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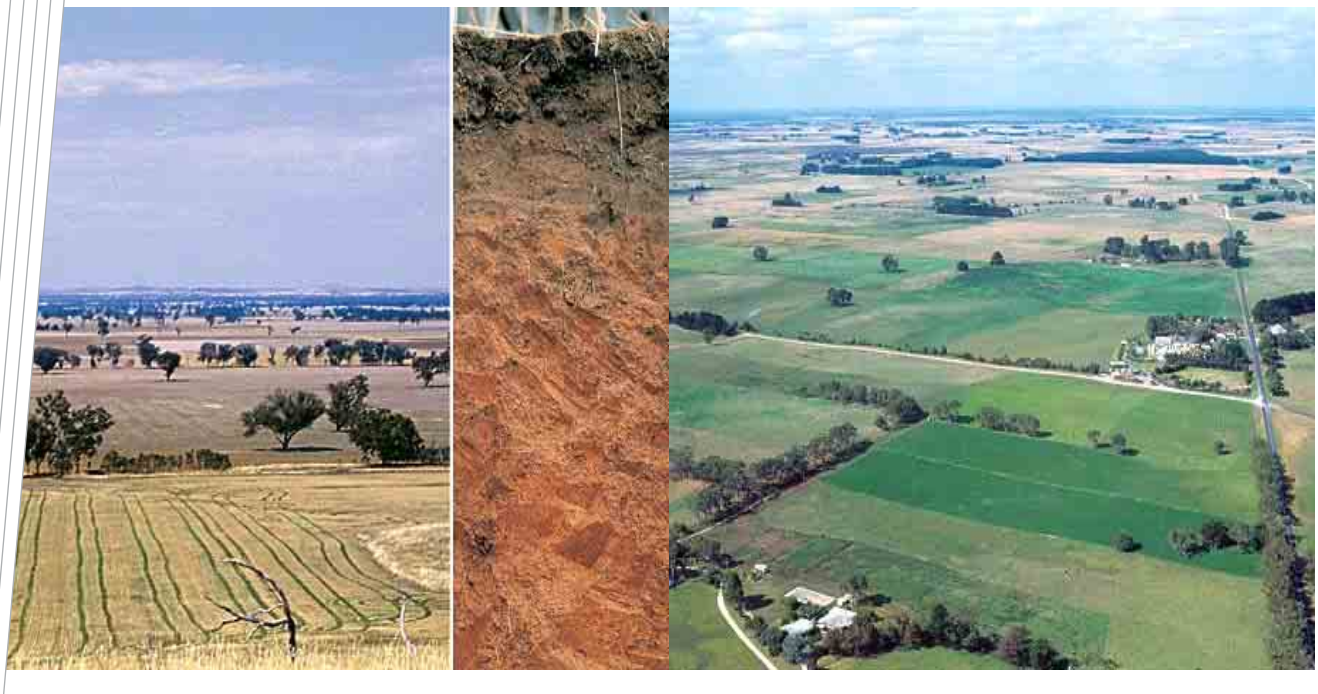

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Building a foundation for soil condition assessment

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CARING FOR OUR COUNTRY

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EXECUTIVE SUMMARY

Introduction

This document presents the results of a project with the objective of designing a national system for monitoring soil condition focusing on two soil indicators: carbon content and acidification.

Soils represent a fundamental resource upon which Australian agricultural systems are reliant. Issues related to food security and environmental safety under increasing global and Australian populations and to greenhouse gas accounting will place considerable demands on Australia's soil resource. Development and implementation of a soil condition monitoring system will be critical to gaining a national understanding of how this resource is being affected by alterations to agricultural management practices and a changing climate. Additionally, such a program will identify regions with soils requiring priority investment to maintain their productive capacity.

In a soil monitoring program, the identification and assessment of 'master' soil variables that exert some level of control or influence over multiple soil properties will provide the greatest return on investment. The quantity of organic carbon present and the extent of acidification are two such "master" soil variables.

Increasing the quantity of soil organic carbon (SOC) will provide positive responses in a range of soil biological, chemical and physical properties with the additional benefit of reducing the concentration of carbon dioxide in the atmosphere. Soil acidification is a consequence of the removal of products associated with agricultural production. Increasing soil acidity adversely affects numerous soil properties and can result in irreparable damage to the soil resource if left unchecked. Recent analyses indicate that some Australian soils are more vulnerable to acidification than previously thought. Ultimately, losses of soil carbon and acidification will restrict future productivity and land use options.

The suggested monitoring system consists of an integration of sampling and analytical protocols with modelling to deliver an accurate assessment of soil condition change across a selection of susceptible and/or important Australian soils and land uses.

The questions to be answered by a national program

The national program is designed around three questions asked of representative soil and land use combinations:

1. What are the current and future influences of land use and management practices on the magnitude and direction of soil carbon and pH change?

2. What are the levels of certainty associated with measured soil carbon and pH changes?
3. Are the direction and magnitude of soil carbon and pH change consistent across different environments?

What constitutes a 'national' program?

A complete and representative national program should provide a network of monitoring sites representative of all soil landscape types under the current and evolving land management. In small countries (e.g. the UK) an intensive sampling grid can form the basis of a comprehensive national coverage. Resource constraints, the size of the managed land base and diversities in climate, soil type, land use and management practices across Australia limit the establishment of such an intensive program. However, a comprehensive monitoring program including important exemplar landscapes with a 'nested' approach for including national, state-based, regional and community effort could be achieved. This report focuses on the stratification used to develop the broadest layer of an Australian national soil monitoring program. It also provides the template for creating additional nested layers that further classify agricultural lands into smaller units so that the overall effort can grow and provide a coordinated assessment.

The proposed national monitoring program will use a hierarchical approach containing the following three levels:

1. Monitoring Regions representative of the major Australian agroecological zones will provide the primary stratification across Australia. Monitoring Regions containing soils most susceptible to losses of carbon and acidification will be given priority in the selection process.
2. Monitoring Units will be selected to exemplify the main combinations of land use, management practice and soil type present within the defined Monitoring Regions.
3. Monitoring Sites will represent a single expression of a land use/management practice/soil type combination defined by the Monitoring Unit. Many Monitoring Sites would be monitored within each Monitoring Unit.

As a component of the monitoring program defined in this report, a well documented set of sampling and analytical protocols that will provide reliable estimates of soil carbon and acidification are defined. Discussions of the science behind soil carbon and pH as well as recommended methodologies can be found in Sections 3 and 4 and Appendices 2 and 3.

The monitoring system will be constructed to allow statistically defensible statements pertaining to:

1. temporal changes in soil condition induced by applied land management practices at Monitoring Sites,
2. comparison of the effects of different land management practices imposed across Monitoring Units within Monitoring Regions, and
3. assessment of the consistency in changes in soil condition between Monitoring Regions.

Temporal and spatial dimensions of a national monitoring program

Spatial stratification has been used to restrict variance and allow detection of changes that are small relative to the range of soil pH and organic carbon values present. This approach will optimise detection of temporal changes and the acquisition of a national perspective of the extent of soil change and its consistency in trends within and between regions. The concept is to ultimately identify approximately 12 Monitoring Regions having distinctive climatic properties and soils. The project has identified 20 candidate regions based on physiographic regions, soil properties, land use intensity and potential resilience of the soil to change (Figure 1). It is envisaged that the number of Monitoring Regions will be reduced to a practical and desirable number through a process of consultation and prioritisation to identify regions with soils that are most susceptible to acidification and/or changes in carbon content.

Within a Monitoring Region, Monitoring Units representative of the major combinations of land use, management practice and soil type will be defined. The number of Monitoring Units within the Monitoring Regions may vary depending on the variety of land use and management practices in use and their potential impact on soil carbon and acidity. Within each Monitoring Unit, soil will be collected from approximately 100 separate Monitoring Sites. The number of Monitoring Sites within Monitoring Units will vary with the number increasing as spatial variability within Monitoring Regions increases. Resource constraints also impose limitations on the total number of Monitoring Sites that can be defined. Ultimately, the number of sites is a compromise between the resources available and the precision of the estimate that can be achieved; it is proposed that priority be given to defining a smaller number of adequately monitored Monitoring Sites if resources become limiting.

Information collected from the individual Monitoring Sites will enable clear statements about the baselines and trends, while the composite of Monitoring Sites within Monitoring Units and

Monitoring Regions will provide more general assessments of the magnitude and uniformity of changes in soil condition induced by land use and management practices.

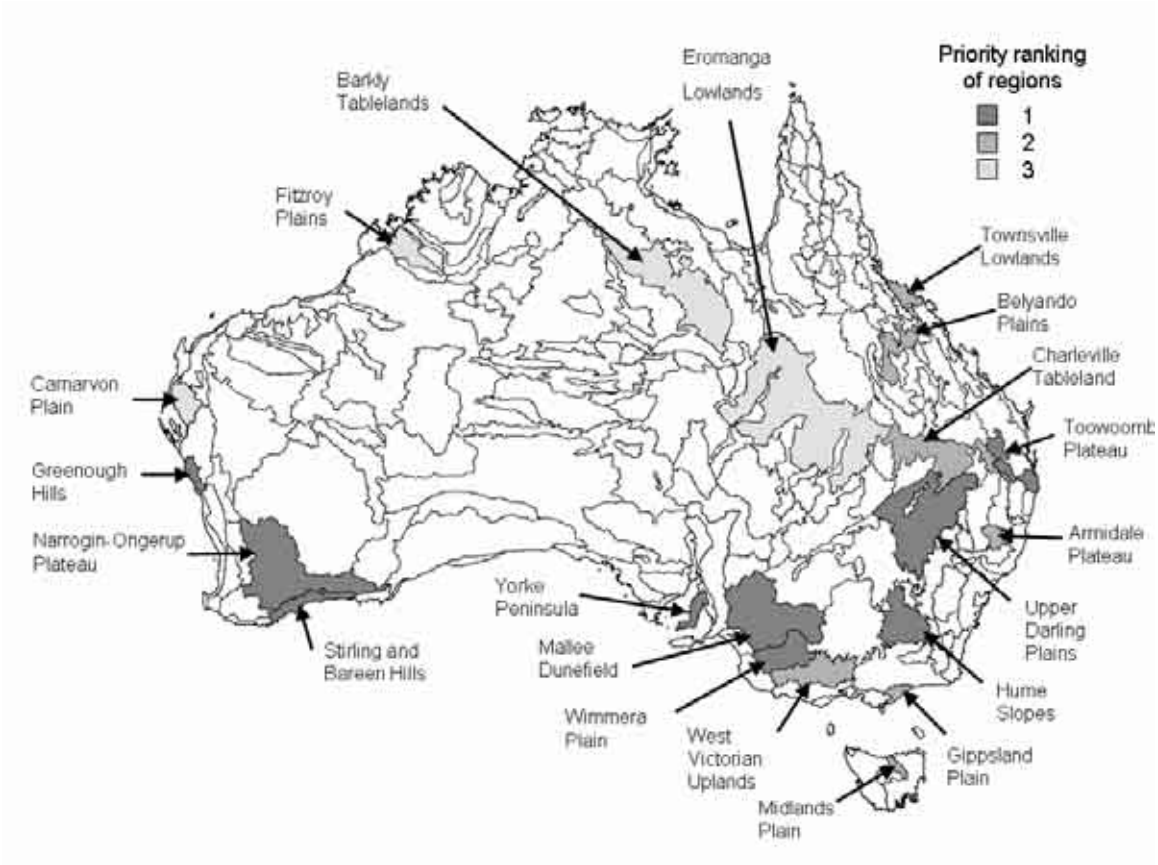

Figure 1: Location of provisional monitoring regions. The priority ranking gives an indication of the importance of including a given region in the monitoring program with highest priority of 1 and a minimum of 3. Region classification is according to Jennings and Mabbutt (1986).

Recommendations pertaining to the temporal and spatial design:

Recommendation: That a national monitoring scheme for change in soil carbon and soil pH be established based on the concept of Monitoring Regions, Monitoring Units and robust Monitoring Sites as defined in Section 1.1.1

Recommendation: That the precise selection of Monitoring Regions, Units and Sites be developed in an implementation phase between CSIRO and the relevant State Agencies under the auspices of the National Committee on Soil and Terrain and technical assistance of the Australian Collaborative Land Evaluation Program (ACLEP).

Recommendation: That the twenty Monitoring Regions identified in this report form the basis for the selection of at least 12 regions to stratify national monitoring – alternatives which better complement state activities will replace some regions where they satisfy similar stratification criteria.

Recommendation: That as part of the implementation phase of the National Soil Condition Monitoring Program, a focussed sampling and measurement project is used to characterise variance in key soil attributes in contrasting land management, soil type and climatic regions – using a combination of desktop studies of existing data, sampling and measurement with rapid measurement technology.

Recommendation: Estimates of within and between Monitoring Site variances are derived for each Monitoring Unit to be included in the monitoring program and used to define the number of soil samples to be collected within Monitoring Sites and the number of Monitoring Sites required within Monitoring Regions. These estimates should be derived from existing datasets. Where no estimates are possible, reconnaisance surveys should be used to derive the required values.

Recommendation: Estimates of within and between Monitoring Site variances should be verified as soil sampling is initiated. Where deviations from estimated values are obtained, the number of soil samples to be collected and Monitoring Sites to be included are altered to maintain the ability to detect differences of the desired magnitude with a defined probability.

Recommendation: A Latin hypercube analysis (Minasny and McBratney, 2006) with soil mapping, terrain, climate and gamma radiometrics data will be used to identify candidate Monitoring Sites; that twice as many sites as required be selected and that an a priori process for identifying sites to be culled and for the selection of replacement sites from within the unallocated sites is developed as part of the site selection process.

Recommendation: That detailed operational guidelines be developed as part of the implementation phase of the National Soil Condition Monitoring Program to describe in detail site establishment, characterisation and long term management; sampling protocols and processes for exhaustion and replacement.

Recommendation: That composite soil samples prepared from the samples collected from the Monitoring Sites are stored in the CSIRO maintained Australian National Soil Archive to quality specification and with accompanying analytical results.

Recommendations pertaining to information system design and support:

Recommendation: That ACLEP with relevant State Agencies and BRS, through collaboration with Australian Collaborative Land Evaluation Program (ACLUMP), develop and agree to support a long-term system to assess, and record land use and land management practices as an integral part of the national monitoring scheme

Recommendation: That ACLEP in conjunction with key database officers in State Agencies amend the NatSoil database to accommodate soil condition indicator monitoring data including expanded land use/management options consistent with Australian Land Use Management (ALUM) codes and develop a field / laboratory database with storing, reporting and analysis tools for pH, OC and related soil indicators

Recommendation: That ACLEP with relevant State Agencies develop confidentiality protocols to ensure that monitoring data acquired for individual paddocks/farms cannot be traced back to individual farmers in any reporting within ASRIS

Recommendation: That the National Committee on Soil and Terrain (NCST) be invited to recommend on governance guidelines for the conduct of the National Soil Condition Monitoring Program, an overview committee and processes for day to day management.

Soil properties to be measured

Soil organic carbon

The potential amount of carbon that can accumulate in a soil is a function of the nature and mass of mineral particles present. Whether this potential can be realised is determined by the balance between inputs of carbon from plant residues and losses as carbon dioxide due to decomposition. Management practices that increase the input of carbon to the soil or decrease the losses will result in an increase in SOC. Losses by erosion (wind and water) may be significant or even catastrophic under adverse conditions.

A monitoring system incorporating measurements of SOC will need to quantify the total amount of organic carbon present and its allocation to component fractions. When combined with a calibrated SOC model, such data will allow an assessment of soil carbon condition at the time of measurement as well as estimates of the likely SOC outcomes of various future management strategies. The collection of these data through time at all sites will also provide a robust and consistent data set to further SOC model development into the future. Changes in SOC are not fast and multiple measurements over decades are often required to detect change. Early indicators of the direction of SOC change may be obtained by measuring rates of mineralisation of carbon and nitrogen under controlled laboratory conditions. Such measures, when repeated on soil samples collected through time will provide an indication of alterations to soil biological functioning.

Recommended methodologies pertaining to soil organic carbon: Total organic carbon is to be measured using a dry combustion analyser equipped with infrared detection to quantify the amount of CO_2 liberated from a sample (Method 2.1: Total carbon analysis, page 128). Where carbonates are present, samples will require pretreatment with sulfurous acid (Method 2.2: Sample pretreatment to remove carbonate carbon, page 129). Allocation of soil organic carbon to its component fractions (particulate organic carbon, humus carbon and charcoal carbon) will be complete by direct measurement (Method 2.3: Fractionation of soil organic carbon, page 129) or mid-infrared (MIR) prediction (Method 2.4: Fractionation of soil organic carbon – indirect measurement by mid infrared spectroscopy, page 133). The proportion of mineralisable carbon and nitrogen will be defined by a laboratory incubation procedure conducted under defined conditions (Method 2.5: Determination of mineralisable C and N, page 133).

Soil acidification

Measuring soil acidification requires detection of a change in soil pH (ΔpH) through time. The key land management and soil attributes required to understand ΔpH measurements

include: net acid addition rate (NAAR) for a particular land use (mol H^+.ha^{-1}.$period^{-1}$); soil pH buffering capacity (pHBC) (mol H^+.kg^{-1}.pH $unit^{-1}$); and soil bulk density (kg.m^{-3}).

The recommended method of measuring pHBC is by titration with occasional shaking over a period of 7 days. However, when entering into a soil monitoring program where a significant number of samples will be analysed, the time and labour commitments required for the titration method become impractical. For the proposed monitoring, the titration method will be used to calibrate and evaluate a promising more rapid and cost-effective Mehlich buffer method having a 1 hr measurement time. Initial results suggest that the Mehlich buffer method is reliable and promising as a rapid method to estimate pHBC.

The simplest and most reliable method to estimate NAAR uses measurement of the change in pH (ΔpH) through time as well as the pHBC of each soil layer. This method integrates net acid addition over several years and relies on few assumptions. Values of layer-specific NAAR are summed to the soil depth of interest to give the soil profile NAAR for the land use being studied. Estimates of NAAR should be complemented with measures of direct acid/alkali inputs to provide an insight on the magnitude of the processes contributing to acidity and how these contributions might be changed by management. Records of land management practices and product removals over the period used to measure ΔpH will provide the required information. An additional benefit of completing such direct estimates is to allow acidification due to leaching loss of nitrate to be estimated.

Recommended methodologies pertaining to soil acidification: Measurement of soil pH is to occur in a 1:5 soil:0.01M $CaCl_2$ solution (Method 3.1: Soil pH in Calcium chloride, page 135). Two approaches to defining soil pH buffering capacity (pHBC) are to be used. The Mehlich buffer method (Method 3.2: pH Buffering Capacity by Mehlich Buffer Method, page 135) offers a more rapid analysis than the titration method (Method 3.3: pH Buffering Capacity by Titration, page 136), but its ability to derive valid estimates of soil buffer capacity remains to be proven. It is suggested that initially both methods be applied and a decision be made later as to the validity of retaining the more cost effective Mehlich buffer method. The amount of lime required to attain critical pH values of 4.8 and 5.5 will be defined (Method 3.4: Lime requirement for liming to critical pH, page 138). Estimates of net acid addition rates will be quantified by measurement (Method 3.5: Estimating NAAR by ΔpH and pHBC, page 139) and estimation based on carbon and nitrogen cycling (Method 3.6: Estimating NAAR by carbon and nitrogen cycles, page 141).

Enabling technologies and information resources

A series of enabling technologies exist that will help in the establishment and analysis of soils within the proposed national soil monitoring program.

1. The availability of spatial information pertaining to environmental and soil properties from the first National Land and Water Resources Audit and augmented through the development of the Australian Soil Resource Information System (ASRIS). As a result of this project, these underpinning resources now include on-line calculators, expanded spatial datasets and spectral libraries of key soil assets to refine rapid measurement technologies.
2. The use of mid-infrared spectroscopy to enhance the number of samples that can be analysed with a specified level of confidence. Such work would be instrumental in establishing sites and defining the potential spatial variability that exists both at individual sites and across sites within monitoring units.
3. Development of a rapid and accurate methodology for measuring soil bulk density on site. Bulk density is an important variable to quantifying the amount of soil organic carbon present and parameters governing acidification (e.g. buffer capacity).

Interactions with other agencies

For this monitoring program to be successful, it will require involvement from various state agencies and NRM Regional Bodies to ensure that the appropriate land uses and soils are monitored. The monitoring system will be established in a manner that allows such groups to perform additional measurements either to enhance coverage or provide more detailed spatial assessment within the regions selected. Additionally, to be successful the program will require involvement and support of land owners and managers as well as sound documentation of land use and management practices implemented both historically and into the future.

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1 A NATIONAL PROTOCOL

1.1 Introduction

A comprehensive monitoring program requires an integration of sampling and analytical protocols with modelling and an accurate assessment of spatial variability and representativeness. This section concentrates on the issues associated with the implementation of a monitoring program across Australia which would provide a robust basis for continuing observations and assessment of change in key landscapes. It does not provide a complete monitoring program but does establish the protocols for nested finer scale monitoring which would extend the network and provide state and regional reporting.

In a soil monitoring program, the identification and assessment of 'master' soil variables that exert some level of control or influence over multiple soil properties will provide the greatest return on investment. The quantity of organic carbon present and the extent of acidification are two such "master" soil variables. Increasing the quantity of soil organic carbon (SOC) will provide positive responses in a range of soil biological, chemical and physical properties with the additional benefit of reducing the concentration of carbon dioxide in the atmosphere. Soil acidification is a consequence of the removal of products associated with agricultural production. Increasing soil acidity adversely affects numerous soil properties and can result in irreparable damage to the soil resource if left unchecked. Ultimately, losses of soil carbon and acidification will restrict future productivity and land use options.

Emphasis in this report is on the design of a program that provides reliable estimates of change in soil organic carbon and acidity across Australia. It builds on the conclusions of a series of reports and deliberations on monitoring (e.g. McKenzie et al. 2000a, 2002, McKenzie and Dixon 2007) to construct a distributed sites model. The most relevant recommendations of McKenzie and Dixon (2007) involve establishing a monitoring program; preparing detailed site establishment and measurement protocols and methods; designing a data management system; refining understanding of remote sensed observations and models; documenting land use and land management practices; understanding biophysical and agricultural system processes; and establishing institutional arrangements. The first three recommendations of McKenzie and Dixon (2007) are the principal focus of this report. However, the others are also examined as they are critical for the interpretation of monitoring results and the operations of the program.

1.1.1 What constitutes a 'national' program? The questions and answers.

In an ideal world, the national program would provide a comprehensive network of monitoring sites representative of all soil landscape types under current and evolving land management. Diversities in climate, soil type, land use and management practices across Australia provide

a significant practical challenge to the establishment of a representative national program. However, comprehensive monitoring could be achieved with a 'nested' approach including national, state-based, regional and community effort. At its simplest level, the national program would provide the template for such a nested approach. In practice, the nesting process will have to be iterative and work with both existing and planned monitoring schemes. Some states and regions have monitoring systems in place. These have not necessarily been derived from a consistent appraisal of the monitoring issues. A national scheme would seek common ground and integration across existing monitoring schemes and provide a consistent framework to guide new schemes.

This report describes the components of a national set of monitoring sites (a subset of the potential 'nested' comprehensive set of sites) which would provide a useful cross-sectional analysis of national baselines and the land use/management practice induced rates of change in soil carbon and acidity across Australia. The proposed monitoring program will not comprehensively examine all Australian landscapes, but will rather identify important exemplar landscapes and land management systems having the potential to induce changes in soil carbon and acidity. With this in place, additional and/or more intensive future monitoring schemes could fit within and inform the proposed national program.

