

Mapping soil sorption capacity as a measure of regional groundwater vulnerability

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Abstract

Groundwater is susceptible to contamination from a range of land-use activities, while remediation is very expensive and often impractical. To help mitigate this problem an effective regional vulnerability assessment, based on existing databases that provide a consistent national coverage, was developed.

One of the critical factors affecting vulnerability in the Manawatu area of New Zealand is the effect of the soil, through its sorption capacity, on the fate of contaminants. Organic carbon content is often the most important factor controlling a soil's sorption capacity, but because carbon content declines sharply below the A horizon, the sorption model developed also considers the cation exchange capacity of the profile, particularly at lower depths.

Soil data were obtained from the New Zealand Land Resource Inventory and the Manawatu – Wanganui regional soil database. Correlation of the two databases allowed the creation of cation exchange capacity, organic carbon content, and soil sorption maps for the study area. An uncertainty ranking system was derived to indicate the reliability of these maps.

Soil sorption is relatively low for the soils over the northern Tararua foothills and other recharge zones, so little, or no, contaminant attenuation occurs there. As contaminants are more likely to reach the aquifer, controls on potentially contaminating land-use activities are particularly important in these areas.

Highest uncertainty in the estimates of vulnerability as a result of soil sorption, reflecting the present lack of chemical data for these soils, is around inland Horowhenua where land use is very intensive and where many bores provide drinking water.

Introduction

Groundwater is a valuable source of drinking water but may pose a serious health hazard if contaminated. Since the late 1970s nitrate, bacteria and, more recently, pesticides have been detected in groundwater world-wide. This has stimulated research on the subsurface fate of contaminants, and ways of mitigating their adverse effects.

Groundwater can be contaminated through a wide variety of human activities, including the land disposal of waste materials and sewage, and through leaching of fertilisers and pesticides. The discharge of domestic, agricultural, and industrial effluent onto, and into, the ground has also increased recently because of more intensive land use and the high cost of alternative disposal systems. This land-based 'treatment' of effluent is often encouraged, with little regard for the possibility for groundwater contamination.

Because most rural communities rely heavily on groundwater as a source of drinking water, groundwater contamination in rural areas has become a major subject of groundwater investigations in New Zealand.

Aquifer vulnerability

Prevention of environmental contamination is of prime importance for effective management of groundwater resources. Groundwater remediation is very expensive and slow. In fact, for many persistent contaminants remediation may not be possible at all within a reasonable time frame. To protect groundwater resources therefore, those areas most prone to contamination by human activity should be delineated for more detailed management. This can most efficiently be done through the assessment of groundwater vulnerability, with vulnerability being defined as:

"The likelihood of contaminants reaching a specified position in the groundwater system after introduction at some location above the uppermost aquifer."

National Research Council (1993)

This paper presents work that is part of a wider study aimed at providing a scientifically defensible procedure for assessing vulnerability to contamination, using existing databases that provide consistent national coverage. This wider study (Bekesi, 1998) brings together data on soils, climate, and the subsurface environment; develops an interpretation system for these data; and presents the findings in the form of maps that can be readily understood by lay-persons.

The selection of physical and chemical factors which affect groundwater vulnerability is not straightforward. A review of vulnerability assessment

methods by the US Environmental Protection Agency (1993) lists 73 physical factors which have been used. The number and diversity of these factors partly reflects variations in hydrogeological settings.

In the Manawatu region of New Zealand, four factors are thought to predominantly control groundwater vulnerability: the properties of the soil, rainfall recharge, and the characteristics of the unsaturated zone and aquifer medium. This is because the majority of the aquifers are shallow, consist of relatively coarse alluvial sediments, and have generally high transmissivities and recharge (Bekesi, 1998).

This paper focuses on estimating the effect of the soil, in particular its sorption capacity, on the fate of contaminants. It also discusses the uncertainty of the derived spatial estimates of soil sorption capacity. The uncertainty associated with our understanding of the subsurface processes and the data used in this analysis make it necessary to quantify the accuracy of the estimates of soil sorption, and consequently aquifer vulnerability.

Study area

The Manawatu region is situated on the west of the lower North Island of New Zealand, about 150 km north of Wellington (Fig. 1). It covers approximately 4200 km² and contains numerous aquifers in unconsolidated Quaternary sedimentary formations. Most of the area's 5,000 bores are shallow, with over 75% being less than 50 m. Of concern is that 20% of bores in the south tap groundwater with a nitrate-nitrogen concentration above the New Zealand drinking water standard (11.3 mg/l).

