly disturbed by the Canterbury earthquakes in 2011.

We have not observed any wide-scale trends of phosphorus enrichment in Canterbury groundwater over the past decade, but more long-term monitoring data would be useful to confirm this statistically.

Geology

Deposits of phosphorus-rich rocks are rare in New Zealand, but sparingly soluble phosphate minerals, such as apatite, may be a source of phosphorus in groundwater (Rosen, 2001). Long residence times and long travel paths are needed for groundwater to dissolve phosphorus from these minerals, so DRP concentrations from these sources tend to be higher in the deeper parts of the aquifers.

We examined Environment Canterbury's bore logs for wells 30 m deep or deeper to see if we could find connections between DRP concentrations and the geology adjacent to the well screens. Groundwater at this depth is less likely to be affected by phosphorus leached from the land surface. Bore logs were of varying quality with some wells having geological formations assigned (mainly in Christchurch and South Canterbury) and others only giving general descriptions of the material encountered by the bore (e.g. gravel). Several wells did not have associated bore logs so we also used the surface geology descriptions from the QMap Series dataset (GNS Science) to try to fill the gaps. Median and maximum DRP concentrations by geological formation are presented in Table 2.

Table 2: Summary of DRP concentrations by geological formation for wells >= 30 m deep

Geological Formation	Number of wells	Median DRP (mg/L)	Maximum DRP (mg/L)
Quaternary (Plains)[1]	366	0.007	0.31
Quaternary (South Canterbury)[1]	43	0.012	0.22
Quaternary (North Canterbury)[1]	27	0.016	0.77
Kowai Formation	26	0.032	0.59
Onekarara Group – Taratu Formation	1	0.093	
Otakou Group – Mt Harris Formation[2]	1	0.51	
Otakou Group – White Rock Coal Measures[2]	1	0.005	

[1] Quaternary could also include older formations not identified on bore logs, particularly in North Canterbury where bore logs have not been geologically coded.
[2] Strata tentatively assigned to Mt Harris and White Rock deposits by geologist coding bore logs.

Most of the wells on the Canterbury Plains are constructed in young sedimentary deposits formed during the Quaternary Period (past 2.6 million years). We have very limited information for wells in older geological formations. Of the 29 wells we know are screened in the Kowai Formation or older units, many have elevated groundwater DRP concentrations, with the exception of one well in the White Rock Coal Measures. Median DRP in groundwater was slightly higher in wells within Quaternary geologies in north and south Canterbury when compared with the central Canterbury Plains. We do not have information available on the mineralogy of the aquifer formations at these wells, so we do not know if elevated DRP is linked to phosphorus-bearing minerals in the aquifers.

Phosphate-rich volcanic rocks of Banks Peninsula provide a constant source of phosphate to the surface waterways on the peninsula. Banks Peninsula streams have higher median DRP concentrations and lower variability in DRP those concentrations than other river types in Canterbury (Stevenson et al., 2010). But we do not have any wells in these volcanic rocks with DRP data to include in our groundwater assessment.

Geochemistry

The concentration of phosphate dissolved in groundwater is indirectly controlled by the redox state. Although phosphate itself is not redox active, the redox state affects the availability and reactivity of substances such as iron oxides, to which phosphate can be absorbed.

We used a system devised by McMahon and Chapelle (2008) to characterise the redox state of groundwater samples, based on measured concentrations of dissolved oxygen, nitrate, manganese, iron and sulphate in the water samples. We grouped our data into three broad classes: oxic, mixed and anoxic. The mixed redox class showed indications that samples were not at redox equilibrium or that oxic and anoxic water sources are mixed.

About three-quarters of the groundwater samples were classed as oxic (75%) while the remaining quarter were almost evenly split between anoxic (16%) and mixed (11%) redox classes. The box plot in Figure 2 shows the distribution of DRP data across the three main redox classes we assigned.