The concept of the national program is based around the identification of a variety of Monitoring Regions around Australia that capture broad differences in soil type, climate and land use. Within each Monitoring Region, specific combinations of land use/management practices and soil/landscapes will be identified and be referred to as Monitoring Units. The Monitoring Unit will be composed of a set of Monitoring Sites identified as being representative of the Monitoring Units selected within the Monitoring Regions. .

Thus a national monitoring program will consist of the following hierarchical elements organised as indicated in Figure 2:

- Monitoring Regions (MR): a priority subset of the regions that together constitute the geographic extent of the country and are monitored for national reporting. The regions chosen represent a cross-section of the major biogeoclimatic zones of Australia.
- Monitoring Units (MU): the main combinations of soil/landscape by land use/management practice within a Monitoring Region. These will constitute a specific subset of the land management systems in place in the country and will be representative of current practice or some designed changes to current practice to achieve specific environmental purposes. Again, not all Monitoring Units that may exist within a Monitoring Region would be monitored in a national program.

- Monitoring Sites (MS): a single expression of a land use/management practice soil by combination designed to be representative of a monitoring unit. Many Monitoring Sites (estimated at 100) would be established within each Monitoring Unit.

Appropriately designed and established, this monitoring program would enable:

- clear statements about the baseline and temporal trend in measured soil properties at each Monitoring Site;
- the composite story told by a set of Monitoring Sites about change in soil properties within the Monitoring Units studied; and
- the identification of trends in soil properties across the identified Monitoring Regions..

An important component of any monitoring program is a justified and well documented set of sampling and analytical protocols that can be used to provide reliable estimates of the soil properties being examined. Section 2 and Appendix 1 describe the process used to select Monitoring regions and considerations related to sampling activities. Sections 3 and 4 discuss the science supporting decisions on what measurements related to soil carbon and acidity should be included in the monitoring program. Appendices 2 and 3 present the proposed analytical methodologies to be implemented for soil carbon and acidity.

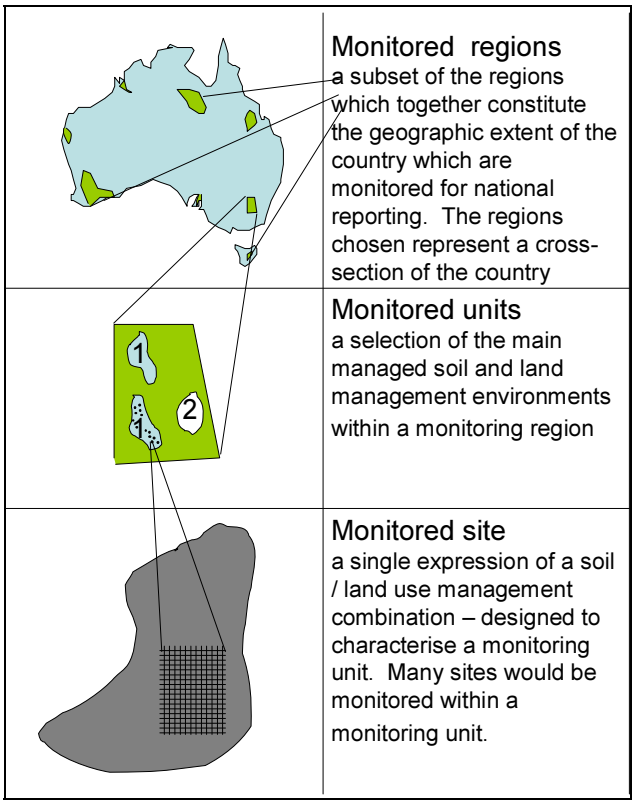

Figure 2: Diagrammatic representation of the hierarchical organisation of Monitoring Regions, Monitoring Units and Monitoring Sites within a national monitoring program.

Recommendation: That a national monitoring program for change in soil carbon and soil pH be established based on the Monitoring Regions, Monitoring Units and robust Monitoring Sites defined in Section 1.1.1

Recommendation: That the selection of the Monitoring Regions, Monitoring Units and Monitoring Sites be developed in an implementation phase between CSIRO and the relevant State Agencies under the auspices of the National Committee on Soil and Terrain and technical assistance of the Australian Collaborative Land Evaluation Program.

The principles underlying this process are developed in the next section.

2 THE SPATIAL ELEMENTS – MONITORING REGIONS, UNITS AND SITES

2.1 Introduction

The proposed national initiative constitutes a specific case within the more general monitoring approach suggested by McKenzie et al. (2002). It concentrates on soil carbon and pH – identified by McKenzie et al. (2002) as soil attributes which are tractable for long term monitoring based on a set of revisited sites. These are also two of four soil attributes selected by the Caring for Our Country program as indicators of soil condition.

The program design addresses a set of critical questions:

1. What are the current and future influences of land use and management practices on the magnitude and direction of soil carbon and pH change?
2. What are the levels of certainty associated with measured soil carbon and pH changes?
3. Are the direction and magnitude of soil carbon and pH change consistent in different environments?

Change in soil pH and soil carbon result from natural variations in climate and vegetation and through anthropogenic activities associated with land use and applied management practices. Rates of change can be mediated by soil properties such that specific combinations of soils and land management will respond uniquely to management or cyclical impacts.

An effective national monitoring program will measure change in important combinations of land management and soils across significant climatic and environmental gradients. Thus the proposed strategy stratifies observations by environments and tests the changes within these environments and then tests for differences between environments. Each environment is a different combination of soil, climate and management.

The spatial design developed in this section recognises that not all environments will be monitored. A method of prioritising regions to be monitored is developed. Within these regions a requirement will exist to identify which combinations of soil/landscape and land use/management practice should be monitored to will provide the most sensitive indication of soil carbon and pH change across Australia.

2.2 Constraints to the design of the national program

McKenzie et al. (2002) describe in some detail the challenges which constrain monitoring choices. Of these the following are considered important in the development of the national program:

1. Many soil indicators change relatively slowly – including the two targeted indicators: soil carbon and soil pH;
2. The spatial variability of soil indicators is often larger than the temporal variation (which also may be significant).
3. Management induced changes can be either gradual or rapid – e.g. the immediate impact of land clearing on soil carbon versus a typically slow decline thereafter; and
4. Temporal variation is influenced by strong seasonal and longer term cycles (such as the *El Niño* and *La Niña* climatic cycles) and the impact may exceed the underlying trend of land management induced change.

It follows that the detection of management effects within climate and other environmental impacts is a key challenge for monitoring systems. To obtain the statistical rigor required to define temporal changes in soil properties, effort should be concentrated on reducing the uncertainty of measured soil properties at specific locations both through space and time. This can be achieved by limiting the spatial extend of a Monitoring Site (area of soil sampled) and collecting temporal samples from a consistent set of Monitoring Sites (representative of a target population). Stratification within environments should be used to increase the efficiency and reduce the number of sites required to detect a change of defined magnitude. Additionally, long-term monitoring will be required to confirm temporal trends and reduce uncertainty imposed by seasonal variation.

The fundamental sampling unit will be the Monitoring Site. These are essentially identical to the soil individuals described in McKenzie et al. (2002). Each Monitoring Site will be established and sampled to ensure reliable measurement of change at the site. Monitoring Sites will be chosen (in terms of number and geographic position) to be representative of the broader Monitoring Unit residing within a Monitoring Region. An example of a Monitoring Unit would be cereal/pasture rotations occurring on Red Chromosols within a Monitoring Region defined as the mid north of SA. A set of provisional Monitoring Regions has been identified in this report based on differences in land use intensity, climate and soil-landscape

resilience. Monitoring Units are identified in broad terms in this report but will be refined in the development of the operational stage of the national monitoring scheme. Monitoring Units will constitute significant national groupings of land use management systems on repeating soil-landscapes.

The program is designed to detect change in soil properties at the Monitoring Sites and across the defined Monitoring Units with monitoring intervals in the order of 5 years. While the monitoring program will not be designed to detect change beyond the included Monitoring Regions, Units and Sites, the national stratification and accent on significant national groupings will provide an indication of change across environments.

Monitoring will be undertaken by relevant State/Regional Agencies in collaboration with CSIRO through the Australian Collaborative Land Evaluation Program.

The national monitoring program is structured so that state-based and regional activities can complement the national program. In many situations, especially where state monitoring regimes are currently being designed or are yet to be designed, a state program could be nested within the national program with similar design concepts and shared technical protocols. Where state monitoring programs exist, design of the national program for Monitoring Regions within the state will accommodate the state system in the design. States may also decide to monitor different or additional indicators beyond those included in the national program. However, inclusion within the national program will require measurement of the parameters described in this report.

2.3 Identifying Monitoring Regions and Monitoring Units

2.3.1 Monitoring Regions

A number of national regionalisations of Australia were considered for identification of managed landscapes where organic carbon and acidification are subject to land use and management induced change. The subdivision into physiographic regions (Figure 3 Jennings and Mabbutt, 1986) was considered the most appropriate. Physiographic regions provide the national hierarchy and context for detailed soil information within the Australian Soil Resource Information System (ASRIS). This regionalisation has two advantages as a basis for national soil monitoring program. Firstly, it is based on differences in geomorphology and parent materials; the primary drivers of soil type and development. Secondly, its derivation and application across Australia is consistent.

The physiographic regions have been revised by the ASRIS partners taking into consideration such products as the digital elevation model (DEM) which provides terrain derivatives that were not available to Jennings and Mabbutt (1986). The revision was not available for this report but is sufficiently different from the original interpretation to change

the broad conclusions. The new boundaries will aid refinement of the regional boundaries as the program is implemented.

2.3.1.1 Prioritising regions for national monitoring

A national monitoring program does not need to capture change in all 200 physiographic regions. The key national monitoring questions (e.g. "*Are grain producing farmers managing soil acidity?*") can be answered by focussing on a defined subset of regions and understanding temporal trends within each region. In this section, the principles (representation, threat and resilience) used in prioritising and selecting Monitoring Regions are described. It should be noted that heterogeneity in some regions may be significant.

Figure 3: Physiographic regions of Australia defined by Jennings and Mabbutt (1986).

Representation

Two key assumptions of the proposed national monitoring program include:

- that a subset of regions can adequately represent the range of soil, land use and land use impacts in Australia, and
- knowledge of soil condition trends of key Monitoring Units within selected Monitoring Regions would provide useful national information on baseline soil condition and trends.

The full reasoning behind the selection of particular regions is detailed in Appendix 1. This section of the report will briefly examine the stages within the selection process and the initial set of Monitoring Regions included.

While an objective regional classification can reliably relate Monitoring Regions to each other and provide a robust basis for grouping, classification procedures are particularly vulnerable to inconsistent data. Landscape and climate parameters and even remote sensed interpretations can now be derived from relatively consistent national datasets. However, despite the progress made in collating the best soil data within ASRIS, there is no comprehensive consistent national soil data set; gaps in soil survey efforts are significant. Major gaps exist outside cropping areas in Western Australia and South Australia and across both cropping and pastoral areas within the eastern states. The only complete and consistent national soil information is the Atlas of Australian Soils (Northcote et al. 1960-1968). Various soil chemical and physical parameters have been ascribed to the polygons within the mapping (McKenzie and Hook, 1992, McKenzie, 2000b). Despite concerns about the level of certainty around these estimates, they remain valuable because of the consistency in application and coverage.

With a spatial intersection process, the physiographic regions were populated with the relevant parameters from the interpreted Atlas of Australian Soils. It was then possible to compare the proportion of each region in terms of these attributes. This part of the classification process is outlined in Appendix 1. Figure 4 is a 10 group classification (PATN, Belbin 1987) of the regions using only the derived soil properties. There are strong geographic patterns in this classification and similarities to a 10 group classification of soil type based on the principal profile form subdivisions of Northcote (1979) (Figure 5). The priority setting process examined 10, 20 and 40 soil unit groupings in priority setting (Appendix 1).

Threat

Soil properties vary in response to soil development processes, climate and land management. Land management is the major contemporary factor and often offers the only anthropogenic mechanism capable of altering soil properties. Thus, land management represents an important component requiring inclusion in the design of a national soil monitoring program.

A six class land use intensity classification (Appendix 1) was developed from a number of sources but principally the 1 km land use mapping assembled by the Bureau of Rural Sciences (BRS, 2006). This intensity classification largely has grazing native vegetation at the low intensity end and horticulture at the high intensity end. (Conservation and forestry were not included in this assessment). Since horticulture and other input intensive agricultural industries are only from small areas (Table 1), they were added to cropping. As a result, the most intense class across a physiographic region was cropping and other intensive agriculture. The distribution of these land use classes across Australia is presented in Figure 6 .Table 1 provides a summary of the land uses included in each defined land use

intensity class. The amount of agriculture present in each of the physiographic regions varies considerably. In Figure 7 those physiographic regions with more than 49% agriculture (defined as cropping and grazing) are indicated by cross hatching. A focus on specific land use within the physiographic regions is the major task in choosing Monitoring Units.

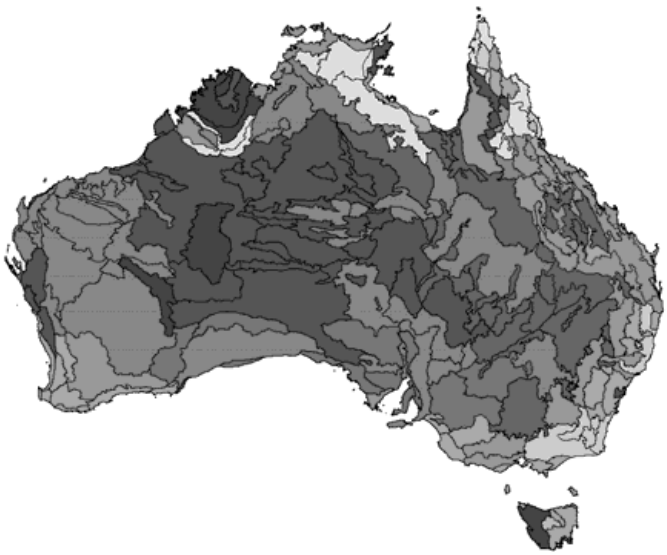

Figure 4: The 10 group classification of Regions using Soil properties.

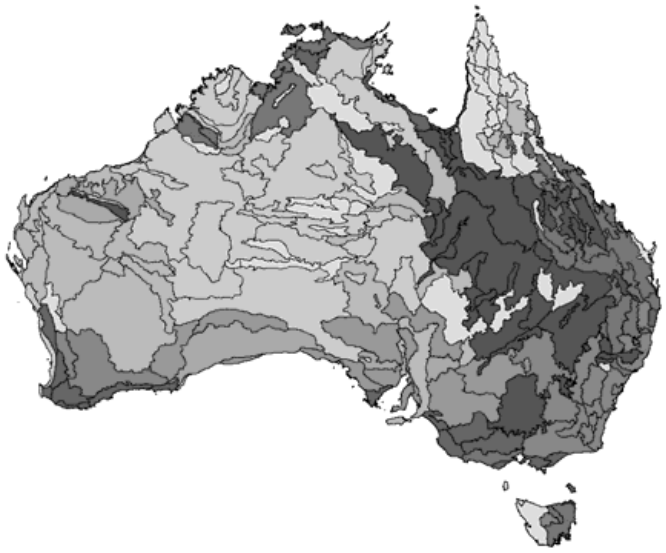

Figure 5: The 10 group classification of physiographic regions using soil types based on the principal profile form subdivisions of Northcote (1979).

Resilience

The ability of a soil to resist modifying processes is a function of its composition, although there is no simple convergence of resilience across different modifying processes. For example, the resilience to changing pH is not simply correlated with the resilience to

changing organic carbon and other properties. This section describes the use of the available datasets to prepare an estimate of resilience to changing pH and organic carbon. The detail of this process is provided in Appendix 1.

A classification aimed at providing an estimate of the resistance to changing pH is presented in Figure 8. This analysis combined an assessment of the neutralising effects of soil carbonate and factors contributing to pH buffer capacity. To a significant degree this is a reflection of alkalinity of the soils and to a lesser extent organic carbon levels (see Section 4 of this report for more detail on soil pH, acidification and buffer capacity).

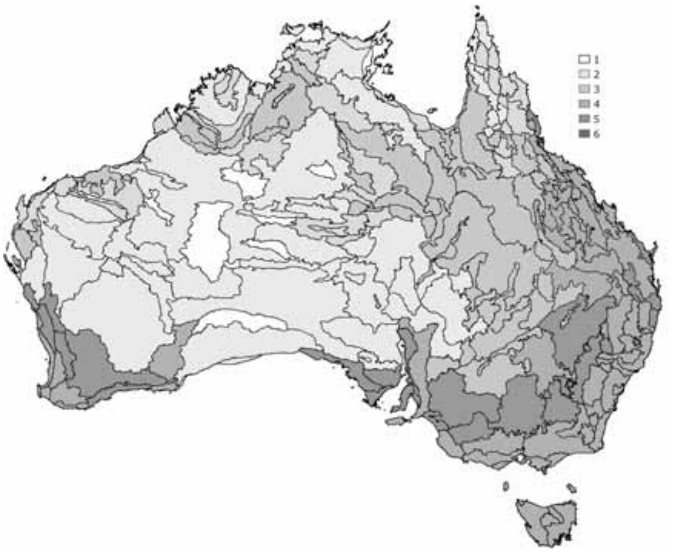

Figure 6: Distribution of the five land use intensity classes delineated – categories listed in Table 1.

Table 1: Land use intensity classes.

Land use class	Description of predominant land uses	Number of physiographic regions	Proportion of Australia's land area attributable to each class (% Australia's land area)
1	nature conservation / natural areas	12	4
2	grazing native pastures (with low stocking rate)	42	41
3	grazing native pastures (with low-moderate stocking rate)	30	9
4	grazing native pastures (with moderate stocking rate)	50	21
5	grazing native pastures (high stocking rate), grazing modified pastures, minor cropping	63	15
6	intensive agriculture and cropping	27	10

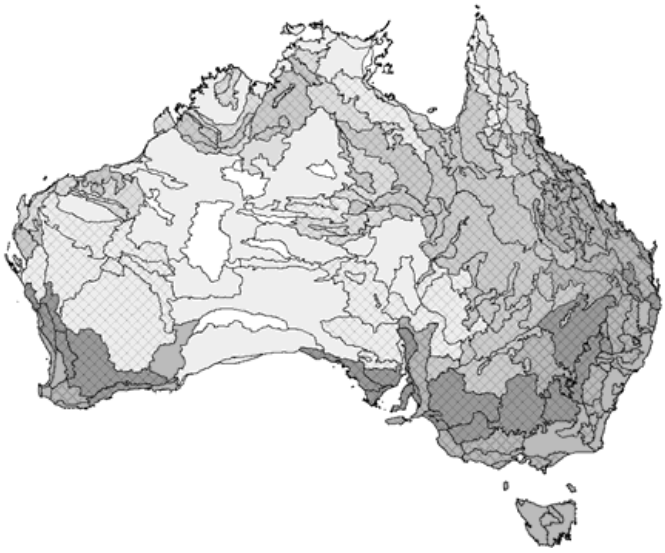

Figure 7: Land use intensity classification with regions having >49% of their land area devoted to agricultural use being hatched (grey scale coding of the regions is the same that used in Figure 6).

The amount of organic carbon present in a soil is defined by the balance between inputs and losses (see Section 3 of this report for more detail on soil carbon). In agricultural systems, inputs of organic carbon are controlled by net primary production (NPP) and the allocation of NPP to residues remaining after harvest or consumption by animals. A potential exception to this occurs where organic amendments (e.g. waste products) are available and applied. Losses of soil carbon result from the processes of microbial degradation and erosion. The same environmental characteristics (e.g. availability of water and heat) govern, to a large extent, both NPP and decomposition rates. As a result, most long term management systems exist in a balance in which inputs and losses of carbon are similar and an "equilibrium" soil carbon content is attained. Production and return of residues to a soil will be optimised by maximising the duration in which actively photosynthesising plants are present in the system. As a result, an index of the persistence of vegetation cover throughout the year should provide an index of the resilience of soil organic carbon content. As the proportion of the year in which growing plants capable of photosynthesising are present increases, potential resilience of soil carbon increases. Figure 9 presents an indication of the resilience to organic carbon loss based on the soil cover index of Donohue et al. (2007).

2.3.1.2 Selection of candidate Monitoring Regions

Of the 224 physiographic regions identified by Jennings and Mabbutt (1986), 12 had little to no agricultural land use. Of the remainder, only those with more than 49% agriculture (163 regions identified by hatching in Figure 7) were considered further in this assessment.

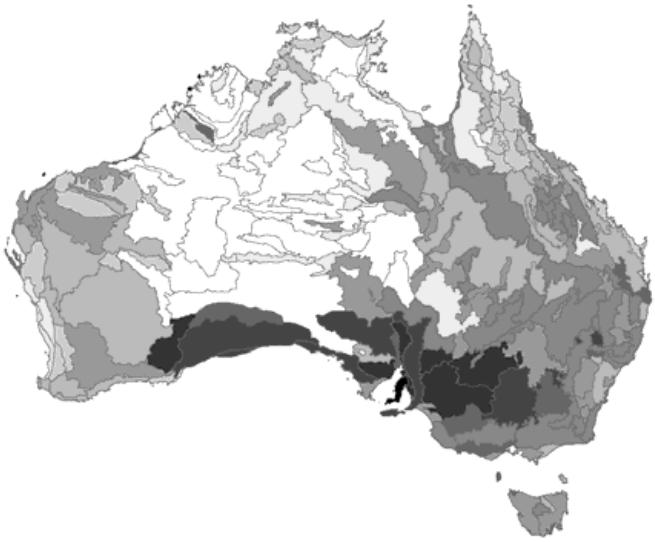

Figure 8: Resilience of Australian soils to pH change (the darker the shading the more resilient the soil is to pH change).

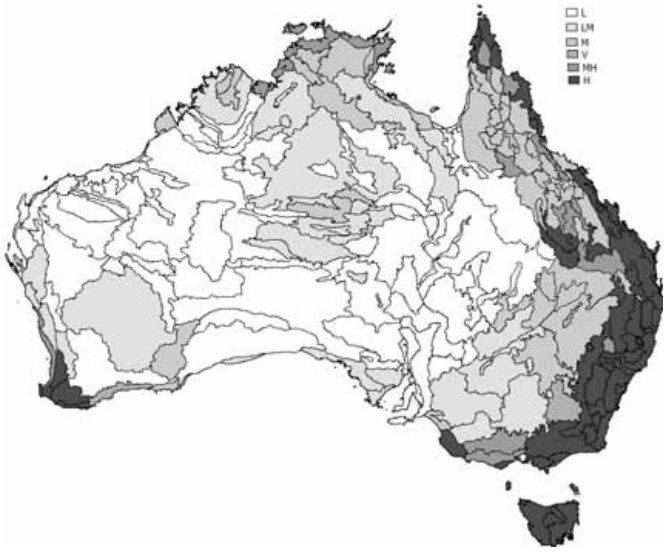

Figure 9 Resilience of Australian soils to changes in organic carbon content based on a persistent vegetation classification (the darker the shading the more resilient the soil is to soil carbon content change).

The process of combining the representativeness, threat and resilience to produce vulnerability classes is presented in several steps. Appendix 1 provides additional details to those presented here. Initially the combination of the land use intensity (Figure 6), resilience to pH change (Figure 8) and resilience to organic carbon change (Figure 9) produced Figure 10 which identifies the 74 potential Monitoring Regions with the highest potential vulnerability of the soil to land use. Vulnerability increases in progressing from yellow through light red to dark red. Significant parts of Australia are not represented as vulnerable in Figure 10 principally because of their low agricultural activity. In Figure 11, the 74 potential Monitoring Regions (the regions with the highest vulnerabilities) have been overlaid with hatching that delineates the areas of agricultural activity. Grazing activities in some of the rangeland areas

and in some parts of south eastern Australia have not been selected because they have high perennial cover. The group of 20 most vulnerable potential Monitoring Regions were also identified (Figure 13).