Groundwater is used extensively throughout the study area for drinking, stock, and irrigation. Total water use is around 520,000 m³/day; with 65% of this coming from groundwater (Bekesi, 1998). In several districts groundwater is the only usable source of drinking water.

The Tararua and Ruahine axial ranges bisect the study area. Regional groundwater recharge areas include these ranges and the Pohangina anticline (Fig. 1). Local recharge areas are situated near Sanson, Feilding, and Himatangi to Foxton.

Sorption

Sorption of contaminants onto soil particles is an important process to consider in a vulnerability assessment. This is because it decreases the concentration of contaminants in the liquid phase, at least until the sorption capacity of the soil is saturated. The rate of sorption, or the accumulation of contaminants on the solid surface, is related to the concentration of the contaminant in the liquid phase through equilibrium isotherms. These equilibrium conditions usually assume that the amount of sorption is not limited by time.

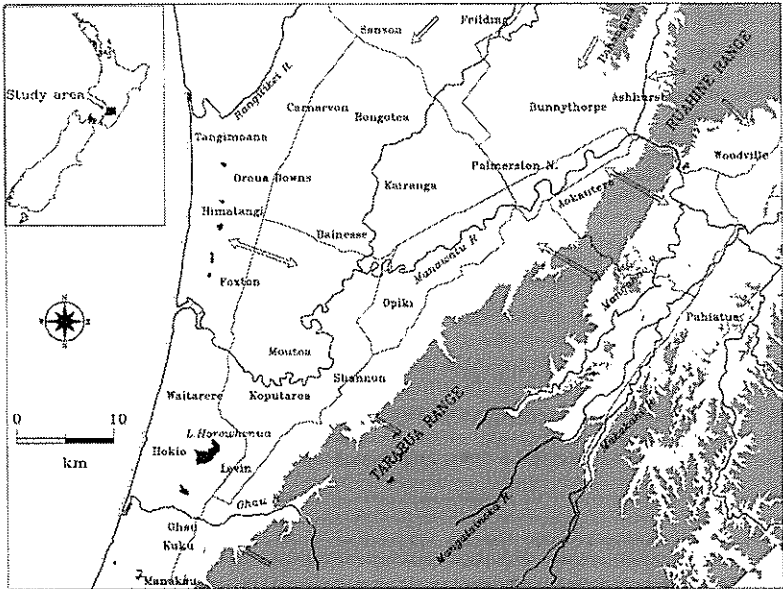


Figure 1 – The study area and localities. Shaded areas have an altitude of 200 m or more above sea level. The main groundwater recharge areas include the Tararua and Ruahine ranges and the Pohangina anticline. Local recharge areas are situated near Sanson, Feilding, and from Himatangi to Foxton. Recharge areas, and approximate groundwater flow directions, are shown by arrows.

Knox *et al.* (1993) argue that the sorption-desorption equilibrium is a first-order process with the rate of chemical sorption, q , being:

$$\frac{\partial q}{\partial t} = K_s \frac{\theta}{\rho_s(1-\theta)} C_l - K_d q$$

where t is the time,

K_s and K_d are the first-order sorption and desorption coefficients (1/time)

θ is the pore-water fraction (dimensionless)

C_l is the concentration of the contaminant in the liquid phase (mass/length³)

ρ is the solid phase density (mass/length³)

At equilibrium,

$$\frac{K_s}{K_d} \frac{\theta}{\rho_s(1-\theta)} C_l = K_p C_l = q$$

where K_p is the linear (or Freundlich) equilibrium partition coefficient, often termed the "partition coefficient".

The above Freundlich isotherm is just one of the many approximations of the physical and chemical processes operating; however, at low contaminant concentrations the difference between linear and non-linear isotherms is negligible. The rate of sorption thus becomes:

$$\frac{\partial q}{\partial t} = \frac{\partial q}{\partial C_l} \frac{\partial C_l}{\partial t} = K_p \frac{\partial C_l}{\partial t}$$

Sorption may also influence groundwater contamination by delaying contaminant movement; conversely, desorption will lengthen the contamination period. If contaminants are released continuously, and for a long time, sorption/desorption in the soil and unsaturated zone will only delay, not prevent, the eventual contamination of the aquifer once the sorption capacity has been exceeded. The complex sorption-desorption relationships and controls are discussed fully by Schwarzenbach *et al.* (1993) and Knox *et al.* (1993). Only a simplified version is presented here.