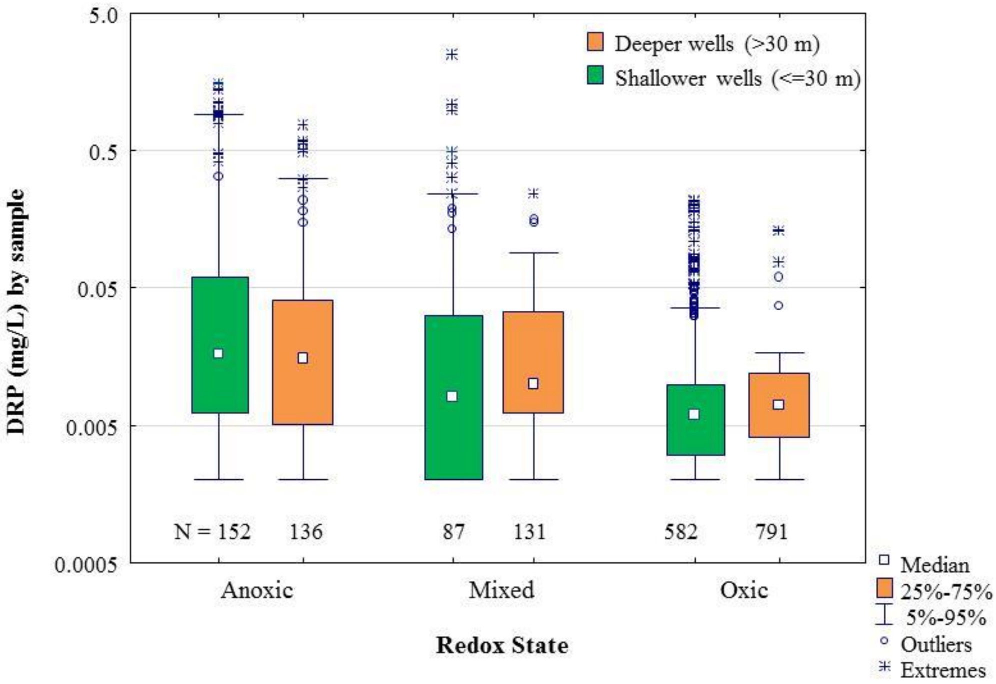

Figure 2: Distribution of DRP concentrations in groundwater samples grouped by well depth and redox class. N = No. of samples. Note that the DRP concentrations are plotted on a logarithmic scale to improve the ease of viewing the data.

Anoxic samples had the highest median DRP concentration (0.016 mg/L). Mixed redox class samples covered a wide range of DRP concentrations with some of the highest and lowest concentrations. The median concentration was 0.010 mg/L. Oxic samples, which make up most of the samples in our records, generally have lower DRP concentrations than mixed or anoxic samples, with a median of 0.006 mg/L.

All redox classes have some samples below the laboratory detection limit and some with elevated DRP above the 0.030 mg/L ‘excessive’ surface water threshold. But we only observed DRP concentrations above 0.25 mg/L when groundwater conditions are not oxic. The samples with these very high DRP concentrations are all from anoxic environments (at all depths) or from shallow wells where the groundwater is of mixed redox state. In shallower groundwater, very concentrated sources of phosphorus, such as effluent discharges, may also contain degradable organic carbon which helps to create anoxic conditions.

If there is a source of phosphorus present, then higher concentrations of DRP can dissolve in anoxic groundwater than in oxic environments.

Land use

One of the aims of this review was to look for potential links between groundwater phosphorus concentrations and land use. McDowell *et al.* (2015) used a national groundwater dataset to show elevated and increasing phosphorus concentrations occur under dairy land use, especially in gravel or sand aquifers. The authors of this paper also concluded that the link between land use and groundwater DRP concentrations was present irrespective of groundwater redox state.

Our Canterbury regional map (Figure 1) showed that wells with higher DRP concentrations are mostly located in the Hurunui-Waiau, Orari-Opihi-Pareroa and Lower Waitaki-South Coastal Canterbury zones. There are some areas with intensive agricultural activities within these zones which could be a source of DRP. But other zones with intensive agriculture, e.g. Ashburton zone, have relatively low DRP concentrations in groundwater samples.