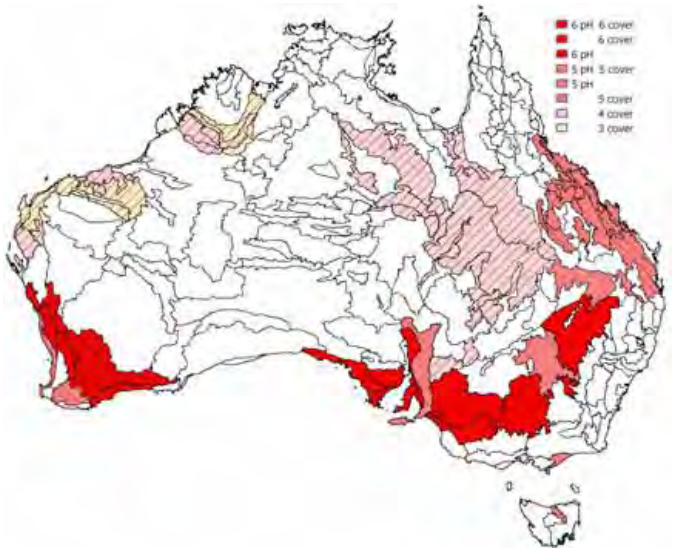

Figure 10: Candidate Monitoring Regions for inclusion in a soil monitoring program selected on the basis of combined land use intensity, pH resilience and organic carbon resilience. Regions selected on the basis of pH are hatched to the left and regions selected on the basis of organic carbon are hatched to the right. Only regions with >49% of the land area devoted to agriculture were considered. In progressing from yellow through to dark red the vulnerability of the soil to change increases.

An attempt to define the relative representativeness of the groups of 163, 74 and 20 candidate regions (Table 2) was completed by constructing a matrix of soil property class by land use intensity class (classes 1-6 shown in Figure 6). Soils were classified into 4, 10 and 20 different groups on the basis of variations in soil properties (see the left side of Table 2). Vulnerability was classified into 6 groups with vulnerability decreasing in progressing from class 6 to class 1 (see the right side of Table 2). The different groupings of potential Monitoring Regions (163, 74 or 20 regions) is located in the central area of Table 2. The values presented in each cell of Table 2 define the number of potential Monitoring Regions that can be allocated to the indicated individual classes of either soils or land use intensity.

Data from Table 2 is presented graphically to show the proportional allocation of potential Monitoring Regions within the 163, 74 and 20 region groupings to soil classes Figure 12a and land use intensity classes Figure 12b. As the number of potential Monitoring Regions declines from 163 to 20, the proportional allocation of regions to soil class declines to zero for soil classes 1, 2, 3, and 10 (Figure 12a). However, for all these soil classes allocation of regions was <5% and was 0% for all Monitoring Region groupings for soil class three. Amongst the remaining soil classes (4-9), all three groupings of potential Monitoring Regions gave more similar allocations with an acceptable proportional allocation being found within each soil class. Thus, the group of 20 potential Monitoring Regions provides a reasonable

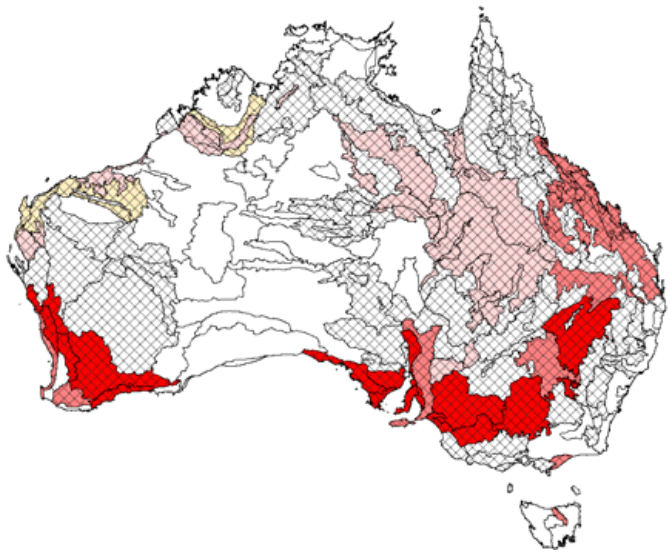

Figure 11: Candidate Monitoring Regions (from Figure 10) overlaid with hatching to define areas of agricultural activity.

Table 2: Summary of the distribution of all Jennings and Mabbutt (1986) physiographic regions, regions with >49% of land area under agriculture and the regions within each agricultural intensity class allocated to each soil group classification. Class 1 conservation lands were not included in the table as there would be little likelihood of a management induced variation in soil properties.

Number of soil groups			All Regions	Regions with >49% of land area under agriculture			Land use intensity class											
							6			5			4			3		2	
4 groups	10 groups	20 groups	total	t*	c#	s§	t	c	s	t	c	s	t	c	s	t	c	t	c
		1	3																
	1	2	12	9	4								3	2		5	2	1	
	2	3	9	2						1						1			
1	3	4	2																
		5	24	13	6	3	1	1		10	5	3				2			
	4	6	9	6	4	2	3	3	2	3	1								
	5	7	36	33	14	6	5	2	3	19	11	2	8	1	1			1	
		8	11	11	3		1	1					4	1		5	1	1	
	6	9	15	15	8	1				1	1		7	5	1	2	2	5	
2		10	11	11	5	1							4	4	1	1	1	6	
		11	6	3	2					1	1		1	1				1	
	7	12	11	8	6	2	5	5	2				2	1				1	
		13	1	1														1	
		14	25	24	11	3	5	3	1	6	3	2	12	5				1	
3	8	15	7	6	6	1							6	6	1				
		16	11	7	2	1	2	2	1							2		3	
	9	17	21	9	2								3	2		3		3	
4		18	4	2												2			
		19	2	1												1			
	10	20	4	2	1											1	1	1	
Total number of regions across the soil classes			224	163	74	20	22	17	9	41	22	7	50	28	4	25	7	25	0

* t = number of regions within each soil class from the total 163 regions with >49% of land area under agriculture

c= number of the potential candidate regions within each soil class from the total of 74 candidate regions identified

§ s= number of selected regions within each soil class from the total of 20 selected regions

coverage of the major soil classes associated with the 74 and 163 region groupings.

In terms of land use class (Figure 12b), a bias towards regions with high land use intensity occurs as the number of potential Monitoring Regions included in the grouping decreases from 163 to 20. Given that land use intensity class is a key driver of vulnerability class and the selection process employed attempted to define the most vulnerable regions, such a bias was both sought after and expected. The allocations of potential Monitoring Regions to land use classes in Figure 12b therefore confirms that the process of region selection was capable of selecting those regions considered most vulnerable to change as a result of their use for agricultural production.

In this initial Monitoring Region selection process, an attempt was made to consider soil classification and the different land use intensities together to maximise coverage. The solution provided in Figure 13 and Table 3 selects 20 potential Monitoring Regions (9 regions from agricultural intensity 6, 7 regions from agricultural intensity 5 and 4 regions from agricultural intensity 4). Additionally these potential Monitoring Regions cover 6 of the 10 soil classes with >49% of land area devoted to agriculture. The soil classes with no representation are found in areas with low intensity grazing and are of less importance to this study.

Taken together, the 20 potential Monitoring Regions cover a range of Australia's managed landscapes. Nonetheless, there will be additional practical and strategic reasons (and additional biophysical factors) which may lead to modifications of the potential Monitoring Regions selected for incorporation into a monitoring program. As such, the set of 20 potential Monitoring Regions should be viewed as a starting point for development of a monitoring system. Discussion with State and Regional stakeholders will be required so that the final set of Monitoring Regions selected meets the conflicting requirements of representativeness and feasibility as a national set of soil Monitoring Regions.

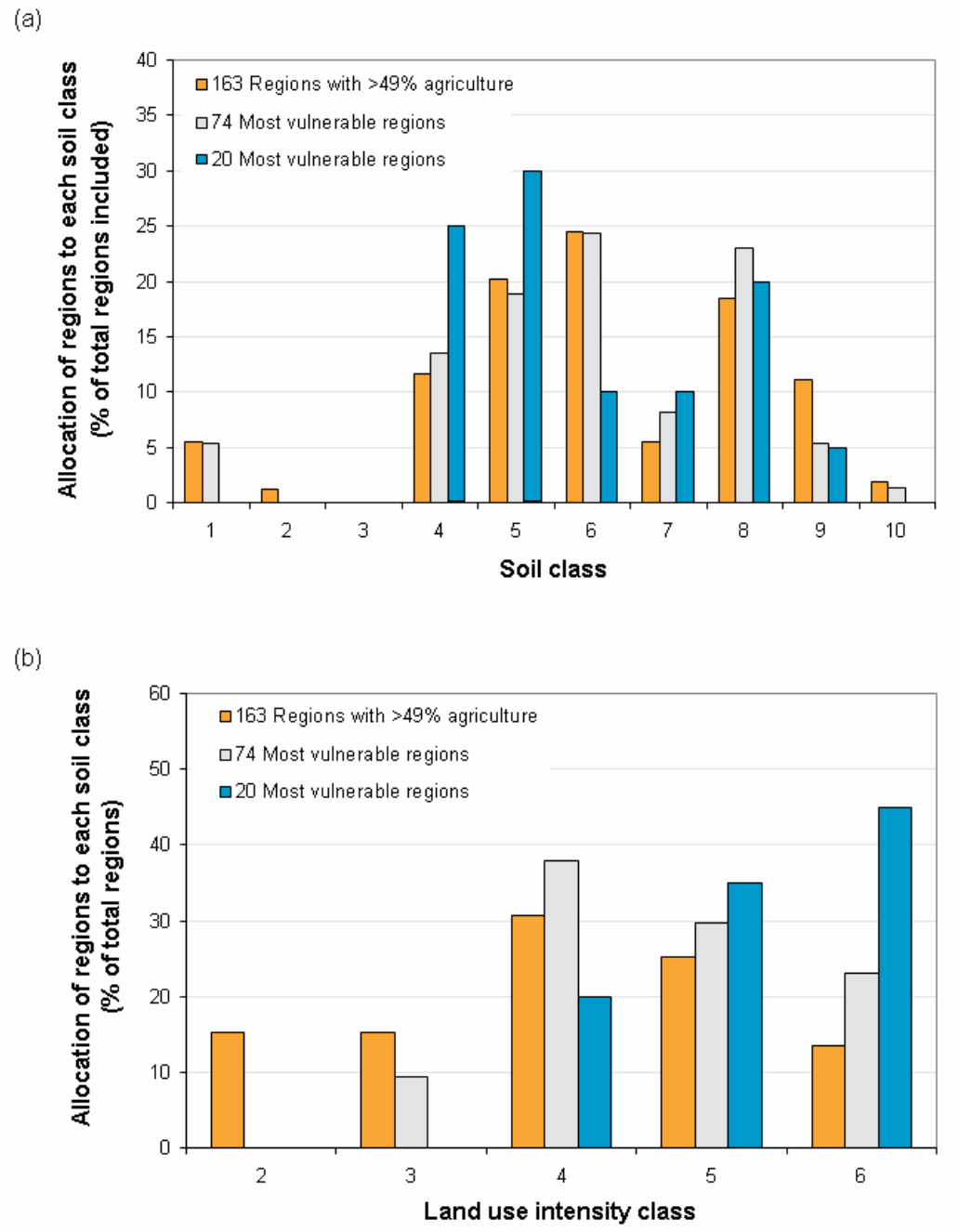

Figure 12: Variation in the proportion of Monitoring Regions allocated to each soil class (a) and land use intensity class (b) for the groupings of 163, 74 and 20 regions.

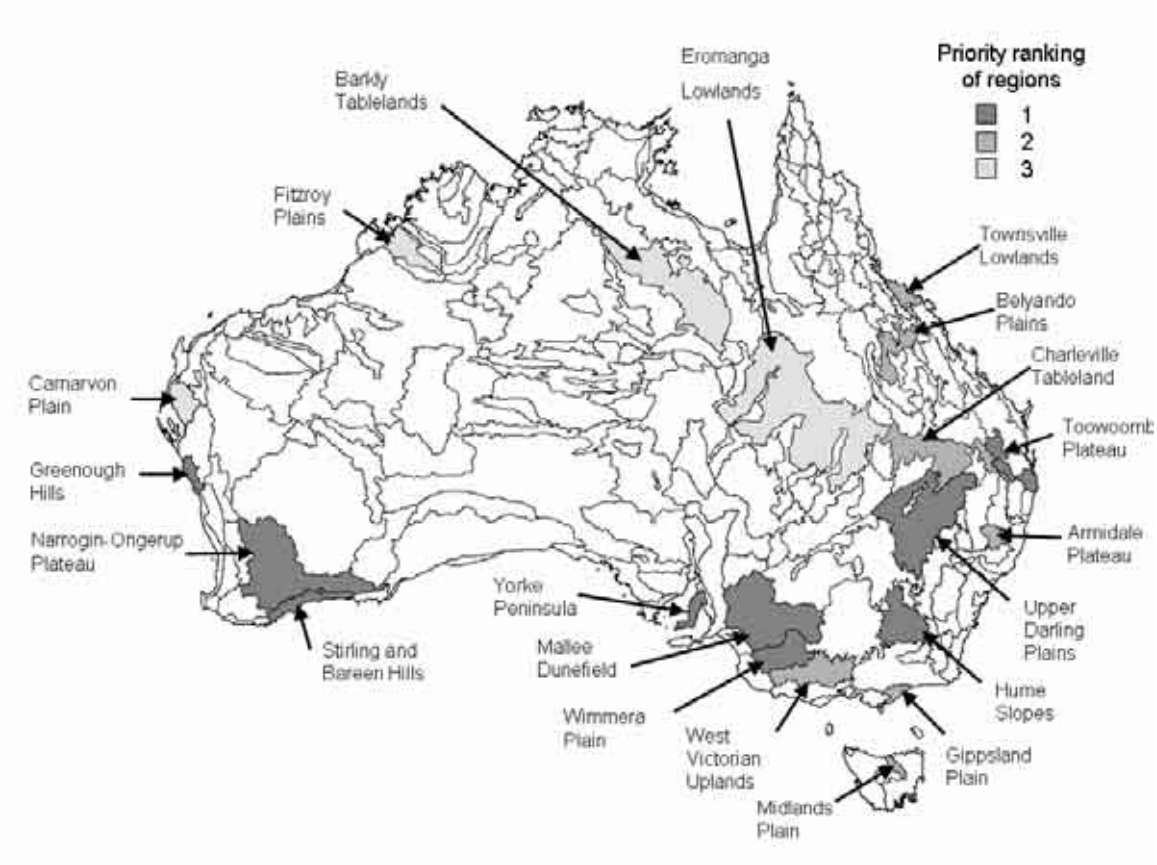

Figure 13: Proposed Monitoring Regions for consideration in the soil monitoring program.

Recommendation: That the twenty proposed Monitoring Regions be used a basis for the selection of at least 12 regions to stratify national monitoring – alternatives which better complement state activities will replace some regions where they satisfy similar stratification criteria.

2.3.2 Monitoring Units

A defined Monitoring Unit within each Monitoring Region constitutes the target population for national soil condition monitoring. Thus if 12 Monitoring Regions are selected across Australia and within each, two Monitoring Units are defined – there are 24 target populations for monitoring.

Monitoring Units are segments of a Monitoring Region that are identifiable land management systems relevant to the monitoring questions in the Region. Broadly, they will be specific soil type by land use combinations (e.g. Brown Chromosols under cereal production). An emphasis will be placed on defining Monitoring Units that are most representative of the agricultural practices employed in a region as well as those where land management is likely to change a soil indicator (pH or organic carbon content). Additional monitoring units may also be included in complementary state and/or regional studies.

Table 3: Twenty regions selected for inclusion in a soil monitoring scheme and their associated priority for entry.

Region name (according to Jennings and Mabbutt (1986)	Priority for entry into the soil monitoring scheme (1=highest, 3=lowest)
Greenough Hills	1
Hume Slopes	1
Mallee Dunefield	1
Narrogin-Ongerup Plateau	1
Stirling and Bareen Hills	1
Toowoomba Plateau	1
Upper Darling Plains	1
Wimmera Plain	1
Yorke Peninsula	1
Armidale Plateau	2
Belyando Plains	2
Charleville Tableland	2
Gippsland Plain	2
Midlands Plain	2
Townsville Lowlands	2
West Victorian Uplands	2
Barkly Tablelands	3
Carnarvon Plain	3
Eromanga Lowlands	3
Fitzroy Plains	3

A recommended set of monitoring units have not been identified in this study; partly because the Regions themselves are subject to change and because of the need to complement existing state monitoring schemes. During the stage of developing the operational specifications for soil condition monitoring, a set of potential Monitoring Units will be developed with GIS overlay techniques from land use and soils information. Full specification of the Monitoring Units will require an area weighted analysis of soil classes by farming systems, local consultation on historic and continuing importance and the degree of flux in soil condition. The farming system concept intended here moves beyond a static definition of land use; in many cases it will involve cycles (phases) of land uses, e.g. cereal, fallow, pasture, canola, cereal etc. A degree of conformity over time to a farming system is implicit, even though the land use and land management will vary. Indeed, different land management is likely within the farming system in response to better resource management and economic conditions associated with various production systems (e.g. commodity prices and costs of inputs).

Recommendation: That at least one Monitoring Unit is defined within each Monitoring Region in the implementation phase of National Soil Monitoring. The Units will be:

- *Representative of agricultural land management, have issues with acidification and/or soil carbon decline / sequestration;*
- *National significant in terms of area covered, impact of the industry or scale of the issue;*
- *Capable of changed land management to address the issue or opportunity.*

2.3.3 Monitoring Sites

The Monitoring Site is a single expression of a Monitoring Unit within a Monitoring Region (i.e. a single soil type by land use/management practice combination). Monitoring Sites represent the base unit in the proposed national monitoring program. For the national program, many Monitoring Sites would be established within each selected Monitoring Unit. The number of Monitoring Sites within any given Monitoring Unit will be specified on the basis of a statistical analysis of the known or estimated spatial and temporal variance and the magnitude of the minimum detectable difference desired. Each Monitoring Site will be selected to allow statements to be made on changes in soil condition at the individual site as well as the aggregate change across Monitoring Sites within a Monitoring Unit. The Monitoring Site is the fundamental and essential unit; established effectively, it will provide a robust statement of change at that site and therefore has value in itself.

2.4 Monitoring sites and considerations in sampling design

The Monitoring Site, as the fundamental unit of national soil condition monitoring, is based on the McKenzie et al. (2002) observation that "*monitoring soil changes relies ultimately on very good quality measurement of representative field sites often over extended periods (i.e. decades)*". The individual field site represents the Monitoring Site and is essentially the "soil individual" defined by McKenzie et al. (2002). This section applies the principles in McKenzie et al. (2002) to the national soil condition monitoring program by expanding on three distinct questions:

1. *What is a Monitoring Site in practice and how is it selected?*
2. *How should a Monitoring Site be sampled?*
3. *How many Monitoring Sites are needed?*

2.4.1 The size and shape of Monitoring Sites

As the size of a Monitoring Site increases the potential spatial heterogeneity in monitored soil properties also increases. Increased heterogeneity across the Monitoring Site will enhance

the variance associated with replicate soil samples and make it more difficult to detect statistically significant variations in soil properties through time. The detection of temporal trends will be advantaged by ensuring that Monitoring Sites are as homogeneous as possible. Thus, the choice of size and shape of Monitoring Sites for the national program will focus on increasing homogeneity.

The 25 m x 25 m site recommended by McKenzie et al. (2002) is also recommended for the proposed national soil monitoring scheme. It is both pragmatic, consistent with the established site concepts (McDonald et al. 1990) and provides room for repeated sampling. While 25 m x 25 m is recommended, it is not essential that the Monitoring Site be a square if there are strong reasons for an alternative shape. This could be the case in complex soil landscapes but it is expected that such landscapes will be the exception. Possible examples of such complexity include:

- gradients (e.g. crests and hill slopes) – rectangular areas with the long axis running perpendicular to the gradient may be more appropriate for increasing homogeneity;
- strong micro relief (e.g. gilgai) – field design may require (contiguous or fragmented) stratification.

2.4.2 Defining the number of Monitoring Sites and sampling locations within Monitoring Sites

McKenzie et al. (2002) proposed a method for predicting how many Monitoring Sites and how many sampling locations (observations) within a Monitoring Site would be appropriate. The methodology is based on prior estimates of the population variance at different scales; effectively scales that equate with within and between Monitoring Sites. The variance values for different scales in Table 7 of McKenzie et al. (2002) are notional and illustrative. In Table 10 of McKenzie et al. (2002), the number of Monitoring Sites is linked with the number of samples at a Monitoring Site.

The within Monitoring Site variability will be used to detect differences between temporal sampling events. Calculation of within Monitoring Site variance requires that all soil samples collected are analysed separately. Compositing of soil samples collected from within the Monitoring Site cannot occur. Estimates of the within Monitoring Site variance will also be used define the number of separate soil samples that must be collected to ensure temporal differences of a defined magnitude can be detected with a desired probability. Additionally, the variance calculated from the first set of collected samples (time zero samples) can be used to inform subsequent sampling campaigns as to the number of individual soil samples that need to be collected from each Monitoring Site to detect a specified minimum temporal difference with a defined level of statistical significance.

The variance measured within Monitoring Sites (equivalent to within Monitoring Units) will be used to detect differences in soil properties between Monitoring Units within Monitoring Regions as well as any temporal trends. As the number of Monitoring Sites within a Monitoring Unit increases the ability to detect differences should also increase. The number Monitoring Sites required within a Monitoring Unit will also be defined using the between Monitoring Site variance.

As an example of the application of this approach, Holmes and Bellamy (personal communication) have used a commercial dataset of soil pH to estimate the number of sites needed to predict change in soil pH and soil carbon over a monitoring timeframe of 5-10 years within various reporting units in a manner similar to that outlined in the previous two paragraphs.

Where no estimates of within and between Monitoring Site variability exist, a reconnaissance survey that randomly samples soils within a subset of the proposed Monitoring Sites will be required. Results from this survey can then be used to guide and define the optimal number of soil sampling points within a Monitoring Site and the number of Monitoring Sites required within a Monitoring Region.

Recommendation: Estimates of within and between Monitoring Site variances are derived for each Monitoring Unit to be included in the monitoring program and used to define the number of soil samples to be collected within Monitoring Sites and the number of Monitoring Sites required within Monitoring Regions. These estimates should be derived from existing datasets. Where no estimates are possible, reconnaisance surveys should be used to derive the required values.

Recommendation: Estimates of within and between Monitoring Site variances should be verified as soil sampling is initiated. Where deviations from estimated values are obtained, the number of soil samples to be collected and Monitoring Sites to be included are altered to maintain the ability to detect differences of the desired magnitude with a defined probability.

2.4.3 Selecting the Monitoring Sites

2.4.3.1 Monitoring Site selection

Selection of the Monitoring Sites requires an adequate spatial mapping of the defined Monitoring Units (combinations of land use, management practice and soil type). In many Australian locations, it is unlikely that any of these components will be mapped in enough detail. It will be necessary to develop an indicative mapping from existing data, remote sensing / airphoto interpretation and expert or local advice. This provisional mapping of

Monitoring Units would provide the base layer for random selection of Monitoring Sites across the Monitoring Unit. Monitoring Sites would then be randomly selected from across the Monitoring Unit. Rapid field checking via a drive by survey could then be used to confirm that the Monitoring Sites are representative of the targeted combination of land use, management practice and soil type. Alternatively, additional Monitoring Sites to the number desired could be identified in the random selection process and each site could be evaluated on arrival to complete the soil sampling. If the Monitoring Site fails to meet the defined combination of land use, management practice and soil type in an initial assessment it is discarded and not sampled.