Solvent-motivated and sorbent-motivated sorption

Knox *et al.* (1993) differentiate between sorbent (porous material) motivated and solvent (contaminant) motivated sorption. A sorbent-motivated process is the sorption of an ionisable contaminant onto a clay surface. Solvent-motivated sorption occurs when a hydrophobic contaminant accumulates onto organic material. It has been observed (Knox *et al.*, 1993) that the organic carbon content of a soil is the most important factor influencing solvent-motivated sorption.

Ion exchange (as a specific case of sorption) involves the transfer of ions from the solute to the solid phase (Bear and Verruijt, 1987). Knox *et al.* (1993) consider ion exchange to be sorbent-motivated sorption, where accumulation of the contaminant occurs on the solid phase because of the affinity of the solid surface for the contaminant.

Sorbent-motivated sorption is therefore primarily controlled by the number of exchange sites available on the medium (which is in turn related to specific surface area) and the availability of electrically charged particles.

Clay particles have by far the largest specific surface area, and are the most electrically charged particles of all sediments. Sorbent-motivated sorption is thus largely controlled by the amount, and type, of clay present in the porous medium. As different clay minerals have differing sorbent-motivated sorption capacities, their *cation exchange capacity* is often used as a measure of this potential. Cation exchange capacity is the ability of a medium to adsorb cations and is expressed as milliequivalents per unit mass.

Cation exchange capacity is related strongly to the specific surface area of the porous medium, and to the availability of electrically charged particles.

Estimating soil sorption capacity

The partition coefficient of a medium is considered to be a function primarily of its organic carbon content and cation exchange capacity:

$$K_p = f(f_{oc}, CEC)$$

where f_{oc} is the organic carbon content and CEC is the cation exchange capacity. Increasing organic carbon and/or cation exchange capacity increases the potential for the accumulation of contaminants onto the solid surfaces. The individual contributions of organic carbon and cation exchange capacity to soil sorption are extremely difficult to separate, because the two parameters are intimately, but not simply, associated (Theng *et al.*, 1998). For example, Parfitt *et al.* (1995) examined 347 soil profiles throughout New Zealand and found that the cation exchange capacity for soils with high smectite content were significantly higher than values predicted from their organic carbon content.

The results of Parfitt *et al.* (1995) and Theng *et al.* (1998) indicate that although organic carbon is the strongest contributor to cation exchange capacity, both organic carbon and cation exchange capacity must be considered in developing soil sorption maps. This is particularly important because of the significant difference between the organic carbon and clay contents of the A horizon, and of the rest of the soil profile.

Soil organic carbon content and cation exchange capacity data are available, or can be estimated, for the study region and indeed the rest of New Zealand. Soil data were obtained from two databases: the New Zealand Land Resource Inventory and the Manawatu – Wanganui regional soil database.

Available soil data

The New Zealand Land Resource Inventory (Newsome, 1992) is a spatial database, mapped at a scale of 1:63,360, consisting of polygons which enclose areas of uniform characteristics; for this study the most important is the 'soil unit'. The minimum size of a polygon is 0.25 km².

The Manawatu–Wanganui regional soil database is a non-spatial database that includes the physical and chemical parameters for most of the soils of the study area. These parameters are expressed as classes and ranges rather than specific values, because the soils are inherently variable, few measurements are available, and the accuracy of specific values varies greatly with each soil survey.

The two primary soil parameters influencing groundwater vulnerability are the organic carbon content and the cation exchange capacity. The various ranges and classes used in the regional soil database are presented in Table 1.

Table 1 – Cation exchange capacity and organic carbon content ranges and classes (based on unpublished notes accompanying the Manawatu – Wanganui regional soil database and Wilde, personal communication 1997)

Cation exchange capacity within 0–0.6 m (meq/100 g)	Organic carbon within 0–0.2 m (%)	Class	Rating
>40	> 20	Very high	5
25 – 40	10 – 20	High	4
12 – 25	4 – 10	Medium	3
6 – 12	2 – 4	Low	2
< 6	< 2	Very low	1

The “Rating” code in Table 1 refers to the potential sorption capacity of soils with cation exchange capacities and organic carbon contents in the ranges indicated. A rating of 5 indicates a high sorption capacity, which consequently should reduce the vulnerability of groundwater to contamination. To take account of the high degree of natural variability in soil properties, and the uncertainty involved in assigning soils to particular classes, two other parameters were developed: “variability” and “reliability”. The variability code is used to indicate the likelihood that a particular soil will have properties within a specific range. Variability is represented by one of the following codes:

- 0 occurs mostly within the nominated class; the middle of the nominated class is the mean
- 1 straddles the rating class above and below; the middle of the nominated class is the mean
- 1- straddles the rating class and class below; the mean is taken at the class boundary
- 1+ straddles the rating class and class above; the mean is taken at the class boundary