We used more detailed land use information from the AgriBase™ dataset (AsureQuality, 2014) to look for possible links between land use and groundwater DRP concentrations. We classified the wells in our study by dominant land use of the surrounding land parcel and excluded those wells where there was no land use recorded immediately around the well. Then we simplified the land use data by grouping them into eight classes. For this analysis we also excluded all wells greater than 30 m deep where we are less likely to see DRP coming from land use. We also divided the data for each land use class by redox class to control for the effects of redox state on phosphorus mobility (Figure 3).

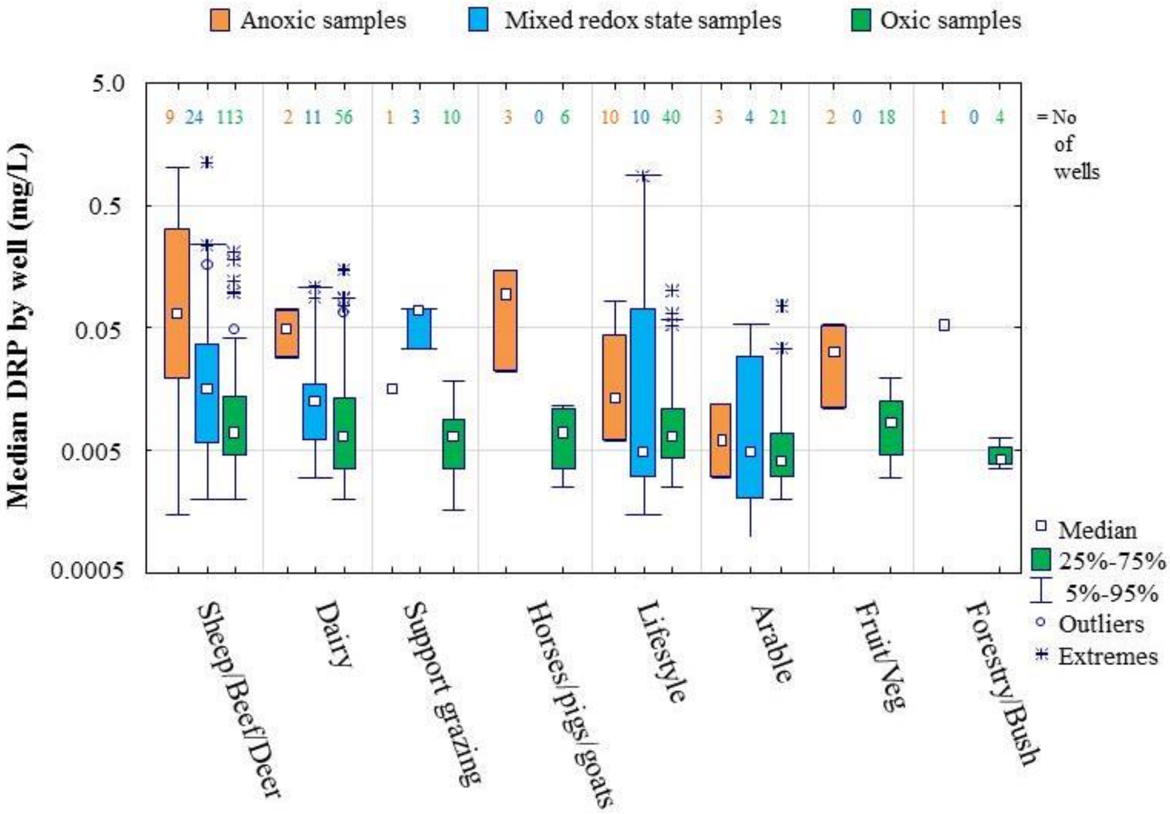

Figure 3: Median DRP concentrations for shallow wells (less than 30 m) by land use class showing the distribution of data for samples with anoxic, mixed and oxic redox states.

We found that land use may have some effect on median DRP, but only if the samples are not oxic. Oxic samples, which make up the bulk of our groundwater data, have very similar median DRP concentrations and concentration ranges across all land use classes. The main difference is the outlier and extreme values, which occur more frequently in the land use classes where livestock (or septic tanks on lifestyle blocks) may be present.