The next phase should assemble key soil covariates such as terrain, climate and lithographic data (e.g. gamma radiometrics) to provide the basic environmental components of soil – landscape gradients within the Monitoring Unit. With these data, it is suggested that a Latin hypercube analysis (Minasny and McBratney, 2006) be used to identify Monitoring Sites that representatively sample any identified gradients within the Monitoring Unit.

Because there will be attrition of Monitoring Sites over the monitoring period, an excess of candidate Monitoring Sites will be selected; in the order of twice the statistical requirement. An *a priori* process for identifying Monitoring Sites to be culled and for the selection of replacement Monitoring Sites from within the unallocated Monitoring Sites will be established at the same time.

Additional issues that will need to be addressed include:

- identification of the land owner associated with each of the randomly allocated Monitoring Sites,
- the willingness of the land owner to participate in the monitoring program,
- identification of any future plans the land owner has for changing land use
- definition of the logistics of site access.

Recommendation: A Latin hypercube analysis (Minasny and McBratney, 2006) with soil mapping, terrain, climate and gamma radiometrics data will be used to identify candidate Monitoring Sites; that twice as many sites as required be selected and that an a priori process for identifying sites to be culled and for the selection of replacement sites from within the unallocated sites is developed as part of the site selection process.

2.4.3.2 Identifying the soil individual

A defined operational approach is needed for the process of establishing the Monitoring Site at the allocated geographic location. The approach will outline the process for identifying a

homogeneous area within the required Monitoring Site dimensions, criteria for adjusting the dimensions, design principles for complex sites and situations where a site should be abandoned. These processes could be informed by sampling strategies with rapid soil measurement techniques or manual field observations applying a range of discriminating characteristics relevant to the Monitoring Unit (e.g. depth to B horizon). The area investigated should be at least 4 times the intended area of the monitoring site. *Ad hoc* transects with an iterative approach to closing spacing within and between transects will probably be time effective.

If the site is too complex to be considered a single soil individual, it should be abandoned unless such heterogeneity is a characteristic of the intended Monitoring Unit (e.g. gilgai) and the periodicity of the complexity is sufficiently predictable to enable a practical site design.

2.4.3.3 Layout of the Monitoring Site

The strongest need in designing the layout of the Monitoring Site is to fit the sampling shape within the spatial extent of the targeted soil individual at the defined location. This may mean that the size, shape and orientation of the Monitoring Site are constrained by the soil spatial patterns that exist at the defined location. The site's origin should be placed with as much randomness as the soil individual's extent allows. It is critical to be able to relocate the corners to within 5 or 10 cm. A number of options are possible from differential GPS to measurements from land marks to buried objects (e.g. EMS II Locator Probe). Each has potential problems (e.g. satellite quality, rebuilding of fences and ripping of paddocks). At least two methods should be employed. From the site corners, internal stratification and/or grid layout can be constructed (reconstructed) by measurement and compass bearing.

2.4.3.4 Characterising the Site

The proposed minimum data set for initial characterisation of the site is that listed in McKenzie et al. (2002) Table 4. Further development of this will depend on adherence to state agency standards for land resource surveys and to the potential wider use of the sites. This is a key task for an operational guide to the national program. The characterisation would be performed from a pit excavated adjacent to the site. Necessary soil chemical and physical analyses to allow classification to Australian Soil Classification great group level should be undertaken. Site description should include land use and surface condition and a description of land use history to as comprehensive an extent as possible.

2.4.4 Exhaustion and replacement

This monitoring program has been designed to allow repeated sampling of Monitoring Sites into the foreseeable future on a 5 year cycle based on a static synchronous sampling approach (de Gruijter et al. 2006). There are obvious constraints to maintaining the full set of sites. For example, the land use component of each Monitoring Unit may not remain

representative of future farming systems. Given the primary objective of the monitoring program is to define the influence of land use on soil condition, repeated sampling of Monitoring Sites through time is a prerequisite of the program. If significant shifts in agricultural production systems occur, additional Monitoring Units will need to be added to the program as needed.

Some Monitoring Sites will need to be removed from a monitoring program and possibly replaced. This could occur for several reasons; a change in farming system[1], a change in owner cooperation, the site is 'too disturbed' by previous sampling, or to reduce any effect of conditioning which having sites within a monitoring scheme might have on the land management. The latter will be difficult to gauge, but it is critical that land management decisions over the area in which a Monitoring Site is located are not influenced by the fact that the area is included in a monitoring program. The monitoring is about observing the results of the management, not influencing or controlling it.

Monitoring Sites will remain in the Monitoring Unit until their removal due to attrition. Therefore, to allow for expected attrition, the number of Monitoring Sites initially included should be twice the expected minimum Clear protocols about removal of the site from the scheme must be developed as operational guidelines of the scheme so that *ad hoc* decisions do not complicate the interpretation. If site replacement is required, candidates should be selected in an unbiased manner from unallocated sites included in the initial random selection process.

Therefore, in the establishment of a Monitoring Site, any future plans of the land owner (e.g. to change to agro-forestry) should be canvassed before establishing the site. Monitoring Sites that stay in any of the land uses within the "farming system", stay within the original Monitoring Unit. If the land use at a Monitoring Site changes (e.g. from cereal cropping to irrigated perennial pasture) it would be in a different farming system and should be removed from the Monitoring Unit unless such change is ubiquitous. Such Monitoring Sites should not be relocated to an alternate Monitoring Unit since they were not part of the selection process for that Monitoring Unit. There may be other benefits in tracking the impacts of the land use change, however.

Soil carbon and soil pH monitoring require destructive sampling. The degree of impact on the site is related to the sample collection method (e.g. core or mini pit) and the size of the site. With a 20 x 20 cm footprint, 20 samples will occupy about 0.1% of the 25 x 25 m site.

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[1] If a change in farming system is representative of what is going on generally in the Monitoring Unit, e.g. adoption of zero/reduced tillage across the majority of WA sands, then the sites should not be dropped. In this case, maintaining the original management would provide data which would not be representative of the system evolution occurring through time.

With a 50 x 50 cm footprint, 20 samples will occupy less than 1% of the 25 x 25 m site. Consider also that the site may be grazed or ploughed a number of times in the 5 years that will elapse between samplings. This is a minimal impact and sampling design can remove the possibility of impact on subsequent sampling.

2.4.5 Timing of sample collection

Inter-seasonal and inter-annual environmental variation will influence the state of soil condition indicators. This is particularly the case where the farming system is dominated by annual plants. The magnitude of cyclical changes in some indicators can be greater than the long term change trends. Thus, a monitoring scheme needs to acknowledge this variation through design, analysis or interpretation.

2.4.5.1 Seasons

Annual variations reflecting summer/winter, wet/dry and physiological growth stage of plants affect soil carbon levels and, to a lesser extent, soil pH parameters in different but possibly predictable ways. Thus, the time of year and/or crop stage that sampling is conducted can be critical. Intensive monthly monitoring, and to a limited degree, quarterly (seasonal) sampling are solutions to derive an appropriate sampling across annual variations. Such intensity of measurement will not be feasible for the proposed monitoring program. The suggested approach will be to structure annual sampling to match times when the rate of change is low. This window is likely to be larger for some perennial systems and challenging for multi phase systems (e.g. crop/pasture/fallow). Sampling in annual cropping systems should be scheduled for non-cropping phases where possible. It will be important to note both the time of year and the growth stage of any plants present at the time of sampling so that future temporal sample collections can occur at the same time of year with plants at a similar stage of development.

Within a Monitoring Region, all sampling of Monitoring Units and their component Monitoring Sites should be conducted within a single year over as short a time frame as possible. It is considered more important to finish sample collections on within a Monitoring Region before moving on or initiating sample collection in additional Monitoring Regions. This may require the use of multiple sample collection crews within a single Monitoring Region. Randomisation of order that the Monitoring Sites are sampled through time within a Monitoring Region should also be implemented to reduce the impact of seasonal variations.

2.4.5.2 Data analysis issues

The primary foci of this monitoring program are as follows:

- The analysis of temporal changes in soil properties (organic carbon and pH for this program) at the individual Monitoring Site.

- The aggregation of all Monitoring Site data within Monitoring Units to detect average and differential behaviour between Monitoring Units within a Monitoring Region.

Differences between Monitoring Regions are of interest. However, since Monitoring Regions will be selected into the program based on evidence suggesting that the soils present have different sensitivities to soil carbon and pH change, an emphasis will not be placed on differences between Monitoring Regions.

2.4.5.3 Return time for sample collection and interpretation issues

The duration between the temporal collection of samples needs to be shorter than the time over which comment is required. Variations in climate (e.g. amount and distribution of rainfall, temperature, occurrence of a frost, etc.) and management strategies (e.g. timing and amount of fertiliser applied, herbicide applications, crop variety selected, etc.) will enhance temporal variability (e.g. see Figure 19 for an indication of this effect). The implication of such variations is that for any given Monitoring Site, multiple measurements will be required to confirm temporal trends in the values of measured soil properties. For comment on a 20 year time frame, it is suggested that measurements be taken on a 4-5 year cycle. As the number of Monitoring Sites within a Monitoring Unit increases, small variations in the management imposed at individual Monitoring Sites will be averaged out; however, if a region is exposed to an abnormal climate event (e.g. a severe frost that limits plant growth and the amount of harvested material removed) all Monitoring Sites within the Monitoring Unit may be affected leading to acquisition of data that may not be reflective of long term trends. Multiple measurements through time are required to ensure the validity of temporal trends.

2.4.6 Sampling at a Monitoring Site

2.4.6.1 Surface organic matter samples

The organic matter residing on the soil surface will be collected using a 0.1 m^2 quadrat. All dead organic material to the organic-mineral boundary should be collected. The collection of this material will define the amount of residue carbon existing at a Monitoring Site and is an important component in monitoring soil carbon. This is described in more detail in the carbon analysis section.

2.4.6.2 Soil samples

The number of soil samples will be determined for each Monitoring Site based on an assessment of variability. Soil samples will be taken with either machine-driven cores or from excavated pits. All collected soil samples will be retained and analysed as separate samples.

Samples will be taken from randomly selected locations within the 25m x 25m Monitoring Site. A 2.5 m x 2.5 m grid will be defined and samples will be collected at the grid intersection points. This gives a total of 122 possible sample collection points within the 25m x 25 m area. If 10 samples are collected with each sampling campaign, this will allow the Monitoring Site to be visited at least 11 times (50 years) before it starts to approach the situation where all potential sampling locations have been utilised.

The soil surface (depth = 0 cm) is to be located at the depth where soil mineral grains are encountered. There is an array of situations where particular soil conditions (e.g. soil micro relief, existing plough patterns or the presence of vegetation) provide challenges to sampling. It is recommended that the operational manual for national soil monitoring should enumerate as many of these as possible (based on existing experience across the states) and suggest standard solutions.

2.4.6.3 Bulk density and volumetric change

Measurement of bulk density must accompany the sampling and analysis of soils for carbon and pH. This provides both a means for converting weighed quantities into volumes for effective comparison (carbon, water, porosity, lime requirement) and for managing the variations in bulk density over time which can mask or confuse real trends in soil parameters.

McKenzie et al. (2000a) outline methods relevant to different soils and sampling needs to measure soil bulk density. In addition, research is currently underway to develop rapid approaches to bulk density measurement using gamma emission.

With the bulk density known, sampling depths can be adjusted to estimate carbon contents to a soil mass equivalent to that sampled initially. Subsequent sample collections will need to extend beyond these depths to allow the adjustment (Figure 14 and Figure 15).

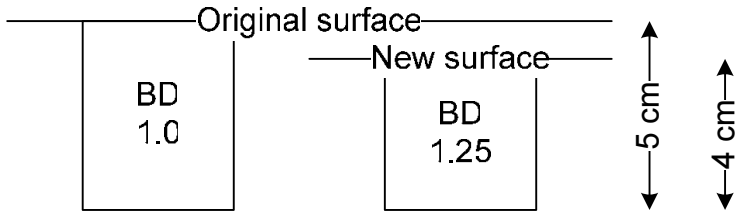


Figure 14: Change of sampling depth because of increase in BD.

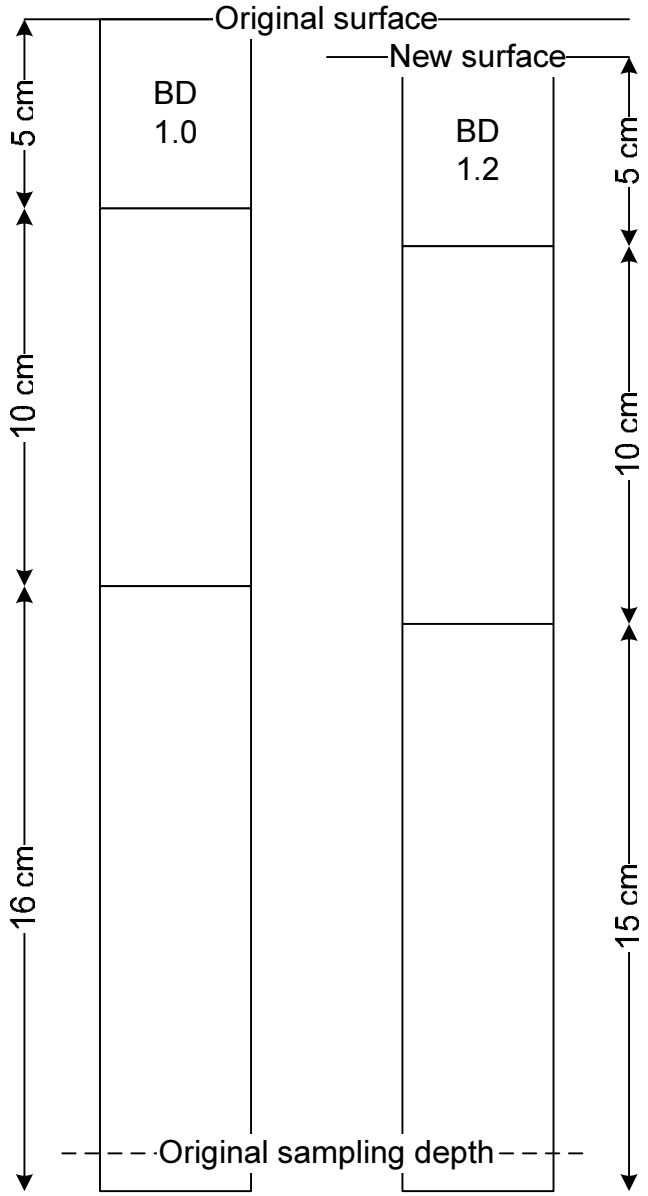


Figure 15: Adjustment of thickness of lower layer to compensate for increased BD at surface.

2.4.7 Sample preparation

A significant potential source of variability within the analysis process is sub sampling and sample preparation and close attention must be paid to this because of the accuracy required for monitoring.

The following sample preparation strategy meets the needs of the organic carbon and pH protocols (In addition, mixing and sub-sampling should also be in accordance with the Australian Standard “AS 4433.2-1997 Guide to the sampling of particulate materials - Preparation of samples”):

- Air dry samples to constant mass
- Screen on 2 mm sieve

- Recover coarse organic matter >2mm, weigh and set the organic material aside for processing.
- The remaining >2mm is progressively commuted through crushing (mortar and pestle or automated crushing device) to break up aggregates of soil primary particles. The >2mm material is not to be ground. The remaining >2mm gravel particles are dried and weighed.
- Weigh <2mm material.
- Thoroughly mix <2mm material by such as passing through a riffle splitter 5 times (returning all to the hopper on each pass).
- Riffle split to segregate sample for moisture content and sample for analysis (3 samples if from bulked sample).

Further discussion of soil samples prior to analysis is detailed in Appendix 2.

Recommendation: That detailed operational guidelines be developed as part of the implementation phase of the National Soil Condition Monitoring Program to describe in detail site establishment, characterisation and long term management; sampling protocols and processes for exhaustion and replacement.

2.4.8 Sample Archive

Sample archiving is essential to the long term value of the monitoring system and has potential value beyond the immediate aims of the project (e.g. Skjemstad and Spouncer (2003) used such samples in modelling organic carbon fluxes in a range of soils under a range of land uses). All bulked samples collected in the national monitoring project will be archived using the standards established for the Australian National Soil Archive. The samples will be stored in the Archive; where there is a similarly maintained state archive smaller sample volumes will be held in these archives for samples collected in that state.

Recommendation: That bulked samples selected during the monitoring program are stored in the Australian National Soil Archive

3 SOIL CARBON: CONCEPTS AND MEASUREMENTS IMPORTANT TO A SOIL MONITORING SCHEME

3.1 Soil organic carbon (SOC) and soil organic matter (SOM)

3.1.1 Definitions

Soil organic matter is a key component of any ecosystem and variation in its abundance and nature has profound effects on many of the processes that occur in the agricultural and native ecosystems (Spain et al., 1983). The term "soil organic matter" (SOM) has been used in different ways to define the organic constituents present in soil. SOM will be defined as per Baldock and Skjemstad (2000) as "*the total of all biologically derived organic matter residing within the soil matrix and directly on the soil surface including thermally altered materials*". As such, SOM consists of a heterogeneous mixture of organic materials originating from plant, microbial and animal residues existing along a decomposition continuum. Since SOM contents are difficult to measure directly, most methods determine soil organic carbon (SOC) content on a per unit mass of soil basis and multiply the resultant values by 1.72 to 2.0 to obtain SOM contents. This factor is based on the assumption that the C content of SOM ranges from 50 to 58% (Baldock and Nelson, 1999). The non-carbon component of SOM is composed of H, O, N, P and S. An average C/N/P/S ratio of 107:7.7:1:1 was presented by Stevenson (1986) for SOM; however, this ratio will vary with the nature of the particular molecular forms of SOM present.

Organic carbon is amongst the most commonly analysed soil constituents. Initially, SOC analyses were performed to investigate processes of soil development and to aid assessments of soil productivity (Gregorich et al., 1997). More recently, defining SOC contents has become important because of the potential for soils to act as a carbon sink and thereby reduce atmospheric CO_2 concentrations. SOC represents a significant reservoir of carbon within the global carbon cycle and has been estimated to account for about 1500 Pg C to a depth of 1 m and for about 2300 Pg C to a depth of 3 m (Houghton, 2005). Comparative estimates of organic carbon contained in atmospheric CO_2 (780 Pg) and living biomass (550 Pg) (Houghton, 2005) indicate indeed that variations in the size of the SOC pool on the order of 5% (75 Pg C) could significantly alter atmospheric CO_2 concentrations.

3.1.2 Distribution of SOC in Australian soils and soil profiles

The content of organic carbon in Australian soils varies significantly. Spain et al. (1983) summarised Australian SOC contents and obtained median values ranging from <3g C/kg soil for desert loams to 81 g C/kg for alpine humus soils (Figure 16). From Figure 16 it is also evident that within a given soil type considerable variation in SOC content can exist. Such variations in SOC content result from differences in climate, soil mineral composition,

soil biota, topography and management. The frequency of catastrophic natural or human-induced events (e.g. fire, floods or water/wind erosion) can also contribute to generating variability in SOC content (Baldock and Skjemstad, 1999).

In addition to spatial variability, SOC content also changes with soil depth and the magnitude of such changes differs between soil types (Figure 17). However, SOC content is greatest at the soil surface and tends to then decrease exponentially with increasing soil depth. This, however, does not necessarily mean that most of the SOC will be present in the surface layers of a soil since considerable amounts of SOC can be found at depth in some soil types (e.g. vertisol, ferrosol, and peats). As a rule of thumb, 30-50% of the SOC can be found in the 0-10 cm layer of a soil, 20-30% in the 10-30 cm layer and 10-30% in the 30-100 cm layer.

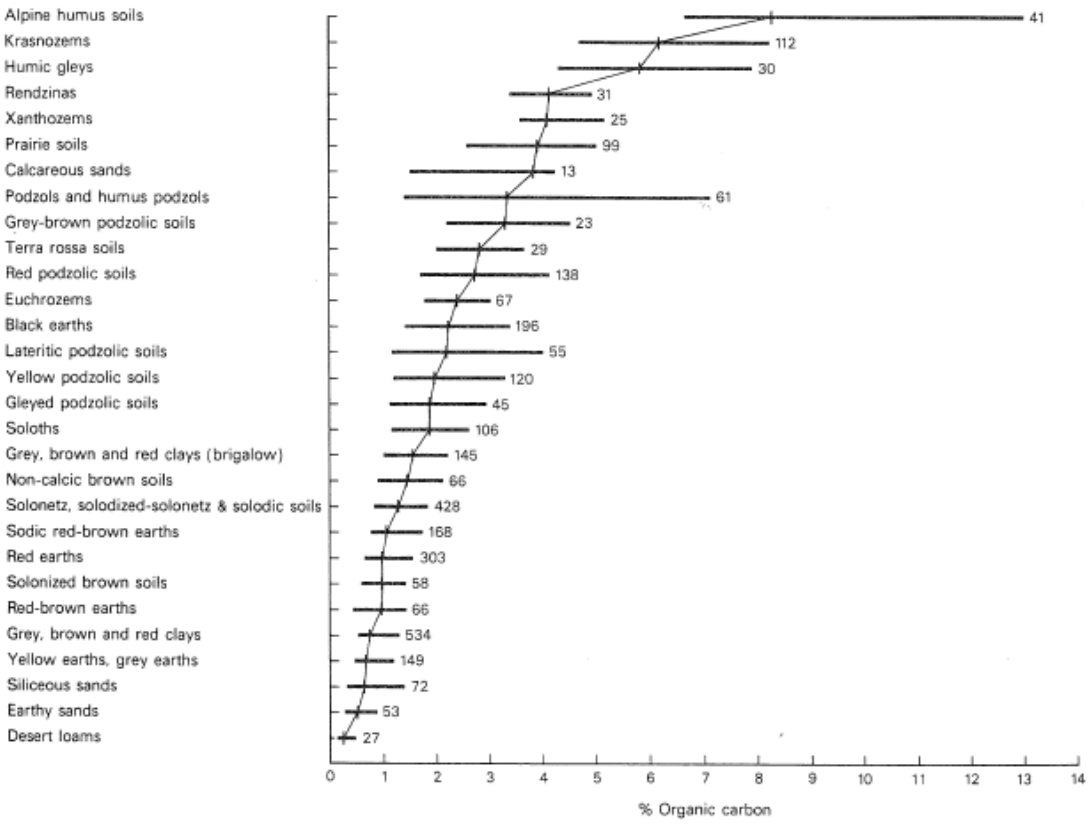


Figure 16: Organic carbon concentrations in Australian soils. Great Soil Group medians, interquartile ranges and the number of records available (from Spain et al., 1983).

The amount of SOC present in a soil is defined by the balance between rates of carbon input in the form of crop residues or organic amendments, and carbon loss as carbon dioxide emitted during decomposition. Losses by erosion or leaching may also be significant in some cases.