The reliability code is used to indicate how the data for a given soil were obtained. The reliability code is defined, in order of increasing certainty, as:

- u from relationship with other soils; quality of estimation is not known
- r from relationship with other soils; estimation thought to be reliable

- m from analysis of the named soil but from another area (different soil survey)
- a from analysis of actual soil

For example, the organic carbon content of the Raumai sandy loam soil, as determined from the Pohangina soil survey, is given by a rating of 3, a variability of 1-, and a reliability of "a". This indicates that the mean organic carbon content is about 4%, but ranges from 2 to 10%. These data were obtained from actual analyses of the Raumai sandy loam, therefore the reliability class is 'a'. The reliability class for the same soil, but in the Rangitikei survey, is 'm' since the properties were not measured directly in this instance.

Linking the databases

Because the spatial Land Resource Inventory data were stored in one database, and the soil chemical properties in another, it was necessary to "match" the soils in each database. The two databases were linked via a hierarchy of four 'matching' steps (Fig. 2): once they were "linked" it was possible to create cation exchange capacity and organic carbon content maps.

Step one: exact matching

Exact match means that organic carbon and cation exchange capacity data are available, in the regional soil database, for a specific soil unit in the Land Resource Inventory.

Step two: matching based on soil form

For soil units without specific physical and chemical data, regional database records were matched using Soil Form. Soil Form Classification (Hewitt, 1993) is based on the principle of grouping soils into classes of similar measurable properties. It was assumed that the physical and chemical characteristics of a soil series can be transferred across surveys. Regional database records without physical parameters were therefore assigned the parameters of soils with the same Soil Form for which parameters were available. It is argued that this type of assignment is valid because the similarity of measurable properties is the basis of Soil Form Classification.

Step three: matching using the General Soil Survey

Not all physical and chemical soil survey data are present in the regional database. As a result it was necessary to use chemical analyses of soils published as part of the General Soil Survey of the North Island (NZ Soil Bureau, 1954). Chemical data presented in this larger scale survey include: total nitrogen, carbon/nitrogen ratio, and base exchange capacity. The organic