Considering only anoxic samples, there does appear to be some enrichment of DRP in groundwater under land uses involving grazing livestock (sheep/beef/deer, dairy and horses/goats/pigs). But with very only a few samples of anoxic groundwater below arable cropping, support grazing and forestry, there were not enough data to draw any strong conclusions about the general impact of these land uses. Our data for forest and natural vegetation in all redox classes is limited by having few wells available for sampling in areas where these land uses occur.

Our assessment is limited by the assumption that the groundwater DRP concentrations we observe are related to the mapped land use class around each well. But groundwater quality is generally a long-term, integrated response to leaching through the soil from land use activities upgradient of the point of measurement. Groundwater composition can also be modified by reaction with aquifer materials and dilution by other recharge sources, such as rivers and water races. Using only broad categories of dominant land use class, we also cannot draw any conclusions about the effects of farm management practices on individual farms.

Soils

Soil characteristics will influence the fate of phosphorus applied to the land. Stony and sandy soils with a low content of clay, carbonate or aluminium- and iron oxide minerals, that help to bind phosphorus, are prone to leaching.

Webb *et al.* (2010) used soil properties to model phosphorus leaching risk in Canterbury. Soils were assigned a leaching potential that gives an indication of the relative risk of phosphorus leaching from different soils under the same land management (Table 3).

Table 3: Phosphorus adsorption index and phosphorus leaching classes for Canterbury soils (from Webb et al., 2010)

P-adsorption index	Rating code	P-leaching vulnerability	Main soils represented
0-50	1	VH	Stony and very stony Recent alluvial soils, young sand dunes, shallow over rock
50-100	2	H	Other alluvial Recent Soils, shallow and stony Pallic Soils
100-200	3	M	Deep Melanic, Gley and Pallic Soils
200-500	4	L	Shallow and stony Brown Soils

We selected wells which were less than 30 m deep to look for relationships between the estimated risk of leaching and the observed concentrations of phosphorus we see in groundwater. We considered these wells most likely to be affected by leaching from land use. But we found no clear relationship between DRP concentrations in wells and the phosphorus leaching risk for soils in Canterbury.

We also plotted the DRP data by redox class to see if this was influencing the results (Figure ***4***). The analysis is limited by having some combinations of soil risk and redox class represented by very few wells. But once again we found the observed concentrations of DRP within a single redox class did not really reflect the assigned soil leaching risk, particularly for the large number of oxic groundwater samples which we find in Canterbury.