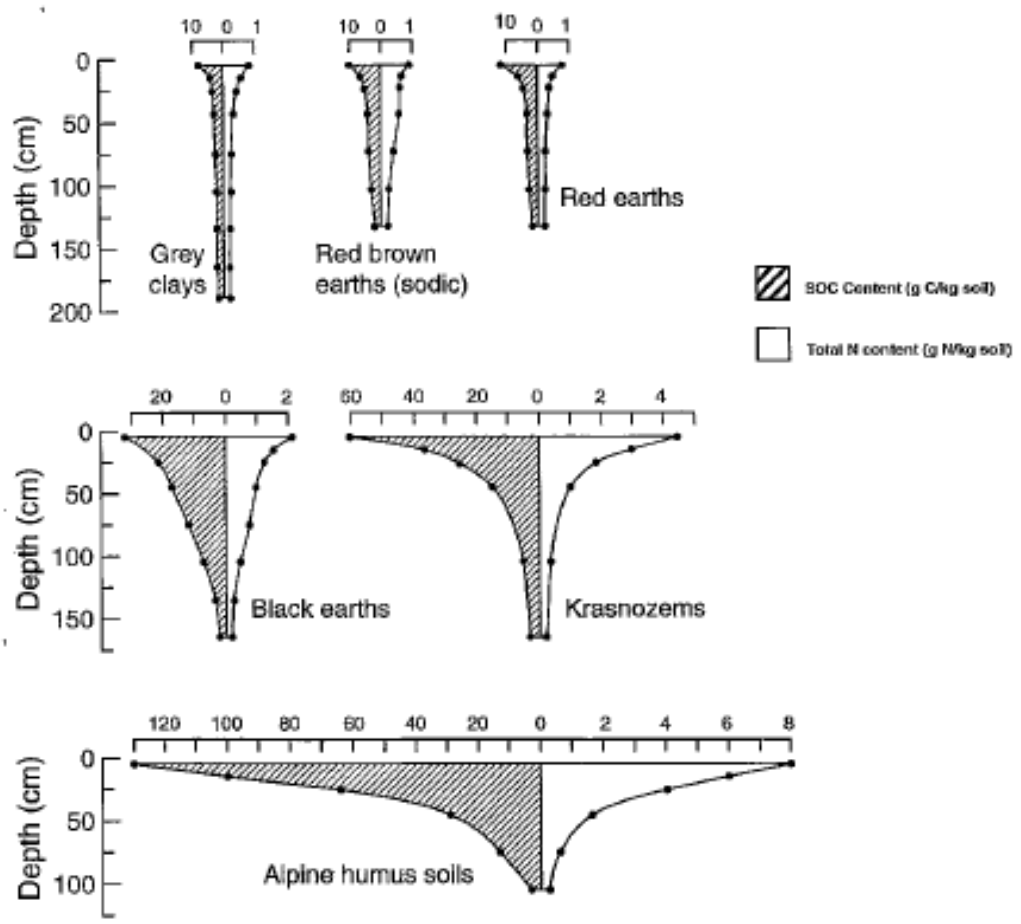


Figure 17: Distribution of organic carbon and nitrogen with depth in selected Australian soils based on a mean of ten profiles (Spain et al., 1983). Note that these C contents are not maximal C holding capacities for these soils but just indicative of the C present in different soil types.

In Figure 18 a bucket is used as an analogy to represent the amount of carbon a soil could potentially hold. The size of the bucket will vary with factors such as soil mineralogy, clay content, depth, and bulk density and is not influenced by management. The bucket will be smaller for a sand than a clay soil due to the increased ability of clay rich soils to protect organic materials against decomposition (Baldock and Skjemstad 2000). Inputs are controlled by the type and amount of plant residue added to the soil. Any practice that enhances productivity and the return of plant residues (shoots or roots) to the soil opens the input tap. For example, appropriate use of fertilisers to maximise productivity will also maximise returns of organic residues to the soil. However, an upper limit of input exists in Australian dryland agriculture because of the limitation that the availability of water places on potential plant productivity. Losses of carbon from soil result from decomposition and conversion of carbon in plant residues and other organic materials present into carbon dioxide. Processes that accelerate decomposition open the losses tap further. The content

of organic carbon in a soil therefore results from the balance between carbon inputs and losses over many years.

Figure 18: Inputs and losses define soil organic carbon content.

SOC contents do not increase indefinitely but rather tend towards equilibrium values dictated by the soil forming factors like climate, biota (vegetation and soil organisms), parent material, and topography. At a given location under constant climate and vegetation, SOC content will move towards an equilibrium value for the system being considered. Natural variations in climate and vegetation or alterations to management will induce temporal variations on intra- and/or inter-annual time scales. Seasonal variations in SOC content measured under an irrigated kikuyu pasture are demonstrated in Figure 19. The data presented in Figure 19 indicate that the most accurate assessment of inter-annual changes in soil carbon is obtained by taking measurements at the same time in each year or perhaps even better at the same physiological stage of crop/pasture growth. If samples are collected at different times of the year, results ranging from a negative to positive change could be obtained. It needs to be recognised that the intra-annual variation depicted in Figure 19 is a more extreme example of the potential variation and arises from the fact that both irrigation and nitrogen fertiliser have been applied to a kikuyu pasture sown into a soil that previously supported a wheat/fallow rotation. As a result rates of pasture production and inputs of carbon to the soil are much greater than would typically be experienced under dryland conditions.

Soil management can induce rapid and large changes to SOC content. For example, the conversion of native ecosystems to agriculture often, but not always, results in a net loss of SOC (Mann, 1986; Davidson and Ackermann, 1993; Paustian et al., 1997). When measurements of SOC are conducted on perturbed systems it must be acknowledged that they may still be in the process of attaining a new equilibrium SOC content. When combined with the potential impacts that variations in climatic conditions can have, it can be difficult to detect the true direction of SOC change induced by alterations to land-use at time scales <10 years. More than 50 years may be required to re-establish equilibrium conditions representative of a new land use (Baldock and Skjemstad, 1999).

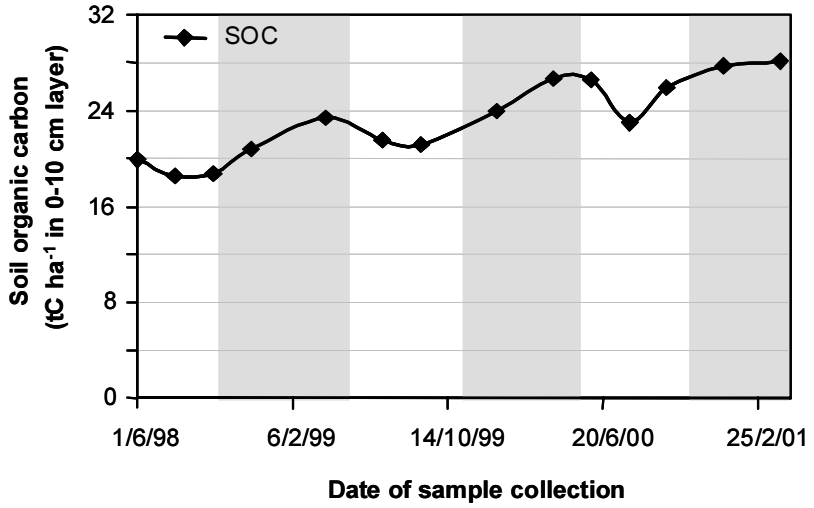


Figure 19: Changes in soil organic carbon over 32 months under an irrigated (grey periods) kikuyu grass pasture.

Variations in SOC content represent the integrated result of the effect of a number of factors and any interaction that occurs between them. The relative importance of these factors has been discussed elsewhere (Baldock and Skjemstad, 1999) and was ranked as follows: management > climate > biota (vegetation and soil organisms) > topography = soil mineral composition.

3.1.3 Composition of SOM/SOC

SOC is composed of a heterogeneous mixture of organic materials that vary in physical size, chemical composition, degree of association with soil minerals, and extent of decomposition. As a result, different components of the SOC will accumulate or be lost at different rates. Experiments using radiocarbon (Anderson and Paul, 1984) and isotopic labelling (e.g. Ladd et al., 1981) have demonstrated the existence of pools of SOC with different turnover rates.

A number of fractionation schemes have been developed to isolate and/or quantify SOC components cycling at different rates. These schemes take advantage of differences in chemical or physical properties of the organic carbon containing materials in soil. Chemical fractionation methods have used solubility in different reagents like water, acids, and bases (Schnitzer, 1978), susceptibility to oxidation (Wolbach and Anders, 1989; Blair et al., 1995), macromolecular techniques for estimation of proteins, polysaccharides, and lipids (Lowe, 1978; Benzing-Purdie and Nikiforuk, 1989; Beavis and Mott, 1996 and 1999; Wiesenberg et al., 2004), and `virtual fractionation` using solid-state ^{13}C NMR (Smernick et al., 2000). Physical fractionation techniques have used differences in particle size or density to isolate particular fractions (Baldock et al., 1992; Cambardella and Elliot, 1992; Golchin et al., 1994). Furthermore, combinations of both chemical and physical methods have been used and

these are often advocated to gain a better understanding of SOC dynamics (Turchenek and Oades, 1979). Fractionation methods based on biological properties have also been developed and used to assess the more labile components of SOC (e.g., soil microbial biomass carbon (Jenkinson, 1976; Brookes, 1995) and the mineralisable C fraction (Campbell et al., 1991; Franzluebbers et al., 1994)).

3.1.3.1 Chemical fractionation of SOC

The earliest attempts to fractionate SOC were based on an alkaline extraction followed by acidic precipitation (Muller, 1887), however, given the mode of extraction and isolation of humic materials from soil and the potential for a variety of inter- and intra-molecular interactions to occur during the process, the probability of mixing older and younger organic species during the extraction is high. Hence, a complete segregation on an age basis can not be expected (Baldock, 2007). Other chemical fractionation methods are based on various extraction or degradative methods considered to be “selective” for a given molecular component. For example, hydrolysis with 6 M HCl or methanesulfonic acid has been used to quantify the proportion of SOC associated with proteins, amino acids and amino sugars (Appuhn et al., 2004; Friedel and Scheller, 2002; Martens and Loeffelmann, 2003). Other methods are suggested for the specific detection of carbohydrate structure (Martens and Loeffelmann, 2002; Rovira and Vallejo, 2000), intact lignin molecules (Tuomela et al., 2000), monomeric species from lignin (Chefetz et al., 2002; Leifeld and Kögel-Knabner, 2005), lipids and lipid like carbon in soils (Poulenard et al., 2004; Rumpel et al., 2004). The main disadvantage of all these chemical fractionation methods is that absolute quantities should be considered as approximate due to the potential for incomplete extraction and/or non-selective action. Furthermore, there is not necessarily a direct link between the chemical reactivity of a certain SOC fraction and its biological reactivity. As an example, consider a polysaccharide material sitting on the edge of a pore wall versus the same material buried within a matrix of clay particles.

Several attempts have also been made to use chemical fractionation procedures in order to allocate SOC to labile and recalcitrant fractions without defining molecular composition. Permanganate oxidation and HCl hydrolysis are two such methods. Quantifying the proportion of SOC oxidised in permanganate solutions of increasing concentrations has been used to define fractions of SOC with different labilities (Blair et al., 1995). However, the existence of strong correlations between the amounts of SOC oxidised at each permanganate concentration and between permanganate-oxidisable carbon and total SOC (Lefroy et al., 1993) question the selectivity of this approach towards identifying differentially labile SOC components (Blair et al., 1995; Mendham et al., 2002). Furthermore, Mendham et al. (2002) showed that the permanganate-oxidisable SOC had little relation to the labile pool of SOC respired over a 96-day incubation period, again questioning the existence of a link between chemical and biological reactivities. The absence of a strong linkage between

chemical and biological reactivities and the lack of a clear definition of the chemical nature of the SOC components attacked by each permanganate solution, can limit the ability of chemical fractionation techniques to be used as proxies for biologically meaningful fractions of SOC (Baldock, 2007).

3.1.3.2 Physical fractionation of SOC

Recent work has suggested that physically isolated fractions may be more useful than the more classical chemical approaches in defining biologically meaningful fractions of SOC (Cambardella, 1998; Sohi et al., 2001; Skjemstad et al., 2004). Methods that fractionate SOC on the basis of particle size and density can be used to isolate components that have different turnover times (Christensen 1996a, 2001). This occurs because, with increasing extent of decomposition of plant residues, particle size is reduced and the chance for interaction with soil minerals increases (Baldock, 2007). When conducting physical fractionation procedures, complete dispersion is essential to ensure quantitative separation of SOC into individual particles with different sizes or densities. To minimise chemical alteration, inclusion of strong acid, alkali or chemical oxidant pre-treatments is avoided, and a combination of sodium saturation and physical dispersion methods is used (Skjemstad et al., 2004).

Typically, SOC is fractionated into four pools: dissolved organic carbon (DOC), particulate organic carbon (POC), humus (HUM) and recalcitrant organic carbon (ROC). DOC constitutes the <0.45 µm diameter organic materials in solution. POC includes any organic fragments with a recognizable plant tissue/cellular structure. HUM is composed of the well decomposed materials typically associated with mineral particles. HUM is usually the largest SOC pool, except in pasture systems where HUM and POC make similar contributions to SOC. In Australian soils, ROC is mainly comprised of highly aromatic charcoal.

Several studies have investigated, with various levels of success, the rate of turnover of SOC found in these different particles size classes based on particle size fractionation (Cambardella and Elliot, 1992; Amelung et al., 1999; Kahle et al., 2003; Schöning et al., 2005), density fractionation (Golchin et al., 1994; Trumbore and Zheng, 1996; Baisden et al., 2002; John et al., 2005; Rethemeyer et al., 2005; Swanston et al., 2005) or a combination of the two (Turchenek and Oades, 1979). Irrespective of the method of physical fractionation of SOC, it is essential that methodologically induced redistribution of SOC amongst the fractions is minimised. It is clear that, although general trends of increasing decomposition and age are associated with decreasing particle size and increasing density, significant inconsistencies can occur. For example, young chemically labile organic carbon can be protected against decomposition through interactions with the soil minerals (physical protection mechanisms), and relatively inert and potentially old charcoal may exist in the form of large particles (Baldock, 2007).

3.1.3.3 Biological fractionation of SOC

A biological fraction of SOC is soil microbial biomass (SMB), often defined as the total mass of microorganisms present in a soil (Brookes, 1995). The importance of the SMB to soil functioning is well recognized (Dalal, 1998, Stockdale and Brookes, 2006) as it regulates all SOM transformations and is considered to be an important component of the active SOC fraction (Smith and Paul, 1990). SMB is routinely measured and expressed in terms of the amount of carbon it contains (SMBC). Various techniques to determine the SMBC exist, but the only direct methods include the chloroform fumigation followed by extraction or incubation (Jenkinson, 1976; Vance et al., 1987a,b). An indirect way of measuring SMB is a substrate induced respiration (SIR) method (Anderson and Domsch, 1978).

SMBC has been found to represent between 0.3% and 7% of SOC (Wardle, 1992) with higher amounts of SMBC in agricultural soils compared to forest soils. Due to its short turnover times of 1-5 years (Jenkinson and Rayner, 1977; Jenkinson and Ladd, 1981; Jenkinson and Parry, 1989; Ladd et al., 1981; Wardle, 1992), SMBC is considered to be an important component of the active or labile pool of SOC and it has been suggested that SMBC provides a sensitive indicator of potential changes in SOC (Powlson and Jenkinson, 1976).

Another way of fractionating SOC biologically is to quantify the product of a biological process. Quantification of the amount of SOC or its associated nutrients that can be mineralised (converted from an organic to inorganic form) over a defined time interval has been used to assess biological availability (e.g. Campbell et al., 1991; Franzluebbers et al., 1994). Mineralisation of C and nutrients results from a complex set of biochemical processes conducted by a wide range of organisms and provides a measure of soil functional capacity. Organic C mineralisation is often called ‘soil respiration’, ‘basal respiration’ or ‘microbial respiration’. The amount or rate of C mineralisation measured over periods from a few days to a few weeks is commonly used as an indicator of general biological activity; whereas, the total amount of CO_2-C released on a longer time frame (>3 months) provides information about the fraction of SOC that is readily available to decomposer organisms. Mineralised C can be expressed either per unit mass of soil (CO_2-C/g soil) or as a proportion of the original SOC present (CO_2-C/g C present) basis. When expressed per unit mass of soil, information regarding the size of the mineralisable C fraction is obtained; whereas, when expressed per g of SOC present, an indication of the degradability of SOC is obtained.

Mineralisable soil organic nitrogen (SON) can provide a measure of the contribution that decomposition processes can make to soil nutrient supply. Mineralisable SON is composed of various organic substrates including microbial biomass, residues of recent crops (mainly POM) and humus. The mineralisable SON can be measured as potentially mineralisable N

using an aerobic incubation under optimum moisture and temperature conditions (Franzluebbers et al., 1994; Chan et al., 2002) or under field conditions (Dalal et al., 2005) using the method developed by Raison et al. (1987). Attempts to correlate mineralisable SON with measures of total SON or SOC have not been very successful. It is suspected that one of the major reasons for this lack of success is related to differences in the allocation of SON and SOC to each type of organic matter and the associated variability in decomposability and C/N ratio. Defining the allocation of SON to the various soil organic fractions should improve our capability to predict the mineralisable N in soils.

3.1.3.4 Consistency between SOC fractionation methods and pools of SOC in simulation models

Often SOC turnover simulation models [e.g. Rothamsted (Jenkinson et al., 1987), Century (Parton et al., 1987) and APSIM (McCown et al., 1996)] are based on SOC pools turning over at varying rates through the microbial biomass. In all these models, however, the SOC pools are conceptual and not measured directly. The construct of these models is similar and includes SOC with a rapid turnover (annual), moderate turnover (decadal), and slow turnover (millennial) as well as an inert component (Skjemstad et al., 2004). It has been recognized that developing a capability to replace these conceptual pools of SOC with measurable pools would offer several advantages: (1) internal verification of appropriate allocations of SOC to pools, (2) greater mechanistic understanding of the implication of management and environment on the components of SOC most affected, and (3) improved confidence in simulation outcomes. A suitable fractionation procedure should be capable of isolating and quantifying the allocation of SOC to pools that differ significantly in their biological availability (Baldock, 2007).

Several methods have been proposed to link measurable pools to the conceptual pools (Christensen, 1996b; Sohi et al., 2001; Poirier et al., 2005; Sohi et al., 2005) by linking biological reactivity to density fractions. However, the biological availability of the carbon in each fraction of these studies was never measured. Furthermore, no attempt was made to substitute the measurable pools of C into a working carbon simulation model to demonstrate the utility of this proposal. The variable contribution of charcoal C to the fractions studied, as indicated by the cross polarisation ^{13}C NMR signal intensity in the aryl-C chemical shift region limits the suitability of such a density based fractionation method (Baldock, 2007). This is particularly true for Australian soils, where charcoal C can account for 0-60% of the SOC and no predictive relationship has been found to exist between the total SOC and charcoal C (Skjemstad et al., 1996, 1998, 1999a, 1999b, 2002). A high recalcitrance of charcoal C to biological mineralisation was demonstrated (Baldock and Smernik, 2002), although priming with glucose was shown to enhance mineralisation of a portion of charcoal C (Hamer et al., 2004; Marschner et al., 2008). Charcoal C has also been found to have a mean residence time in the order of 5000 to 10000 years (Skjemstad et al., 1998; Swift, 2001, Krull et al.,

2003, Krull et al., 2006). Therefore, it is logical to link the charcoal C with the “inert” pool of carbon in the SOC simulation models.

Skjemstad et al. (1996) proposed a three-component fractionation scheme to identify measurable SOC fractions that could potentially be substituted into a computer simulation model (Figure 20). Soil is initially sieved to <2mm. All carbon associated with the >2 mm soil fraction is referred to as buried plant residue (BPR) carbon. The fractions isolated from the <2mm fraction of soil were: POC (particulate organic carbon >53µm), HUM (humus carbon <53 µm particles minus resistant organic carbon) and ROC (resistant organic carbon <53 µm particles from which non-resistant C was removed using a combination photo-oxidation and ^{13}C NMR analyses). Subsequently, Skjemstad et al. (2004) showed that the pool structure of the RothC model could be approximated by using this soil fractionation scheme. They demonstrated that the POC, HUM, and ROC fractions could be used to replace the resistant plant material (RPM), humus (HUM) and inert organic matter (IOM) pools of the RothC model, respectively. This was an important step forward in simulating SOC dynamics and demonstrates the potential for `modelling the measurable` (Christensen, 1996b; Magid et al., 1996; Baldock, 2007).

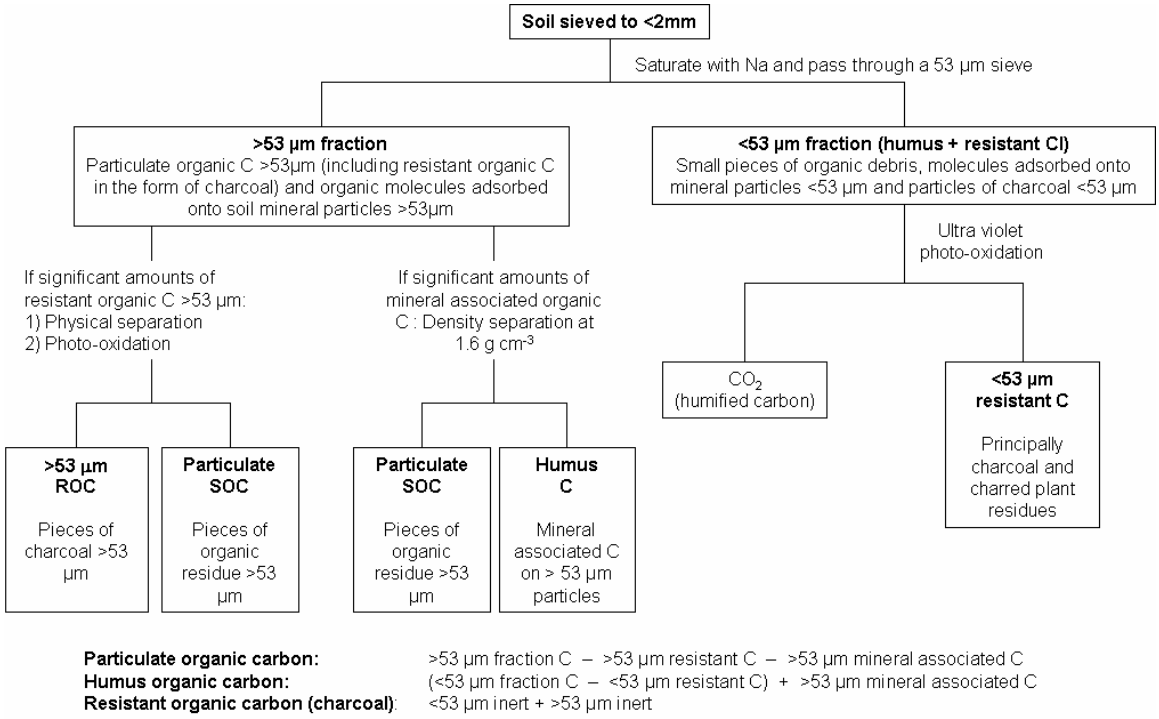


Figure 20: Methodology used to isolate measurable SOC fractions that define the allocation of carbon to particulate organic carbon, humus carbon and resistant (charcoal) organic carbon (modified from from Baldock, 2007 and Skjemstad et al., 1996).

It must be noted that the soil microbial biomass (BIOf and BIOs in the RothC model) and decomposable plant materials (DPM in the RothC model) are absent from the fractionation

scheme (Figure 20) of Skjemstad et al. (1996). The mains reason for this are the difficulty in quantitatively separating the microbial biomass from the various fractions and the fact that the contributions made by these fractions to the total SOC are small compared to the other fractions.

Recently, some modifications/additions have been made to the fractionation scheme of Skjemstad et al. (1996) to cover all organic matter on and in the soil. Surface plant residues (SPR) and buried plant residues (BPR) have been included. SPR accounts for plant stubble located on the soil surface and is measured as a mass of stubble per unit area. BPR accounts for the >2mm pieces of plant residues residing within the soil matrix and is measured as BPR carbon per unit mass of soil. These two additional fractions have been included for carbon accounting purposes and not for simulation modelling because all calibrations completed for the model were carried out on soil sieved to <2mm. Furthermore, the term inert organic matter (IOM) was replaced by resistant organic carbon (ROC) as it was indicated that charcoal has a mean residence time in the order of 5000 to 10000 years (Skjemstad et al., 1998; Swift, 2001, Krull et al., 2003, Krull et al., 2006), and is therefore not truly inert.