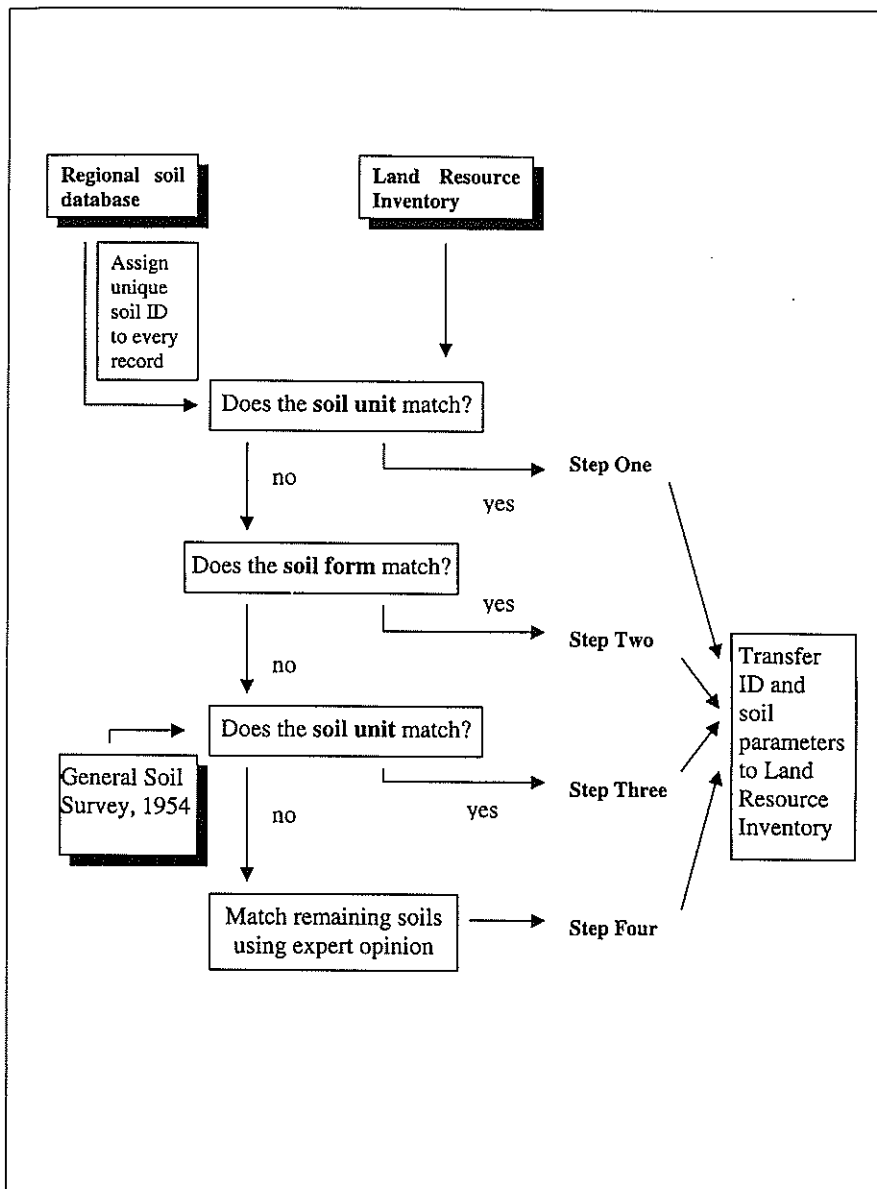


Figure 2 – Flow chart showing the process by which the data in the Regional Soils and Land Resource Inventory databases were linked.

carbon content can therefore be calculated by multiplying total nitrogen by the carbon/nitrogen ratio; while base exchange capacity is identical to the cation exchange capacity. This process allowed the reliable estimation of chemical properties for soils having no data in the small-scale soil surveys.

Step four: matching using “expert knowledge”

The remaining soils for which no chemical data were available were matched with the help of John Bruce (ex Chief Soil Correlator, for the Soil Bureau, DSIR), now with the School of Earth Sciences, Victoria University of Wellington. The basis for matching was the physical similarity of soils from the various surveys. Table 2 summarises the process used to match the soil data from the Land Resource Inventory and Regional databases.

Table 2 – Summary of soil matching

Match phase	Number of polygons	Area of polygons (km ²)	Per cent of total area
Step one	499	687	17
Step two	654	911	23
Step three	671	1300	32
Step four	546	1031	26
<i>Non-normal type polygons*</i>	30	81	2
Total	2400	4010	100

* These non-normal polygons include those covering towns and water for which no soil data are available

Organic carbon and cation exchange capacity maps

Figures 3 and 4 present the soil organic carbon and cation exchange capacity data for the study area. The darker the shade, the higher the organic carbon or cation exchange capacity of the soil and hence the lower the potential groundwater vulnerability.

The system used to assign the soils to specific categories is shown below:

Description	Very low		Low		Medium		High		Very high	
Rating	1		2		3		4		5	
Variability	1-	0,1	1+	0,1	1+ 1-	0,1	1+ 1-	0,1	1+1-	0,1
Category	0	1	2	3	4	5	6	7	8	9

For example, a soil with a medium organic carbon content, a rating of 3, and a variability of 1+, will be placed in category 6.

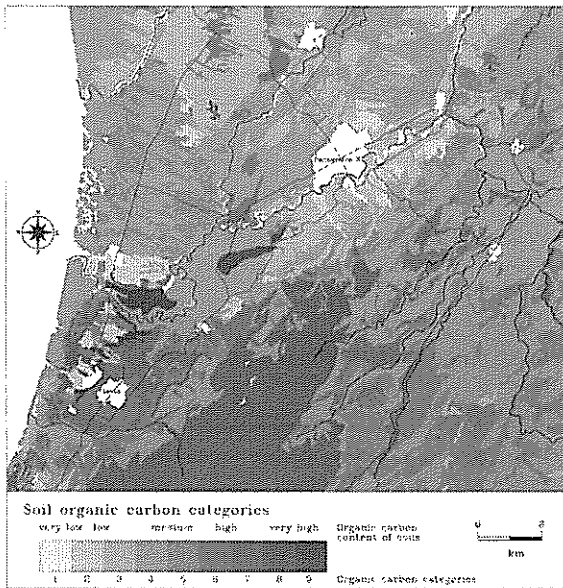


Figure 3 – Variation in soil organic carbon content (Note: the white polygons are lakes and urban areas for which no data exist).