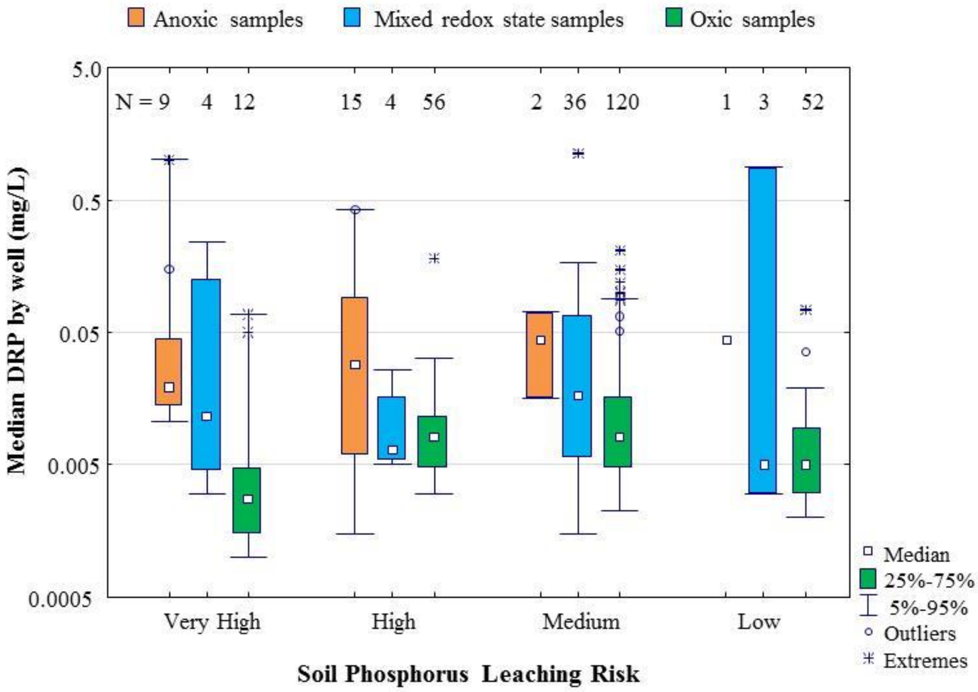

Figure 4: Median DRP concentrations for shallow wells (less than 30 m) in four soil leaching vulnerability classes showing the distribution of data for samples with anoxic, mixed and oxic redox states. N = indicates the number of wells in each category.

We found many wells in our study that have low DRP concentrations even though some of them are located in areas which are mapped as high or very high phosphorus leaching risk areas. The highest DRP concentrations measured in groundwater also did not correspond to the very high risk soils, but were spread across the high, medium and even low risk soils.

It is possible that phosphorus has not been applied in excess to the soil near the wells where we have groundwater DRP data in the higher risk classes. Dilution by river recharge could also be a factor because several of the very high risk soil areas are adjacent to major rivers. Overall it appears that the assessed leaching potential of these soils is a poor predictor of whether or not we will find elevated DRP concentrations in groundwater.

Conclusions

Comparing groundwater quality data for DRP with surface water quality thresholds we may need to rethink some previously-held views that phosphorus concentrations too low to be an issue in groundwater. Around 40% of shallow wells (<30 m deep) sampled in Canterbury could be described as ‘enriched’ and 15% as having ‘excessive‘ phosphorus if the groundwater discharged directly to streams. Phosphorus is not completely immobile in our groundwater systems and phosphorus-enriched groundwater could cause adverse effects if it discharges to surface water, especially if the waterways are already subject to nutrient enrichment.

Some of the dissolved phosphorus in groundwater comes from natural deposits (such as peat and older marine deposits), which likely contribute DRP to coastal groundwater north of Christchurch and south of Timaru. Concentrations of DRP are relatively low (median 0.007 mg/l) in the Quaternary age gravel aquifers of the Canterbury Plains, where the sediments are naturally poor in phosphorus and geochemical conditions unsuitable for phosphorus mobilisation.

Reducing conditions in groundwater play an important role in the mobilising phosphorus from natural and man-made sources in Canterbury groundwater. If there is a source of phosphorus present, then higher concentrations of DRP will dissolve in anoxic groundwater than in oxic environments.

There are some indications that land use has locally affected groundwater DRP in Canterbury. Median DRP concentrations appear to be higher in shallow groundwater below pastoral farming, lifestyle blocks and horticulture than under arable cropping or forested land, although we have fewer samples from wells in areas of non-pastoral land uses for comparison. But redox state still appears to be the overriding factor. We find low concentrations of DRP in Canterbury's mostly oxic groundwaters. Repeat sampling and long-term monitoring have also not shown evidence of DRP concentrations changing in the region over the past decade, despite the intensification of pastoral land uses that have occurred in Canterbury in recent years.

Targeted management of point sources of phosphorus would help to reduce the number of sites with elevated groundwater DRP concentrations. Upgrading of older soakage pits to better onsite septic systems could also help to eliminate some sources of very high DRP discharges.

Control of phosphorus sources is more critically needed in zones where the groundwater is naturally anoxic and closely connected to spring-fed surface waterways. But catchment scale management of diffuse phosphorus leaching to groundwater from diffuse sources based on soil leaching risk maps may not be urgent or practical in areas where most of the groundwater is oxic.

The behaviour of phosphorus in oxic and anoxic environments is broadly the opposite of what we see for nitrate. Nitrate is very soluble and stable in oxic groundwater, but anoxic conditions can lead to denitrification, which decreases nitrate concentrations. In cases where denitrification is proposed as a solution for high nitrate concentrations in groundwater, we also need to consider the potential effects on phosphorus mobility. The opposing behaviour of the two major nutrients in groundwater should also be a consideration in selecting management practices to control nutrients in a catchment.

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