3.1.4 Functions of SOC in soils: why is SOC an important soil component

It is now recognized that SOC plays an important role in a variety of functions in soils. The functions can be broadly classified into three types: biological (provision of substrate and nutrients for microbes), chemical (buffering and pH changes) and physical (stabilisation of soil structure) properties (Figure 21). These functions contribute significantly to defining the potential productivity of soils and are important to the maintenance of soil health and resilience. Strong interactions (represented by the grey arrows) often exist between these different functions. For example, the biological function of providing energy that drives microbial activity also results in improved structural stability and creates organic materials that can contribute to cation exchange and pH buffering. Each fraction of SOC will have a different contribution to the identified functions. Figure 22 illustrates this selective importance of SOC fractions in performing specific functions.

3.1.4.1 Biological functions

The most fundamental function of the SOC is the provision of metabolic energy which drives soil biological processes and the direct and indirect effects this has on other soil properties and functions. As a result of the decomposition of SOC, macronutrients (N, P, and S) associated with the carbon will be mineralised into inorganic forms. These inorganic forms can be either immobilised by soil organisms or taken up by plants (Baldock and Nelson, 1999). Whereas the POC fraction plays the biggest role in the provision of energy for the

biological processes, it is the humus carbon fraction that contains the most nutrients (Figure 22).

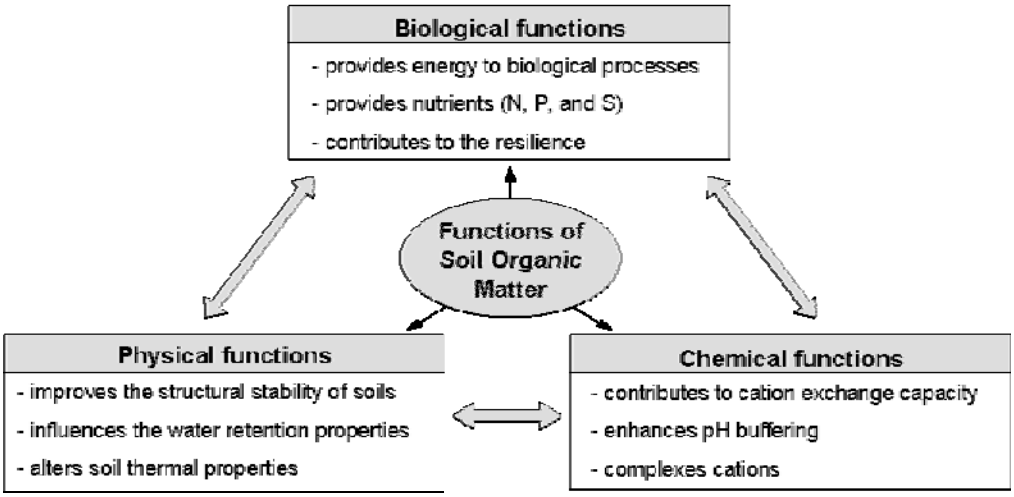


Figure 21: Functions performed by organic matter present in soils (adapted from Baldock and Skjemstad, 1999). Note that interactions occur between the different soil functions.

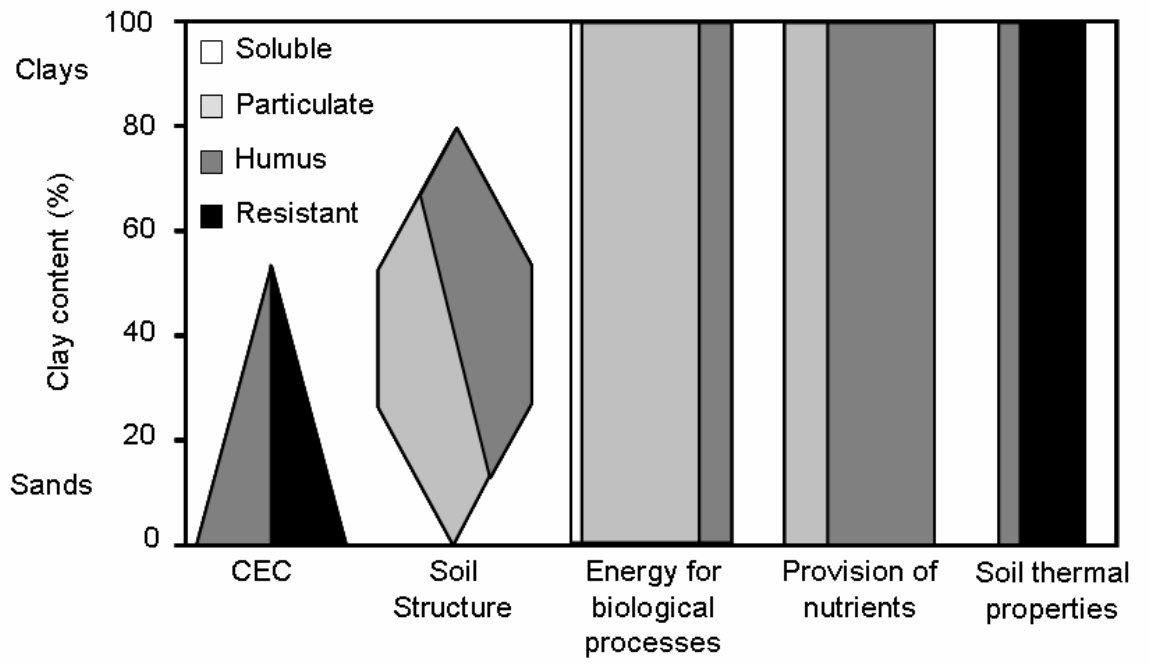


Figure 22: The optimal expression of each SOM function requires different proportions of soil organic carbon pools (soluble, particulate, humus and recalcitrant). The degree to which SOM can influence a particular soil property is given by the width of the various shapes and is expected to vary as a function of clay content (Krull et al. 2005).

3.1.4.2 Chemical functions

SOC and its associated elements can contribute about 25-90% of the cation exchange capacity (CEC) of the surface layer of mineral soils (Stevenson, 1994). The relative contribution of SOM to CEC is greatest for soils with a low clay content, where the soil clay fraction is dominated by minerals with a low charge density (e.g. kaolinite) or where soil minerals have an anion exchange capacity. The relative contribution will be lowest for soil with high clay contents of highly charged minerals (e.g. vermiculite, smectite). The presence of acidic chemical functional groups on soil organic molecules that can act as conjugate acid/base pairs make SOC an effective buffer over a wide range of soil pH. The presence of these various functional groups also provides the capacity for complexation reactions with inorganic cations (Baldock and Nelson, 1999). It is the humus carbon fraction that is responsible for most of the CEC derived from SOC (Figure 22); however, the formation of carboxylic structures on the surface of charcoal (resistant organic carbon) during weathering can make substantial contributions if present in high enough quantities.

3.1.4.3 Physical functions

It is well established that increased SOC content can not only lead to reduced bulk density and increased water holding capacity, but can also increase soil aggregate stability. Water retention can be influenced both directly and indirectly by increasing amounts of SOC. SOC can absorb and hold substantial quantities of water, up to twenty times its mass (Stevenson, 1994). SOC can also reduce evaporation and increase the infiltration of water. The indirect effect comes from the impact on soil aggregation and pore size distribution. Thus SOC can influence plant-available water holding capacity. The influence of SOC on soil structure is provided and maintained by both the humus carbon and POC fractions. The POC fraction plays a greater role in sandy soils as a means of physically binding particles together; however, in high clay content soils, both humus and POC are required to develop and maintain optimal structure as both chemical and physical binding plays a role.

Good soil conditions are generally associated with dark brown colours near the soil surface, which is associated with relatively high SOC contents, good soil aggregation and high nutrient contents (Peverill et al., 1999). The effect of the SOC on soil colour is important because of the thermal properties, which in turn contributes to soil warming and enhancement of biological processes (Baldock and Nelson, 1999). The main fraction contributing to soil colour is the inert carbon pool, which consist of highly aromatic structures such as charcoal.

3.1.5 Rates of change

3.1.5.1 Total SOC

Rates of change in SOC (typically less than 0.5 Mg C ha^{-1} $year^{-1}$) are quite small compared to the large amounts of SOC often present (as high as 100 Mg C ha^{-1}, or more, in the top 60

cm soil layer) (Ellert et al., 2008). Thus temporal trends in SOC can only be reliably measured over a period of years or even decades (Post et al., 2001). Since the distribution of SOC in space is inherently variable, temporal changes (e.g. attributable to management practices, environmental shifts, successional change) must be distinguished from spatial ones (e.g. attributable to landform, long-term geomorphic processes, non-uniform management) (Ellert et al., 2008).

3.1.5.2 Fractions

A measure of the change of the total SOC of a particular soil will provide little information on the changes in the relative size of the various carbon fractions. Figure 23, for example, shows the simulation output from the RothC model for a soil from the Waite Agricultural Research Institute (Skjemstad et al., 1998). Predictions of the changes in the size of the total SOC and its various fractions upon the conversion of a wheat/fallow rotation to permanent pasture are presented. The wheat-fallow rotation resulted in a more rapid decrease in the POC fractions and a more gradual decline in the HUM fraction. In this example, Skjemstad et al. (1998) considered the ROC as a constant. Furthermore, the size of the SMBC was small and therefore not included. When a continuous pasture was introduced, the POC fraction increased rapidly and the HUM pool began to increase but more slowly.

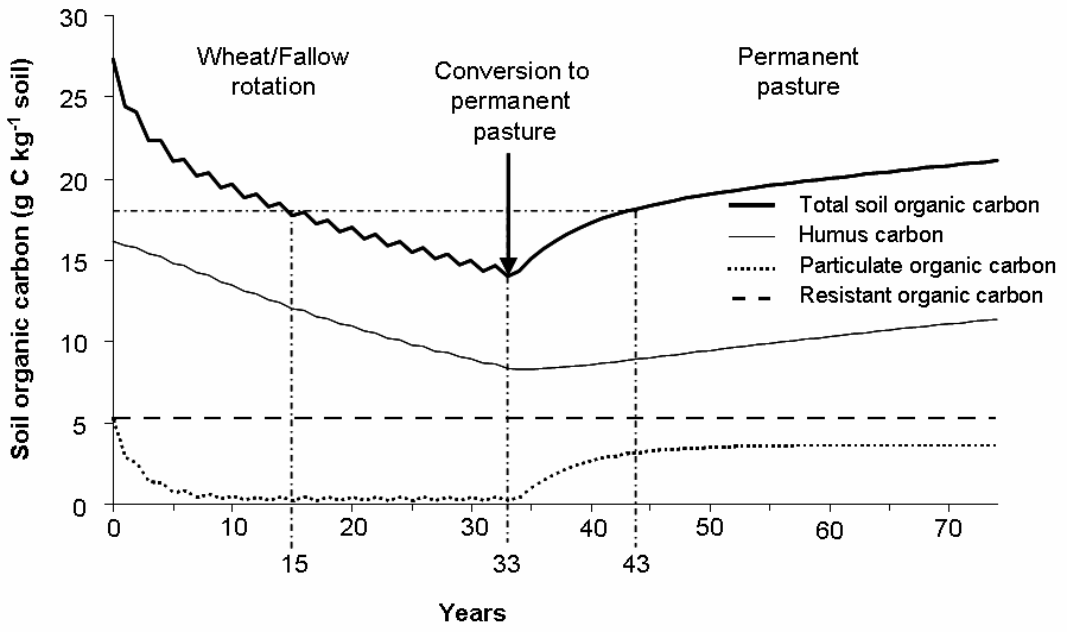


Figure 23: Predicted changes in the contents of total SOC, POC, humus C and resistant organic C (ROC) on conversion (after 33 years) from a wheat/fallow management system to a permanent pasture by using the Rothamsted soil carbon model (Skjemstad et al., 1998). At two different times (15 and 43 years) the soil organic carbon content attained a value of 18 g C/kg soil; however, the composition of the carbon, and thus the functioning of that carbon, was quite different at the two times (from Baldock and Skjemstad, 1999).

The total SOC content was the same after 15 and 43 years, but the distribution of the C in the fractions differed. Compared with the wheat/fallow soil at 18g C/kg soil, the pasture soil at 18 g C/kg soil had a greater content of POC and a lower content of HUM. As a result, many of the physical, chemical and biological properties of the soil at these separate times would be different. Figure 23 indicates that a total SOC measurement would be of less value than measurement of the allocation of SOC to its component fractions in estimating the impact of land use change on SOC content and functioning within a soil (Skjemstad et al., 1998).

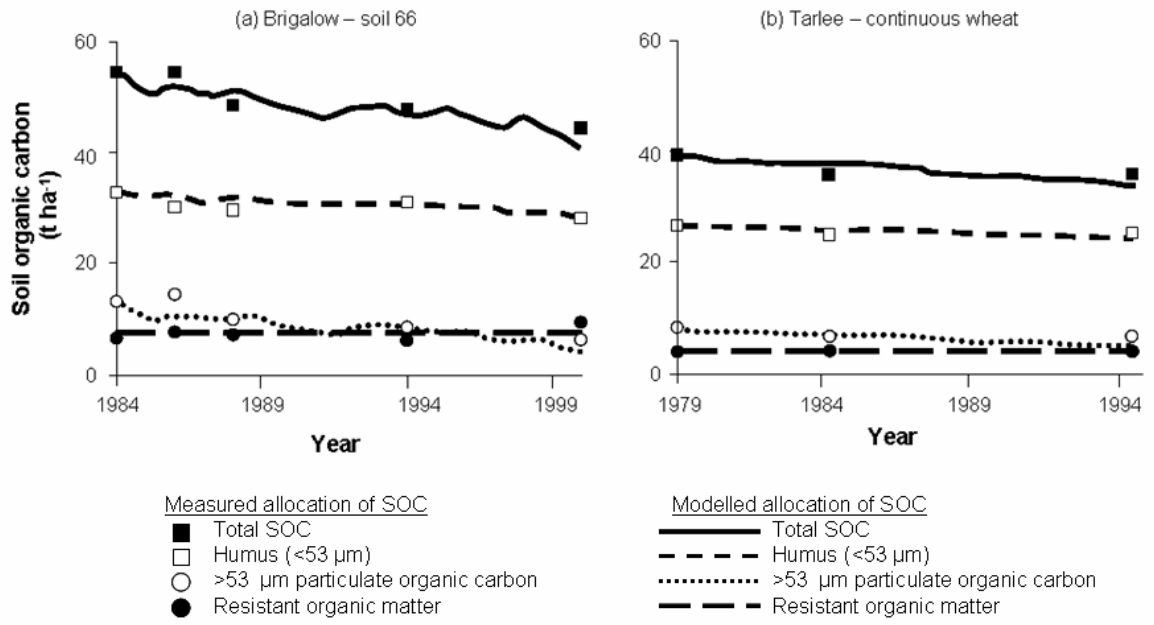


Figure 24: Comparison of measured and modelled (using RothC) total soil organic carbon and carbon allocations for (a) the Qld Brigalow cropping soil (continuous cropping) and (b) the continuous wheat treatment at Tarlee, SA. Points represent measured values and lines represent modelled data.

The Brigalow site (Figure 24a) was originally a forested catchment (native brigalow forest) and was cleared in 1982. Subsequently, wheat or occasionally sorghum was planted until 2000. A good agreement between measured and modelled total SOC and the different fractions was obtained. Total SOC decreased from 54 Mg C/ha to 45 Mg C/ha with changes noted in the first 2 years (average net C loss of 4.8 Mg C/ha/year) being greater than those noted during the last six years (average net C loss of 1.1 Mg C/ha/year). On examining the dynamics associated with the SOC fractions, the loss of total SOC over the measurement period was due predominantly to a decrease in the POC fraction. The decrease in the HUM fraction was less. Neither the measured nor the modelled amount of ROC changed over the timeframe of the measurements. The RothC DPM and BIO (microbial biomass) pools made only small contributions to the SOC present throughout the measurement period. .

The second example shown (Figure 24b) is from the Tarlee Rotation Trial located near Tarlee, South Australia. This site was previously farmed land and over the course of the measurement period was under continuous cropping (wheat) with stubble retention and no N additions. SOC changes were less pronounced at that site than at the Brigalow site, consistent with the fact that the Tarlee site had been cleared for agriculture for some time before the trial was imposed and was thus closer to its new (but lower) equilibrium state. Both the POC and the HUM fraction were responsible for the decrease in SOC noted over the measurement period.

An ability to allocate SOC to its component fractions and to model the dynamics of these fractions will increase our capability to accurately predict the influence of land use and management practices on soil carbon contents and the vulnerability of soil carbon to change into the future.

3.1.6 Early indicators of SOC change

Attempts have been made to identify SOC fractions that respond most rapidly to changes in land-use or management to derive early indicators of the potential impacts of management on total SOC. An ability to predict or detect SOC change at an early stage is important to allow land managers or policy makers to make informed decisions that can limit fertility decline, erosion or greenhouse gas emissions. A number of labile SOC fractions have been proposed for use as early indicators of SOC change including `light` fraction (Spycher et al., 1983; Janzen et al., 1992), particulate organic matter (Cambardella and Elliott, 1992), microbial biomass (Sparling, 1992), mineralisable C (Franzluebbers et al., 1994), and permanganate-oxidisable C (Blair et al., 1995). There seems to be little consensus as to which method or combination of methods is most suitable. Decisions as to which method to use are often based on available equipment or on answering particular questions about SOC dynamics (Skjemstad et al., 2006).

3.1.6.1 Light fraction (LF)

Light fraction (LF) organic carbon is the non-humified fraction of SOC composed mainly of plant residues in an intermediate state of decomposition and is known to decompose faster than the whole SOC (Sollins et al., 1984; Bonde et al., 1992). The separation of LF organic carbon from soils utilises the difference in particle density between organic and mineral particles. Most studies where light fractions have been isolated have used heavy liquid densities ranging from 1.5 – 2.0 Mg m^{-3}. However, as the density of the liquid used for separation increases, the potential of including less labile forms of carbon associated/bound with soil minerals increases. The use of density fractionation to isolate labile LF carbon can be complicated by the presence of charcoal. Due to its low density, charcoal carbon will be measured as LF carbon resulting in a potential overestimation of the amount of labile SOC and an underestimation of the amount of more stable SOC.

Responses of LF carbon to changes in cropping sequences (Angers et al., 1999) and rates of N fertiliser application (Janzen et al., 1992; Malhi et al., 2003) were shown to be greater than but correlated to that of SOC. This suggests that the LF provided a more sensitive parameter to measure variations in response to soil management. Janzen et al. (1992) also found a significant correlation between whole soil respiration rates and the amount of LF carbon present. However, due to its transient nature, LF carbon is more reflective of short-term effects (Janzen et al., 1992).

3.1.6.2 Particulate organic carbon (POC)

POC is dominantly associated with pieces of plant residues and thus has a reasonably restricted chemistry determined by the type of the vegetation present (Skjemstad et al., 2006). The more labile nature of POC, relative to total SOC, HUM and ROC, across a range of environments and land-uses was demonstrated by Skjemstad and Spouncer (2003). In all situations where significant positive or negative changes in SOC were measured, the POC fraction was the first to change and provided an indication of the direction of subsequent changes in SOC. Isolation of this fraction in an intact state is accomplished by passing a dispersed sample through a 53µm sieve and collecting the material remaining on the sieve. The collected POC materials can be analysed by elemental, spectroscopic and microscopic techniques to quantify their chemical and morphological compositions. The presence of charcoal C in a POC fraction can be accounted for using such analyses and when combined with incubation studies, the role of chemical composition on biological availability can be assessed directly.

3.1.6.3 Soil microbial biomass (SMB)

SMB has been suggested to provide a more sensitive indicator of changing soil conditions when compared to the total SOC (Powlson and Jenkinson, 1976). Sparling (1992) used SMB measurements to show changes in climatic, vegetation, cropping and management history in a range of topsoils in New Zealand and concluded that SMB provided a more sensitive index than SOC alone. However, under typical climatic and land use conditions in New Zealand, the SMB values were not readily transferrable between soils indicating that other factors were also influential. In a recent study on a set of different Australian agricultural soils, Wakelin et al. (2008) found that soil pH was the primary driver of both soil microbial diversity and function. Additionally, Mendham et al. (2002) were unable to show any difference in SMB due to changes in land use management in field sites in Western Australia. Another study of several Australian field trials indicated that very high numbers of field replicates (up to 93) were needed to significantly detect a 20% difference from control treatments (Broos et al., 2007). The high spatial and temporal variability in SMB commonly observed at a field scale will limit the value of the SMB as a sensitive and robust indicator of SOC changes. Broos et al. (2007) suggested that, although the SMB remains the `eye of the needle` through which all organic matter must pass as it is mineralised to its basic inorganic

components (Jenkinson, 1977), one should focus on the measurement of the rates at which components of SOC pass through the eye, rather than the measurement of the size of the eye itself.

3.1.6.4 Mineralisable SOC and nutrients

Changes in the amount of SOC and nutrients that can be mineralised within a given time period can also be used as an early indicator of potential SOC changes. Depending on the methodology employed, both the size of the mineralisable SOC fraction and the rate of SOC mineralisation (*k*) can be defined. For example, Riffaldi et al. (1996) studied the effect of soil properties on both the mineralisable SOC and the mineralisation rate (*k*) in different soils. They used a modified first order model to describe the SOC mineralisation in the soils and found that the size of the potentially mineralisable SOC fraction was positively correlated to cation and anion exchange capacity and that the mineralisation rate was higher in fine-textured soils with low C:N ratios. The rate of SOC mineralisation was also shown to be influenced by soil pH (De Laune et al., 1981), clay content (Sigmard and N`dayegamiye, 1993) or soil C and N content (Zak et al., 1993).

Quantification of the mineralisable fraction of SOC has been used as a sensitive indicator of changes in organic matter composition and quality (Bauhus et al., 1993; Hassink, 1994; Franzluebbers, 1999; Mendham et al., 2002, Hoyle et al., 2006). Miller et al. (2005) used the size of the mineralisable SOC and SON pools to define the effect of short-term drying and wetting pulses on long-term C and N fluxes. Cumulative CO_2-C release data, which was 2.2-3.7 times greater in rewet soils compared to soils maintained at equivalent mean soil moisture. Miller et al. (2005) found that SON mineralisation relied primarily on the shifting balance between utilisation of active and slow SOC fractions, whereas the increased SOC mineralisation under drying and wetting cycles appeared to involve a physical process that exposed organic matter to microbial attack. Cookson et al. (2006) found that mineralisable SOC and SON were greater in high fertility than in low fertility sites and generally greater at tillering and sowing than at harvest and flowering. Additionally, Cookson et al. (2006) found that the mineralisable fraction of SOC could be used to predict the magnitude of gross N fluxes consistent with the results of other studies (Bengtsson et al., 2003; Murphy et al., 2003).

3.1.6.5 Permanganate-oxidisable C

Permanganate-oxidisable C is an approach that has been used to measure land-use-induced changes to the labile organic pool in the cropping systems of New South Wales (Blair et al., 1995; Conteh et al., 1998) and Queensland (Blair et al., 1995; Moody et al., 1997; Bell et al., 1998). In Western Australia, however, Mendham et al. (2002) were only able to show an influence of land-use management on permanganate oxidisable C with the most dilute permanganate concentration (i.e. 33 mM MnO_4^-). This result supported the findings of

Moody et al. (1997) and Bell et al. (1998) that the 33 mM permanganate fraction was most sensitive to change. Mendham et al. (2002) were unable to detect any differences in C respired before and after permanganate treatment. Therefore Mendham et al. (2002) suggested that the permanganate oxidisable C had little relation to the most biologically available forms of SOC and concluded that the permanganate oxidisable C was a poor indicator of the labile C fraction for the soils used in their study.