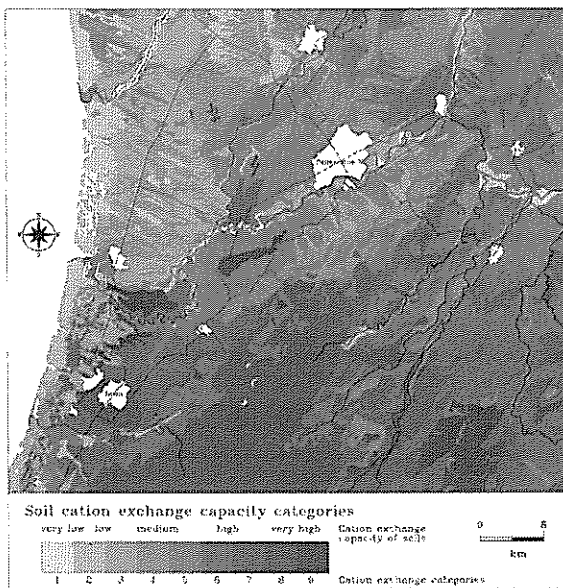


Figure 4 – Variation in soil cation exchange capacity (Note: the white polygons are lakes and urban areas for which no data exist).

Combined soil sorption map

Most users of groundwater vulnerability maps require a “combined” soil sorption map, incorporating both cation exchange capacity and organic carbon, or even a combined aquifer vulnerability map. In creating a combined soil sorption map the independence of organic carbon and cation exchange capacities of a soil must be considered. After all, soils are developed under certain conditions that will influence both organic carbon and cation exchange capacities, and as discussed above, the two parameters are intimately, though not simply, related.

Parfitt *et al.* (1995) and Theng *et al.* (1998) argue that although organic carbon is the strongest contributor to cation exchange capacity, both organic carbon and cation exchange capacity should be considered in constructing soil sorption maps. This is because the separation of the two factors is difficult and the relationship between the two varies with individual soils, and with depth in the profile. Figure 5 compares organic carbon content with cation exchange capacity values (not classes) using data contained in the Regional Soil database. The general trend is that soils with a higher organic carbon content have a higher exchange capacity. However, several soils do not fit this pattern and have high carbon contents but relatively low cation exchange capacities. These are the soils with a high organic carbon content in the A horizon but a low exchange capacity throughout the entire profile. This confirms that while there is some “double accounting” involved by using both parameters, considerable errors would result in estimates of vulnerability relying solely on organic carbon content or the cation exchange capacity. Also any “double accounting” which is present is likely to be common throughout the study area and would therefore not affect the relative vulnerability rankings assigned to the soils.

Figure 5 shows the ‘rules of combination’ for developing the unified soil sorption map. The different markers correspond to the final nine categories, ranging from very low to very high sorption capacity. Unlike most previous vulnerability studies, this final soil sorption classification is based on the actual physical and chemical properties of the soils, not simply on subjective divisions of ranked soil parameters.

For example, soil sorption category 4 (represented by ‘diamonds’ in Figure 5) is characterised by organic carbon levels of around 7% and a ‘corresponding’ cation exchange capacity of approximately 12meq/100 g. Cation exchange capacity was, however, allowed to vary for this category between 5meq/100 g (if the organic carbon level was high, 10%) and 18meq/100 g (for a low organic carbon level of 3%).

Figure 6 shows the “combined” soil sorption capacity map of the study area. The darkest polygons, indicating the highest soil sorption capacity, are assigned to the peaty loam soils. The lowest soil sorption capacity (pale

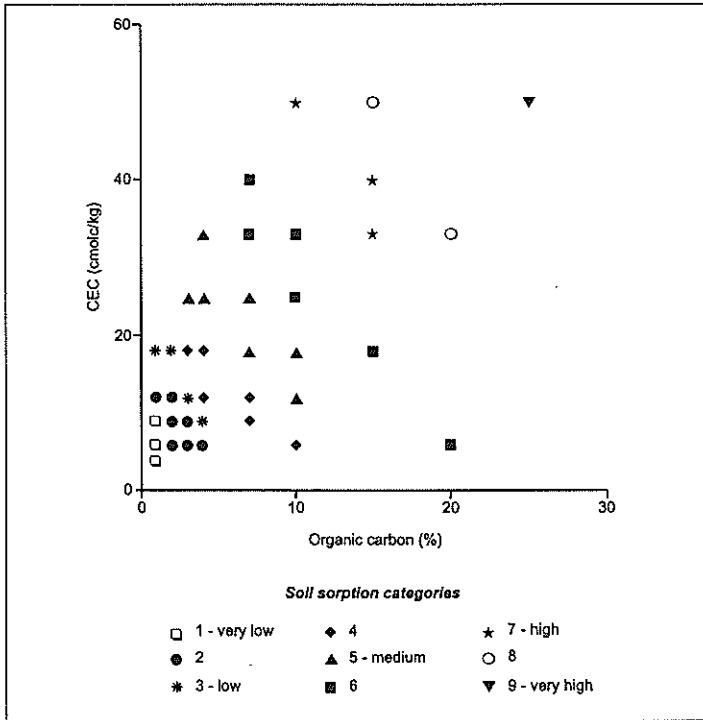


Figure 5 – The relationship between organic carbon content and cation exchange capacity for soils in the study area.

shades), not surprisingly, is applied to the gravelly or sandy soils and along the present river channels.