In a comparison using both the POC and the permanganate oxidisable C methods as measurements of the `labile` organic carbon, Skjemstad et al. (2006) showed that the POC method was more sensitive by a factor of approximately two to rapid loss in SOC as a result of management or land-use change. Although there was some correlation between the two methods, the permanganate method was shown to be particularly sensitive to the presence of lignin or lignin-like compounds and insensitive to SOC gains under pasture. These findings suggested that the nature of the vegetation and its residues may have a strong influence on the measured amount of permanganate oxidisable carbon. The presence of charcoal was an issue with both techniques; however, in the POC method any contribution of charcoal could be assessed and corrected for. Such correction was not possible with the permanganate method because the method could not distinguish between charcoal and other biomolecules found in soil. Due do these limitations, Skjemstad at al. (2006) concluded that the permanganate method should not be applied indiscriminately across different soil types and management practices as a means of quantifying the labile fraction of SOC.

3.1.7 Summary

In addition to its importance in the global carbon cycle, SOC contributes positively to a range of biological, physical and chemical properties important to defining the potential productivity of a soil. SOC and its associated elements (H, O, N, P and S) in organic materials provide a positive impact on many properties important to defining soil productivity. Understanding the dynamics of SOC, both in its entirety and its various fractions, and the influence of environmental and soil properties is essential to adequately characterise the effects of management and land use on fluxes of carbon and soil productivity (Baldock, 2007).

SOC is composed of a heterogeneous mixture of organic materials and several chemical, physical and biological fractionation schemes have been applied to identify its various fractions. The physical fractionation scheme of Skjemstad et al. (1996) has proven to be compatible with the pool structure of the RothC model which is an important step forward in our capability of modelling the measurable. Furthermore, the fractions separated are shown to be biologically significant and strongly influential in their contributions to the different functions of SOC. Therefore, a better understanding of the composition of the SOC will provide a better understanding of the influence of land management on the C cycling in general. The POC fraction has been shown to be a sensitive indicator of future SOC

changes, offering an important predictive capability. Mineralisable SOC and nutrients integrate both a biologically significant fraction and a functional capability of a soil to decompose this fraction making it another early indicator of SOC and an excellent measure of soil functioning and the implications of SOC changes

3.2 SOC protocols for a soil monitoring scheme

3.2.1 Approach

Plant residue and soil samples are to be collected as discussed in Section 1 of this report. This section of the report provides a summary of the protocols to be followed to complete the various analytical procedures associated with the measurement of SOC and its component fractions. A detailed presentation with a step by step description of the methodology associated with each analytical procedure is given in Appendix 2

The organic carbon content of plant residues and soil will be measured on a dry weight basis (g C/kg sample). When combined with measured values for the mass of residues per unit land area or mass of soil per unit soil volume, the mass of carbon per unit land area (t C/ha) will be calculated and used to express the amount of carbon that resides at a given location.

The sampled soil will be fractionated according to the scheme presented in Figure 25 to measure the allocation of SOC to its component fractions. All allocations will be expressed in units of t C/ha for each depth layer (0-10, 10-20 and 20-30 cm). Additionally the sum of total organic carbon and carbon in each fraction across the three depth layers will be calculated. Values obtained for the 0-30 cm soil layer will be consistent with the requirements of FullCAM (the national soil carbon model being developed by the Department of Climate Change) and will facilitate ongoing testing and improvement of the modelling system, where required, across a wide range of sites representative of Australian soils.

Mineralisable C and N fractions will be determined using a standard laboratory incubation process. This analysis will provide an assessment of the functional capacity of the soil decomposer community to mineralise carbon and the proportion of the SOC that is mineralisable. By also measuring the mineralisation of N, an indication on the implications of land-use on the potential delivery of nutrients will be defined.

3.2.2 Recommended analytical methods

Two approaches to the analysis of carbon in soil samples will be used in the monitoring program. The actual measurement of SOC content and its allocation to fractions is expensive (in the order of thousands of dollars per sample for a complete analysis). Recent research

activities have indicated that mid infrared (MIR) spectroscopy when combined with a partial least squares (PLS) data analysis technique can provide cost-effective estimates of the amount of SOC and its allocation to fractions with a defined level of precision. Actual measurements of SOC and its allocation will be carried out at each monitoring site on a single composite sample. The data acquired will be used to optimise the MIR/PLS calibrations used to predict SOC and its allocation to fractions. All soil samples collected from a monitoring site (a minimum of 10) will be analysed by MIR/PLS to provide estimates of SOC and its allocation with defined levels of confidence. The individual MIR/PLS analyses will be used to provide estimates of the mean and variance of the SOC parameters measured at each monitoring site.

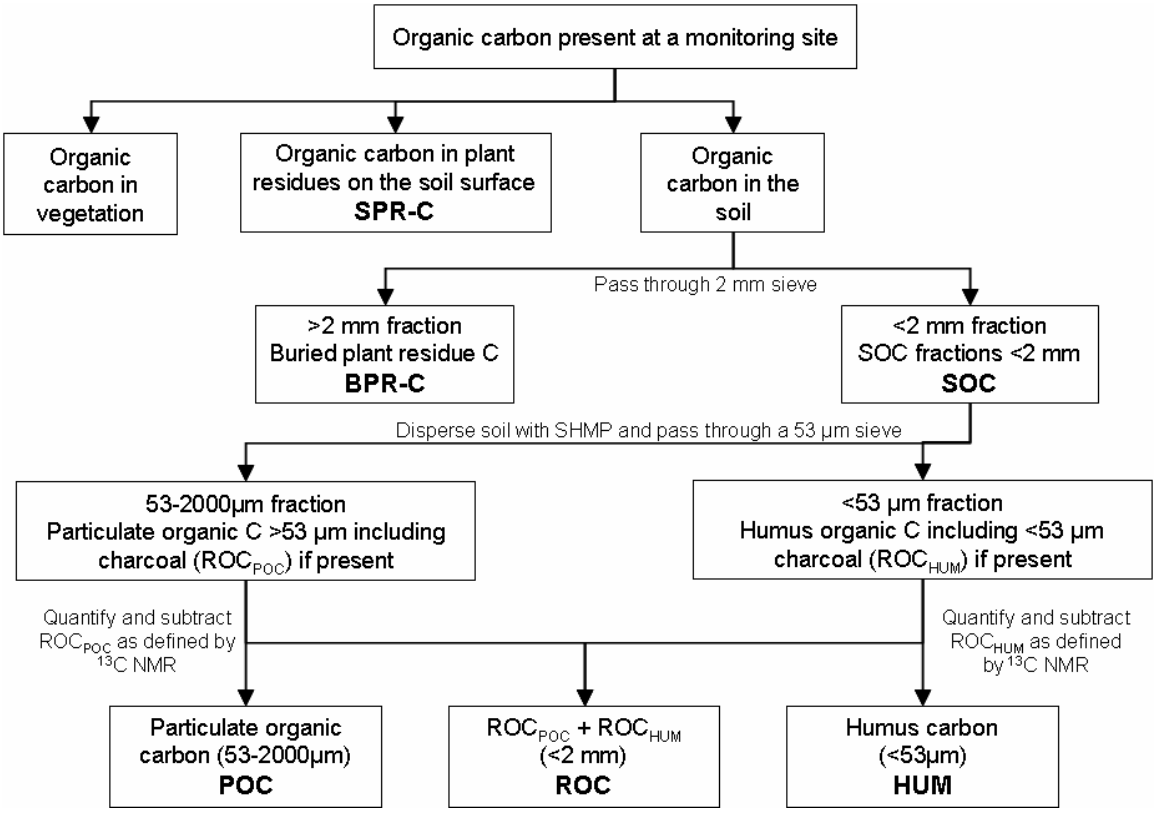


Figure 25: Proposed methodology to quantify soil carbon and its allocation to fractions at a monitoring site. SPR-C is the carbon associated with plant residues located on the soil surface quantitatively collected on an area basis. BPR-C is carbon associated with plant residues >2mm buried within the soil. POC is the organic carbon in the particles 2mm - 53µm excluding any ROC in this size fraction. HUM is the organic carbon in the particles <53µm excluding any ROC in this size fraction. ROC is the resistant organic carbon measured as charcoal carbon in the 2mm – 53µm and <53µm fractions. SHMP is sodium hexametaphosphate.

3.2.2.1 Total Organic Carbon (TOC)

Total organic carbon (TOC), whether associated with surface plant residues (SPR-C), buried plant residues (BPR-C) or the SOC fractions (POC, HUM, ROC) requires measurement using a dry combustion automated analyser equipped with an infrared or thermal conductivity

detector which directly measures the amount of CO_2 emitted during the combustion process. The preferred instrument is a LECO C-144 C analyser used as described by Merry and Spouncer (1988). Where necessary, adjustments for the presence of carbonate-C will be made by acid pre-treatment to remove all carbonate-C prior to completing the analysis.

3.2.2.2 Fractionation scheme and carbon fractions

The carbon fractionation scheme as described in Figure 25 will be used. The carbon content of each fraction will be measured using the method outlined above for TOC analysis, except for the charcoal residing in the 53-2000µm fraction (ROC_{POC}) and the <53µm fraction (ROC_{HUM}). The ROC (charcoal) contents of the two 53-2000µm and <53µm fractions will be defined by a combined use of ^{13}C NMR spectroscopy and a mixing model described in Baldock et al. (2004). The recalcitrant organic carbon (ROC) fraction will calculated as the sum of both the ROC_{POC} and the ROC_{HUM} fractions, that is the sum of the charcoal residing in the 53-2000µm and <53µm fractions.

3.2.2.3 Mineralisable SOC and mineralisable soil organic nitrogen (SON)

The mineralisable SOC and SON fractions will be defined using incubation studies conducted at a constant temperature (20°C) and moisture content (70% water filled pore space) using soils packed to a constant bulk density of 1.4 Mg m^{-3}. CO_2-C emissions will be measured using an infrared gas analyser (Servomex CO_2 headspace analyser). The incubation experiments will be continued until the rate of change of the cumulative CO_2-C values with time becomes negligible. The amount (g CO_2-C kg^{-1} soil) and proportion (g CO_2-C g^{-1} SOC) of mineralisable SOC will be defined based on the CO_2-C emission measurements. Inorganic N contents (NH_4-N + NO_3-N) will be quantified at the start and at the end of the incubation by extraction with 2M KCl. The amounts of NH_4-N and NO_3-N in the extracts will be measured colourimetrically (AlpKem Flow Solution III, O.I. Analytical, Wilsonville, OR, USA). The mineralisable N fraction will be defined as the difference between the final and the initial inorganic N contents.

4 SOIL ACIDIFICATION: CONCEPTS AND MEASUREMENTS IMPORTANT TO A SOIL MONITORING SCHEME

The importance and implications of increasing soil acidity in limiting yields, land use options and in damaging the natural resource base have been extensively reviewed by Dolling et al. (2001) as part of the National Land and Water Resources Audit. The essence of that report is summarised here to provide background and context to this work.

Soil acidification is, and will remain, a major limitation to agricultural production in Australia if not addressed in terms of ameliorating the effects of previous acidification and preventing further acidification.

Some 50 million ha of agricultural land, occupying approximately 50% of current agricultural land, have a surface soil pH (in $CaCl_2$) below the optimal value of pH 5.5. Of this acidified area, 25-50% (13-25 million ha) has a surface soil pH less than 4.8. While surface soil pH can be ameliorated with applications of lime, if acidity moves down the soil profile or is generated in the deeper layers, it is much more difficult to correct. Again, there are substantial areas already with pH levels, in these deeper layers, at or below the two critical values of pH 5.5 and 4.8.

The significance of these two critical values of pH 5.5 and 4.8 is of particular importance in soils with high levels of aluminium or manganese. At pH 5.5 even acid sensitive agricultural species will maintain 90 to100% of yield produced at higher pH under the same conditions. However, once pH drops below this value, all crops show some loss of productivity, even the most acid tolerant species. At pH 4.8, highly tolerant, slightly tolerant, moderately sensitive, and extremely sensitive crops will have yield reduced to the order of 90, 80, 65, and 35%, respectively, of the yield expected if grown at pH 6.5. Reducing pH to 4.5 will result in yields approximately 80, 50, 35, and 5%, respectively, of the yield expected if grown at pH 6.5. Thus, the potential negative effect of lowered soil pH in on productivity is substantial.

While using acid tolerant crops may retain acceptable levels of productivity in the short term, such a strategy (a) limits flexibility in land use, and (b) is not a long term solution because decreasing pH affects the soil resource itself – not just the plants that grow in it. Prolonged acidification especially of the subsoil may be very difficult to reverse. As pH decreases, the vulnerability to nutrient loss increases, especially for cations such as Ca, Mg and K under leaching conditions due to loss in cation exchange capacity and displacement due to the formation of exchangeable aluminium. In addition to direct effects on nutrients and their availability, at pH less than 4.3 dissolution of clay-sized minerals, such as Fe and Al oxides, may occur. Leaching of these dissolved minerals will lead to permanent loss of clay as well as any nutrients, cation exchange capacity, or pH buffer capacity associated with those clay minerals; resulting in permanent damage. So while it might be possible to reverse soil acidity

through the application of lime, it is not always possible to reverse all of the detrimental effects caused by allowing such a high degree of acidification to occur.

As pointed out by Dolling et al. (2001), of the 50% of agricultural soils with a pH >5.5, it was estimated that, depending on land use and management practices, 28 to 80% will take less than 10 years to reach pH 5.5 if no lime is used. Similarly, of the 75 to 87% of agricultural soils with a surface pH >4.8, it was estimated that 33-71 % will take less than 10 years to reach pH 4.8 if no lime is used.

This means that in 10 years from ~2001 to ~2011, between 64 and 90% of Australia's agricultural land (64 to 90 million ha) will have a surface soil pH of 5.5 or less; and some 21 to 74% of agricultural land (21 to 74 million ha) will have a pH of 4.8 or less if no lime is used.

For a more complete analysis, and further details on the above summary, and other important information, please refer to Dolling et al. (2001). In addition, Slattery and Hollier (2002) have provided a recent treatise of the important issues relating to soil acidification and its amelioration in Victoria.

In the rest of this section, we concentrate on the technical aspects of measuring and predicting pH change, ameliorating soil acidity, and setting protocols for including acidification in a soil monitoring program.

4.1 Parameters important to defining the extent of soil acidification

In order to define the impact of land use and management practices on rates of soil acidification, quantification of the net acid addition rate (NAAR), soil pH buffer capacity (pHBC), soil bulk density and the volume of soil affected by is required. With an understanding of the impact of land use or management practice on these parameters, it is possible to define a potential change in pH according to Equation [1] where: ΔpH is the change in pH over a specified period (pH unit period^{-1}); NAAR is the net acid addition rate for a particular land use (mol H^+ ha^{-1} period^{-1}); pHBC is the pH buffering capacity of the soil (mol H^+ kg^{-1} pH unit^{-1}); BD is the bulk density of the soil (kg m^{-3}); and V is the volume of the soil being affected (m^3 ha^{-1}). If the period is expressed in years, then ΔpH will be the annual pH change (Helyar and Porter, 1989).

$$\Delta\text{pH} = \frac{\text{NAAR}}{\text{pHBC} \times \text{BD} \times \text{V}} \qquad [1]$$

Once a ΔpH has been defined, the number of years required to reach a critical soil pH can be calculated using Equation [2] (Dowling et al., 2001) where: Years is the number of years predicted until the critical soil pH is reached (yr); pHcurr is the current pH of the soil (pH

units); pHcrit is the critical pH chosen (pH units, e.g. 4.8); ΔpH is the annual change in pH (pH units yr^{-1}).

$$\text{Years} = \frac{\text{pHcurr} - \text{pHcrit}}{\Delta\text{pH}} \quad [2]$$

In either case there is a requirement to determine the pHBC and the NAAR for the system being examined. Thus pHBC, NAAR, and ΔpH are inextricably linked. Theoretically, each parameter can be estimated from the other two. So for example, if pHBC and ΔpH are measured experimentally, then NAAR can be estimated. Additionally, to define the influence of management on soil pH values, ΔpH can be predicted if pHBC and NAAR are determined. Further, if current pH is know, time to critical pH (Years) can also be predicted. The subsequent sections present a review of the determination of pHBC and NAAR values for soil.

4.2 pH Buffer Capacity (pHBC)

The pHBC provides a quantitative description of the ability of a soil to resist a change in pH on addition of acidity or alkalinity. Therefore pHBC determines both the amount of lime required to increase soil pH to a specified value (lime requirement, McLean, 1973) and, when combined with estimates of NAAR, the time required for soil pH to shift to a critical lower pH. The critical pH is often defined as the pH at which production losses are likely (e.g. Helyar and Porter, 1989). If the value of pHBC for a soil is known, it can be used to deduce NAAR from observed changes in soil pH over time or over spatially different treatments (as in paired sites). The pHBC is commonly determined experimentally and expressed as the amount of acidity (or alkalinity) required to change the pH of one kilogram of soil by one pH unit (cmol H^+ kg^{-1} pH^{-1}). Its value is determined by a range of reactions that can occur in soils.

4.2.1 Reactions involved in soil pH buffering

Soil pH defines the amount of acidity present at the time a soil was sampled and analysed; however, it does not define the response in pH to acid or alkali addition because buffering is involved. Buffering in soils occurs because of the presence of a variety of reactions that adsorb and/or release protons (H^+) from the soil solution. These reactions help explain the magnitude of pHBC and its correlations with soil properties. The constituents of soil, such as its organic matter and clay content, can adsorb and release protons (H^+) depending on the ambient soil solution composition.

Soil organic matter contains functional groups that are weak acids. A weak acid dissociates and releases its protons according to pH (Equation [3]). For a weak acid (HA), the dissociation constant K_A is defined according to Equation [4],

$$HA \quad H^+ + A^- \qquad [3]$$

$$K_A = \frac{[H^+][A^-]}{[HA]} \qquad [4]$$

The dissociation constant of a weak acid is normally expressed as -log K_A or pK_A. The pK_A is effectively the pH when half of HA is dissociated. The pH buffering capacity of a weak acid is not constant but is maximised at its pK_A. Carboxyl (pK_A ~4.8) and phenolic hydroxyl (pK_A ~9.0) groups present in the organic components of a soil provide weak acid properties that contribute to soil pH buffering (Equation [5]). Adsorption or release of protons by organic materials present in a soil is the most important component of pH buffering in topsoil layers. In West Australian cropping soils, pHBC was found to be strongly correlated only with total soil organic carbon (Moore et al., 1998).

$$SOM-COOH \quad SOM-COO^- + H^+ \qquad [5]$$

Soil mineral components with a permanent net negative charge can also contribute to pH buffering through cation exchange reactions (Equation [6]). These minerals are created by isomorphic substitution of higher valence cations with lower valance cations during mineral formation. The presence of minerals with a high permanent surface charge density and a high surface area will contribute most to this form of pH buffering.

$$Soil-H+M^+ \quad Soil-M+H^+ \qquad [6]$$

The combined negative charge provided by soil organic and mineral components defines the cation exchange capacity (CEC) of a soil. As soil pH is lowered, adsorption of protons offsets some of the net negative charge resulting in a corresponding loss of effective cation exchange capacity (ECEC).

Acidity residing on the exchange complex of mineral soils is mostly present in the form of exchangeable aluminium instead of H^+. Exchangeable aluminium is hydrated in water and releases protons to form aluminium hydroxide when neutralised. The sum of exchangeable H^+ and aluminium defines the amount of exchangeable acidity present in a soil. In many soils pHBC can be predicted by changes in ECEC and exchangeable aluminium (Conyers et al., 2000). The amount of lime required to neutralise exchangeable Al in these soils will exceed the amount of exchangeable Al because part of the lime will be used to increase ECEC. Thus, depending on the composition of the soil, basing lime requirement on

exchangeable acidity alone (Kamprath, 1970) is likely to lead to underestimates as other reactions are ignored (Aitken et al., 1990a).

Highly weathered soils can contain significant quantities of minerals with a pH dependent charge. This buffering reaction is important in soils rich in high surface area kaolinite and/or oxides of aluminium and iron such as Ferralsols of the humid tropics but may also be of importance to highly weathered soils in Mediterranean environments in Australia (Wong and Wittwer, 2009). These minerals have variable charge surfaces and can adsorb or release protons depending on soil pH. The surface charge of these minerals varies from negative ($HO\text{-}AlO^-$) to zero charge (HO-AlOH) to positive charge ($HO\text{-}AlOH_2^+$) according to soil pH and proton adsorption (Equations [7] and [8]). As is the case with soil organic matter, buffering provided by variable charge mineral surfaces is not constant but is at its minimum at the point of zero charge; that is, the pH when the variable charge is zero (Noble, 2001). Changes in surface charge due to this reaction can consume an average of about 50% of the lime added to such soils to raise pH from 4-6 (Gillman and Sumpter, 1986).

$$HO-AlO^- + H^+ \quad HO-AlOH \qquad [7]$$

$$HO-AlOH + H^+ \quad HO-AlOH_2^+ \qquad [8]$$

Dissolution of carbonates is an important buffer against lowering of soil pH in recently limed and calcareous soils. Loss of calcium carbonate can occur in these soils as a result of dissolution of carbonic acid formed when carbon dioxide in the soil atmosphere dissolves in water or when acidity generated by agricultural production reacts with carbonate or bicarbonate (Equation [9]). The bicarbonate formed is further acidified to carbon dioxide following loss of carbonates (Equation [10]).

$$CO_2 + H_2O \quad H_2CO_3 \quad HCO_3^- + H^+ \qquad [9]$$

$$CaCO_3 + HCO_3^- + H^+ \quad Ca(HCO_3)_2 \quad Ca^{2+} + 2HCO_3^- \qquad [10]$$

Dissolution of clay minerals in acid soils can also buffer soil pH change, but rates of reaction are slow and require long time frames. This process is not captured in pHBC measurements but can provide a source of dissolved aluminium in acid soils.

Each of the reactions described above can influence the rate of change in soil pH and make different contributions to pHBC depending on the starting pH value and soil composition. Since the pHBC of each of the reactions discussed varies with soil pH, the overall soil pHBC also varies when examined across a wide range of pH values. Changes in CEC on organic matter and clay surfaces are a major determinant of pHBC in acid soils (Aitken et al., 1990). pHBC is high at pH_{Ca} <4.5 due to reactions involving variable charge hydrous iron and aluminium oxides and clay dissolution. pHBC is also high at pH_{Ca} > 7.5 due to charging

reactions (Moore et al., 1998). However, over the pH_{Ca} range of 4.5 to 6.5, pHBC is approximately constant when expressed in units of proton consumption per unit change in pH (Thomas et al., 2004).

4.2.2 Methods of measuring soil pH buffer capacity

Direct determination of pHBC requires measurement of equilibrium soil pH following incremental additions of acidity or alkalinity. Several methods of measuring pHBC are used in Australia. Valence and ionic strength of the acid and base used in titration were found to impact on pHBC measurement (Aitken and Moody 1994). The pHBC determined by titration of the soil suspension in water with calcium hydroxide was about twice the pHBC measured by titration with sodium hydroxide. In contrast, pHBC measured in sodium hydroxide and hydrochloric acid was not significantly different for the majority of soils studied. This implies that when a water suspension is used, calcium hydroxide or carbonate should be used to estimate lime requirement but hydrochloric acid or sodium hydroxide should be used to estimate NAAR and time to critical pH during acidification to mimic the likely cation valances encountered during liming or acidification processes. A marked increase in measured values of pHBC occurs with increasing ionic strength at values <0.03 M. A need therefore exists to carry out pHBC measurements at ionic strengths similar to those encountered in the field. Aitken and Moody (1994) suggested the use of 0.002 M $CaCl_2$ (ionic strength=0.006 M) for pHBC measurement. Soil pH and pH change are normally measured in 0.010 M $CaCl_2$ and it is beneficial to measure pHBC also in 0.010 M $CaCl_2$ to ensure consistent conditions under which measurements are made. This is important when pHBC is in turn used to estimate lime requirement, NAAR and time to critical pH as the soil pH used would be in 0.010 M $CaCl_2$.