Field checking

Before the information in the soil sorption capacity map (Fig. 6) is presented, it needs to be checked using soil organic carbon and cation exchange capacity data obtained independently from that used in developing the map. Only a limited amount of independent data were available. For these data, obtained from Landcare Research Ltd, soil sorption categories were calculated using the organic carbon and cation exchange capacity measurements. Table 3 shows good agreement between these independent data and that derived from the estimated soil sorption capacities. There is an exact correspondence for four sites; and the difference between actual and estimated soil sorption is only one unit for the remaining five sites. Although the independent data listed in Table 3 are spread throughout the study area, more observations are needed for a full quantitative validation.

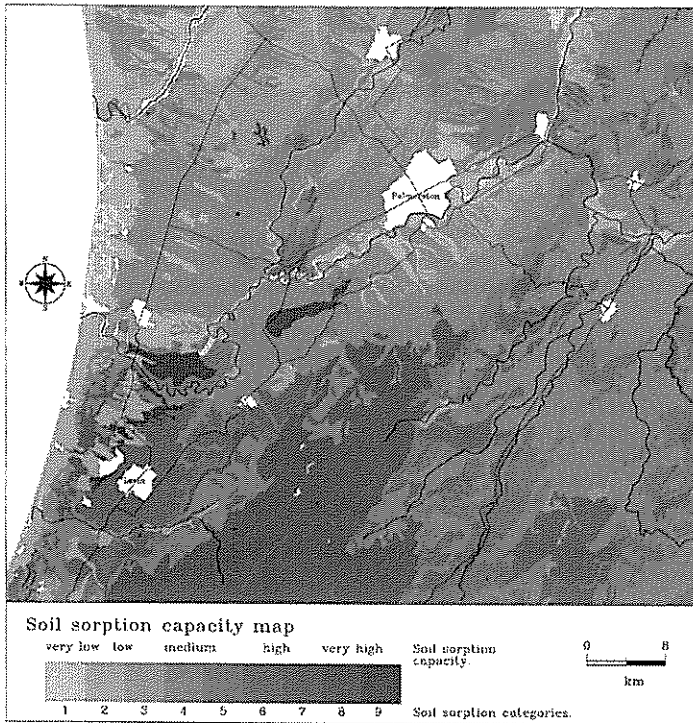


Figure 6 – Variation in soil sorption capacity (Note: the white polygons are lakes and urban areas for which no data exist). High soil sorption capacity, and hence low vulnerability to contamination, are represented by dark shades.

Table 3 – Comparison between estimated and independent soil sorption capacity data

Site	Soil sorption capacity category		
	Independent	Estimated	Difference
1	6	7	-1
2	6	6	0
3	4	5	-1
4	4	3	1
5	6	7	-1
6	6	5	1
7	6	6	0
8	8	8	0
9	6	6	0

Results

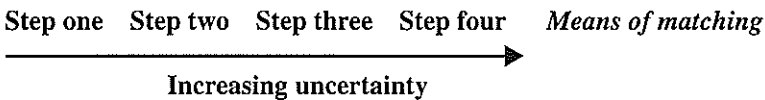
Figure 6 shows the low sorption capacity of soils overlying the northern Tararua foothill recharge zone (south and southeast of Palmerston North and near Aokautere in Figure 1). This is because of the low organic carbon content of these soils. Soil sorption is low to medium over the Pohangina area and near Feilding and Sanson. All these areas act as recharge zones.

In these low sorption capacity, and therefore high vulnerability, soils in recharge areas little contaminant attenuation will occur. Any contaminants introduced at the surface will therefore quickly saturate the available sorption capacity and then migrate to the underlying aquifer. This will lead to potential water quality problems both in the immediate vicinity, and in a down-flow direction.

Uncertainty

The process by which the soil properties were matched to the soil units contains some uncertainty, from both the uncertainty inherent in each database, and from the matching process itself.

There is no documentation of uncertainty for the Land Resource Inventory, besides that relating to scale, although any uncertainty associated with the original soil surveys would be carried through to the Inventory database. The reliability classes derived for the Regional Soil database, however, can be used as a measure of uncertainty of the vulnerability assessment. Uncertainty from the actual matching process can be related to the particular "step" which needed to be used: 1) exact matching, 2) Regional database matching based on soil form, 3) matching using the General Soil Survey, or 4) matching using "expert knowledge".



The uncertainty resulting from having to use steps one or three is similar; the only difference being that the organic carbon and cation exchange data are derived from detailed surveys (step one) or from the more general North Island Survey (step three). The basic unit for the matching (the soil unit) however, is more refined because of the more detailed soil surveys used in step one matching.

Therefore the reliability classes assigned to the Regional Soil database and the particular "step" needed to be used for matching the soil units can be used to create a combined soil uncertainty index. For example, reliability

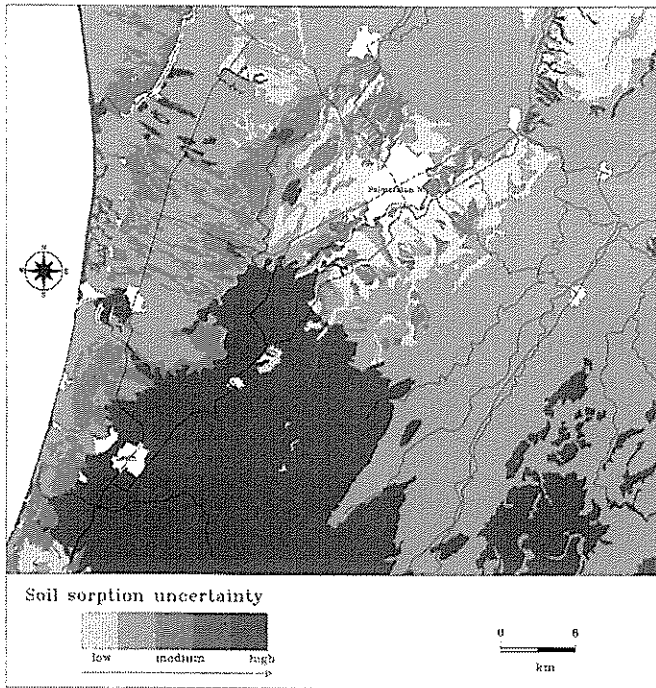


Figure 7 – Variation in the uncertainty of estimates of soil sorption capacity (Note: the white polygons are lakes and urban areas for which no data exist). The dark area around Levin represents high uncertainty in the estimation of sorption capacity because of the lack of detailed data.

class 'r' means that it can be considered as having uncertainty equivalent to that resulting from having to use step two for matching. Similarly, use of step one for matching can be viewed as equivalent to a reliability of 'a'. The uncertainty ranking system based on these two measures (reliability class and "step") is presented in Table 4. Because there are only minor differences in the organic carbon and cation exchange capacity reliability classes for a given soil, Figure 7 portrays uncertainty associated with each of the organic carbon and cation exchange capacity maps. The grey-scale used in Figure 7 corresponds to the uncertainty categories of Table 4.

Table 4 – Uncertainty categories: based on reliability classes and how the data were matched

Regional database reliability	Matching phase	Uncertainty category	Area (km ²)	Area %
a	One	1	364	9.3
m	One	2	2080	53.0
	Three			
a	Two			
m	Two	3	377	9.6
r	One			
r	Two	4	26	0.6
u	One	5	1080	27.5
u	Two			
	Four			

Excellent data coverage from the Kairanga and Otaki Soil Surveys, and good data coverage of the Manawatu Soil Surveys produce low uncertainty around Palmerston North, and in the southwestern margin of the study area.

Highest uncertainty exists for the soils of 'inland' Horowhenua (south of Foxton and Shannon in Figure 1), reflecting the lack of chemical data for these soils. This is unfortunate from the perspective of this study because of the intensive land use in the area, and the large number of bores which are used for drinking water.

Conclusions

The method developed to assess soil sorption, and its potential influence on groundwater vulnerability, can be applied throughout the country. The use of existing national databases ensures consistent standards and quality, and relatively low cost. Uncertainty associated with the vulnerability assessments can be evaluated to provide a measure of the reliability of the soil sorption maps.

The vulnerability assessment presented highlights the relatively low sorption capacity of soils overlying the Tararua foothills and other recharge zones. The significance of the low sorption capacity, and therefore high vulnerability, soils in recharge areas is that little, or no, contaminant attenuation will occur. This highlights the risk both in the immediate area, and to water resources in a down-flow direction.

These results can be used to direct resources, by focusing attention on the most vulnerable areas. This will help to safe-guard water quality and mitigate adverse affects on the groundwater resource in a cost effective manner.

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