The generic approaches to the measurement of pHBC are described below. Several pH buffering reactions such as mineral dissolution and proton diffusion are slow. The technical response is to carry out the measurement of pHBC over a range of reaction times selected in which it is assumed that the various reactions are complete.

4.2.2.1 Incubation

Moist incubation of soil with incremental additions of calcium carbonate is regarded to be one of the most reliable methods of estimating the potential change in soil pH due to liming under field conditions (Bache, 1988). Varying amounts of calcium carbonate are added to soil in aliquots to give predicted final pH values in the range of 4 to 6.5. The soil is then incubated at a water content near field capacity and room temperature for several weeks before measuring pH. For example, Aitken et al. (1990) measured pHBC by moist incubation of the soil with calcium carbonate for 6 weeks at 25^{o}C. The incubation time used in this approach is pragmatic as reaction of lime with moist soil can take months to reach near completion at room temperature (Barrow and Cox, 1990). Incubation methods are commonly used as the

benchmark against which to test methods with shorter reaction times such as titration and buffer methods (Aitken et al., 1990a). The rate limiting reaction during incubation with lime appears to be diffusion of protons into and out of soil particles (Barrow and Cox, 1990). The effect of this rate limiting step is minimised by using a slurry. Suspension and agitation of the soil slurry increases the rate of reaction by breaking or decreasing the size of soil particles and reducing the dependence of the change in pH on proton diffusion through a soil matrix. This approach is used in titration methods to determine pHBC.

4.2.2.2 Titration

Titrations are performed by adding small incremental amounts of base such as calcium carbonate, calcium hydroxide or sodium hydroxide and/or acid to a soil slurry. These amounts are aimed at giving a range of final pH values from ~4.0 to ~6.5. The final pH of the slurry is then measured when the reaction is complete and the pHBC determined.

A strong correlation between pHBC (and lime requirement) measured by incubation with calcium carbonate and by titration with calcium hydroxide often exists. The titration method has been shown to measure >90% of the lime requirement assessed by incubation (Aitken et al., 1990a, Alabi et al., 1986, McLean et al., 1977). The difference between pHBC measured with a 7-day calcium hydroxide titration and a six-week moist incubation with calcium carbonate was not statistically significant in 40 eastern Queensland soils (Aitken et al., 1990a). Discrepancies between the incubation and titration results sometimes occur and may be due to differences in rates of microbial transformation of nitrogen during incubation and titration (Godsey et al., 2007). Bache (1988) recommended incubating at low temperatures to minimise microbial activity but this slows the rate of reaction (Barrow and Cox, 1990). The Natural Resource Chemistry Laboratory in Western Australia measures pHBC by titration and uses chloroform to inhibit microbial activity. In this method, the soil is suspended in a ratio of 1:5 in 0.002 M $CaCl_2$. Incremental amounts of either HCl and/or NaOH are added and equilibrated with occasional shaking over a period of 7 days at 23^{o}C (Aitken and Moody, 1994). Titration is considered to be a reliable way of determining pHBC, lime requirement (Aitken and Moody, 1994, Aitken et al., 1990a) and acidification rates (Helyar and Porter 1989, van Breemen, 1991). Although the time involved in titration is decreased compared with incubation, it is still too long for routine test and diffusion limiting reactions are not expected to reach completion.

Most of the changes in pH following additions of acid or alkali occur rapidly but a slow reaction likely due to diffusion of protons into or out of soil particles continues for a long period (Barrow and Cox, 1990). Barrow and Cox (1990) showed that the rate of this slow reaction can be increased at high temperatures so that it is possible to achieve in one day at 60^{o}C the same pH change as reaction for several months at 25^{o}C. High temperature moist incubation or titration with lime is not used in Australia. It has the potential to provide a quick

and simple way to measure pHBC overnight and provide values that are more realistic for forecasting long term changes in soil pH and for estimating NAAR.

4.2.2.3 Buffer method

Use of a buffer method to determine lime requirement to a given pH (typically 5.5 to 6.5) provides an alternative to estimate pHBC more quickly than incubation or titration methods carried out at room temperature. Lime requirement is estimated by calibrating the change in pH when a soil sample is equilibrated with a buffer solution against other measurements. Single and double buffer methods (which require two pH measurements) with equilibration time of up to ~1 h at room temperature were well correlated with lime requirement measured by moist incubation with lime for six weeks at 25°C (Aitken et al., 1990a). Buffer methods that used high initial buffer pH and high buffer strength were less well correlated with pHBC than those that used lower initial buffer pH and lower buffer strength. The Mehlich (1976) single buffer method (initial pH 6.6) fitted these two criteria and gave good correlation with measured lime requirement to pH 5.5 (r^2 = 0.78) and pH 6.5 (r^2 = 0.80). Lime requirement calculated from changes in Mehlich buffer pH was in good accord with lime requirement to pH 5.5 estimated from measurements (Figure 26). These initial results suggest that buffer methods, particularly the Mehlich single buffer method, should be considered as a rapid method to estimate lime requirement.

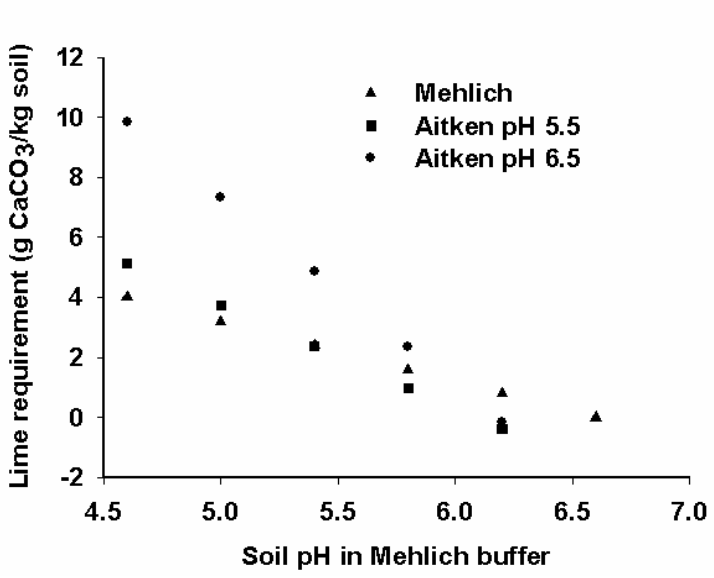


Figure 26: Lime requirement calculated from change in pH of Mehlich buffer on one hour contact with soil and from regression equations for lime requirements measured by moist incubation with lime for target pH values 5.5 and 6.5 (Aitken et al., 1990).

4.2.3 Estimating soil pH buffer capacity from other soil properties

The direct methods of measuring pHBC are still time consuming and are largely not routinely available at commercial laboratories. Pedotransfer functions based on other more easily

measureable soil properties have been developed and used to estimate pHBC indirectly. pHBC pedotransfer functions have included soil properties such as organic matter and clay content, effective cation exchange capacity (ECEC) and field texture (McBratney et al., 2002). Pedotransfer functions to estimate pHBC in Australian soils were reviewed by Noble, (2001). Similar pedotransfer functions are widely used internationally. For example, a pedotransfer function using organic matter and clay content to estimate pHBC was recently developed for the Georgian coastal plain of the USA. There, a multiple linear regression of pHBC measured by soil titration with calcium hydroxide against organic carbon and clay content was used to map pHBC (Weaver et al., 2004). Similarly, organic matter and clay contents have long been used to estimate pHBC of British soils (Bache, 1988).

The review of pHBC in Australian soils by Noble (2001) did not cover highly weathered Mediterranean cropping soils such as those of Western Australia. We accessed pHBC, soil organic carbon and clay content data for 42 topsoil samples from Department of Agriculture and Food Western Australia to test two commonly used pedotransfer functions in Australia (Aitken et al., 1990, Merry, 1997) based on soil organic matter and clay content. The pedotransfer function of Aitken et al. (1990), derived for tropical soils of Queensland, overestimated pHBC in these Mediterranean cropping topsoils by a factor of 2-3 (Figure 27a); whereas, that of Merry (1997) provided reasonable estimates of measured pHBC values (Figure 27b).

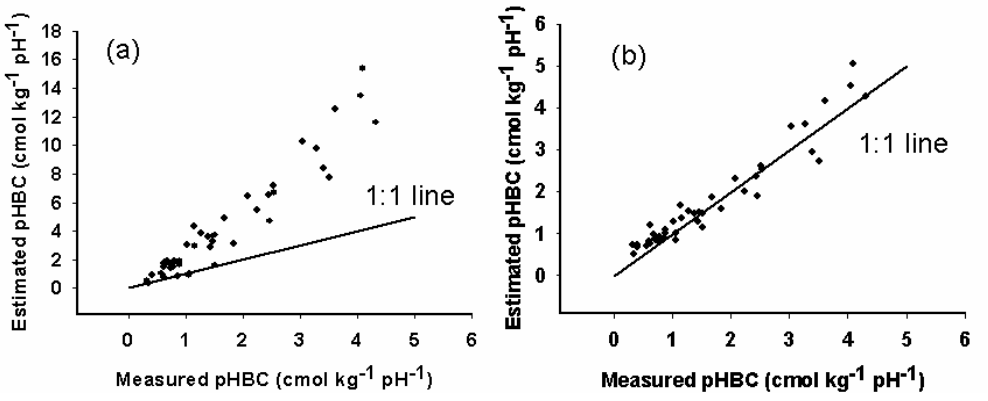


Figure 27: Comparison of measured and estimated pHBC using Aitken et al.'s. (1990) (a) and Merry's (1997) (b) pedotransfer functions based on soil organic matter and clay content for 42 cropping topsoil samples of Western Australia. Please note different y-axis scales.

Important implications of the results presented in Figure 27 include:

1. A single pedotransfer function may not be universally applicable across all soil types. Given the empirical nature of the generation of pedotransfer functions it is important not to apply the function outside of the range of soils used in its generation.

2. The Aitken et al. (1990) pedotransfer function may be of limited value for soils in Western Australia. Additionally the discrepancy in suitability noted between the Aitken et al. (1990) and Merry (1997) functions suggests that the Aitken et al. (1990) function is not applicable to the South Australia and western Victoria soils used by Merry (1997). The Merry (1997) pedotransfer function should be used for these soils

The overestimation of pHBC by the Aitken et al. (1990) pedotransfer function is systematic suggesting that, while organic matter and clay were important in estimating measured pHBC in Mediterranean and temperate soils, their relative contribution is smaller than elsewhere. The clay mineralogy of these soils is dominated by kaolinite which has little pHBC compared with 2:1 clays (Coleman and Thomas, 1964) found elsewhere. The pHBC of organic carbon can be 300 times larger than that of kaolinite (Bache, 1988). Regional difference in the chemical composition of soil organic matter in particular its carboxyl and phenoxy-hydroxyl group content will further result in varying contribution to pHBC per unit carbon content. These differences in type of clay and surface chemistry of soil organic matter undermine the development of a single unifying function that is widely applicable without local calibration.

The pHBC of Western Australian surface cropping soils can be estimated accurately from their organic matter content alone (Moore et al., 1998). This is an advantage as measurement or estimate of clay content is not required. The pHBC expressed as cmol H^+ kg^{-1} pH^{-1} for the 42 WA topsoils examined as part of this report also indicated that pHBC could be predicted from their percentage organic carbon content (% OC) as measured by the Walkley and Black method as follows (Equation [11] and Figure 28):

$$\text{pHBC} = 0.48 + 0.54(\%\text{OC}) \qquad \left(r^2 = 0.91,\ n = 42\right) \qquad [11]$$

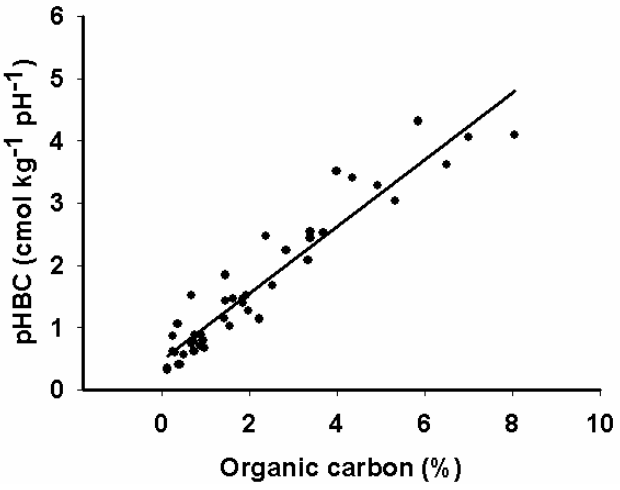


Figure 28: Regression of measured pHBC on soil organic matter content for 42 cropping topsoil samples of Western Australia.

The pHBC of the 42 Western Australian soils was measured by titration of the soil suspended in 0.005 M KCl with KOH and HCl and reading pH after reaction for 17 h at room temperature. The percentage organic carbon content of the soil samples ranged from 0.13 to 8.04% and clay content ranged from 1.8 to 15.4%. Inclusion of clay content to the regression equation above only increased the variance accounted for (r^2) slightly from 0.91 to 0.93. Lime requirement in these soils can vary by a factor of about 10 depending on soil organic matter content. Testing of the pedotransfer function derived for these Mediterranean cropping soils (Moore et al., 1998) with more recent independently measured pHBC data from Department of Agriculture and Food Western Australia showed that it performed well for seven out of the eight topsoil samples measured (Figure 29). The pHBC measurement to derive the test data differed from the calibration data and was performed by titration of the soil suspension in dilute calcium chloride over a 7 day period at room temperature. Soil organic carbon content (Walkley and Black) in the eight topsoil samples ranged from 0.19 to 2.97% and clay content ranged from 2.2 to 15.2%. The outlier with pHBC not well predicted with the Moore et al. (1998) pedotransfer function had 2.97% organic carbon and 7.2% clay. It had one of the two lowest exchangeable aluminium contents of 0.04 $cmol_c\ kg^{-1}$ of the group of soils (range 0.04 to 0.9 $cmol_c\ kg^{-1}$) and it is possible that it contained undissolved lime. The Aitken et al. (1990) pedotransfer function based on both soil organic carbon and clay content again overestimated pHBC whereas that of Merry (1997) estimated pHBC with similar accuracy to the Moore et al. (1998) method (Figure 29). Evidence from these data sets suggests that the Moore et al. (1998) pedotransfer function is more suitable for Western Australian surface cropping soils than the Aitken et al. (1990) method. It should be used locally pending a better understanding of pHBC in these soils and more thorough testing of the pedotransfer functions.

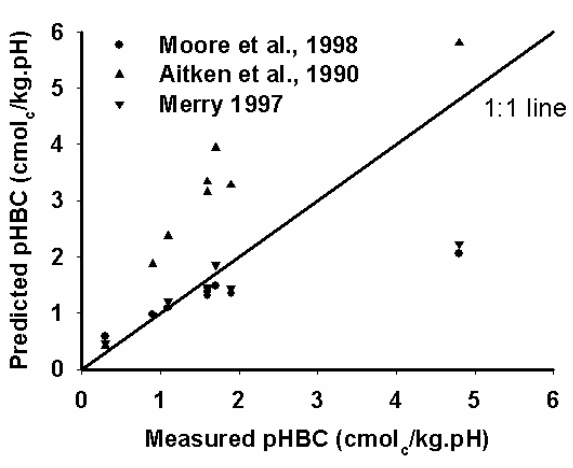


Figure 29: Comparison of measured pHBC with estimates using pedotransfer functions of Moore et al. (1998), Aitken et al. (1990) and Merry (1997).

4.2.4 Pedotransfer functions assessed by NLWRA

The pHBC was highly correlated with the organic carbon and clay contents of topsoil from eastern Queensland locations ranging from the Atherton Tableland to south of Brisbane, (Aitken et al., 1990). Organic carbon accounted for more variance in pHBC (r^2 = 0.52) than clay (r^2 = 0.25). The 40 topsoil (0-15 cm) samples used in this study had 0.3-4.7% OC measured by the Walkley and Black method and 1-77% clay and pHBC of 0.2 to 5.4 g $CaCO_3$ kg^{-1} pH^{-1} measured by moist incubation with calcium carbonate for 6 weeks at 25°C. The regression equation for pHBC (g $CaCO_3$ kg^{-1} pH^{-1}) is given in Equation [12].

$$\text{pHBC} = 0.955\ \%\text{C} + 0.011\ \%\text{Clay} \quad \left(r^2 = 0.83,\ \text{n=40}\right) \qquad [12]$$

Adding exchangeable acidity to the regression equation above only increased the variance accounted for (r^2) from 0.83 to 0.85. The unit of pHBC used in this pedotransfer function can be converted from g $CaCO_3$ kg^{-1} pH^{-1} to $cmol_c$ H^+ kg^{-1} pH^{-1} by multiplying the result by 2.

Clay content of soils is often not available and Merry (1997) developed pedotransfer functions to estimate pHBC based on total soil organic carbon content and ECEC expressed as $cmol_c$ kg^{-1} soil (Merry 1, Equation [13]) or clay content estimated from field-texture (Merry 2, Equation [14]) (Table 4). Total soil organic carbon content was determined by LECO combustion. The pedotransfer functions were based on surface and near-surface soils from South Australia and Western Victoria. The pHBC was measured by titrating 1:5 suspensions of the soil samples in 0.002 M $CaCl_2$ with sodium hydroxide and equilibrating for 7 days at room temperature. The pHBC was expressed as t lime ha^{-1} pH^{-1} for a 10 cm layer with assumed bulk density of 1.4 t m^{-3}. The pHBC can be divided by 1.4 for comparison with units used before (g $CaCO_3$ kg^{-1} pH^{-1}) or it can be multiplied by 1.428 to give units of $cmol_c$ kg^{-1} pH^{-1}.

$$\text{pHBC} = 0.310 + 0.28\ \%\text{TOC} + 0.0546\ \text{ECEC} \quad (\text{Merry1},\ r^2 = 0.71,\ \text{n=121}) \qquad [13]$$

$$\text{pHBC} = 0.200 + 0.364\ \%\text{TOC} + 0.0213\ \text{FT-Clay\%} \quad (\text{Merry2},\ r^2 = 0.76,\ \text{n=158}) \qquad [14]$$

An earlier pedotransfer function developed by Hochman et al. (1989) used the soil specific slope (SL_s) of the linear regression of ECEC expressed as a function of (pH-2.04) to derive an equation for ECEC that explained 96% of the variance in ECEC expressed as $cmol_c$ kg^{-1} pH^{-1} (Equations [15]).

$$\text{ECEC} = \text{SL}_s\left(\text{pH} - 2.04\right) - 0.96 \quad (r^2 = 0.96,\ \text{n=16}) \qquad [15]$$

Rearranging Equation [15] to predict SL_s from measured values of ECEC and pH, describes the way in which ECEC varies with pH (Equation [16]). Hochman et al. (1989) then found that pHBC, expressed as $cmol_c$ $kg^{-1}pH^{-1}$, could be predicted from SL_s according to Equation [17].

$$SL_s = \frac{ECEC + 0.96}{pH - 2.04} \quad [16]$$

$$pHBC = \left(\frac{34.24}{SL_s + 9.5}\right) - 1.741 \quad \left(r^2 = 0.88\right) \quad [17]$$

Table 4: Clay content assigned to field textural classes (Merry, 1997).

Field texture	FT-Clay%
Sand	5
Loamy and clayey sand	8
Sandy loam	15
Loam and silt loam	25
Sandy clay loam	27
Clay and silty clay loam	32
Sandy, silty light clays	38
Medium and heavy clays	50

The pHBC was assumed to be equal to the change in ECEC and exchangeable aluminium over the nominated pH range. This pedotransfer function is used in the Limeit model which in addition to changes in ECEC also takes into account changes in exchangeable aluminium with soil pH as an additional buffering reaction (Noble, 2001).

4.2.5 Testing of pedotransfer functions on Australian soils

The pedotransfer functions described here were tested for their ability to estimate pHBC with six data sets derived from published and unpublished sources (Noble, 2001). The data sets used included:

1. The unpublished data from the Dalrymple Shire, North of Queensland referred to by Noble (2001) had pHBC measured by titration of the 1:5 soil to 0.002 M calcium chloride suspension with HCL or NaOH at 25^{o}C over a period of seven days (Aitken and Moody, 1994).
2. Data from Hochman et al. (1995) and Hochman et al. (1992) had pHBC measured by incubating soil with agricultural lime under field conditions over a period of twelve months.
3. Data from Aitken et al. (1998) had pHBC determined on samples collected from field plots five months after application of agricultural lime.
4. Two unpublished data sets from Gillman for soils derived from granite and metamorphic rocks referred to by Noble (2001) had pHBC measured by adding incremental amounts of saturated calcium hydroxide solution to a soil suspension and allowing the reaction to take place at room temperature over a period of seven days.

The availability of measured values for soil properties in addition to pHBC (e.g. soil clay and carbon contents) within each data set was variable. Additionally, the methods used to

determine pHBC varied. Potential differences in pHBC methodology and the absence of some measured values for additional soil variables imposed some limitations on the comparison of the pedotransfer functions.

The Aitken et al. (1990) pedotransfer function based on soil organic matter and clay content could be tested on four data sets (unpublished data from the Dalrymple Shire, North of Queensland, data from Aitken et al. (1998) and two unpublished data sets from Gillman for soils derived from granite and metamorphic rocks). Ferrosols and hydrosols from the Aitken et al. (1998) data set were omitted from the test as their pHBC was poorly estimated presumably because of their high content of variable charge clays (Noble, 2001). The estimated pHBC ($pHBC_{est}$) of the remaining 66 topsoil samples was correlated with measured pHBC ($pHBD_{meas}$) (Equation [18] and Figure 30).

$$pHBC_{est} = 0.83\left(pHBC_{meas}\right) + 0.82 \quad \left(r^2=0.70,\ n=66\right) \qquad [18]$$

Differences in pHBC measurement methodology appeared to affect the agreement between estimated and measured pHBC. Data from Aitken et al. (1998) had pHBC determined on samples collected from field plots five months after application of agricultural lime. This long field incubation time and likely microbial activity and nitrate leaching in the field resulted in greater measured than estimated pHBC values as indicated by all data points falling below the 1:1 line (Figure 30). The short titration reaction times of seven days used by Noble and Gillman to measure pHBC for the remaining data sets resulted in many measured values being smaller than estimated values as evidenced by data points above the 1:1 line. These differences highlight the importance of using a nationally agreed method of measuring pHBC to ensure that results obtained can be compared nationally. The issues highlighted here are expected to involve slow reactions, microbial activity and nutrient cycling that are not fully captured by short titration experiments. Nitrification and nitrate leaching which would result in apparently greater pHBC measured in the field unless they are accounted for through the inclusion of estimates of NAAR (using a rearranged version of Equation [1] to solve for pHBC). There is a clear danger that field measurement of pHBC may therefore result in double accounting as these processes are unlikely to occur at the same rate in the control and limed plots. In spite of these limitations, the Aitken et al. (1998) function gave reasonable estimates of pHBC across the available data sets. The function has not been tested in Queensland soils with 2:1 clay minerals and alkaline soils. Its performance is uncertain in Calcarosols, Dermosols, Sodosols and Vertosols (Bloesch et al., 2006).

Based on available soil test data on soil organic carbon and ECEC, the Merry 1 pedotransfer function could be tested with five data sets (Hochman et al., 1995, Hochman et al., 1992, Aitken et al., 1998 and two data sets from Gillman for soils derived from granite and metamorphic rocks). This pedotransfer function worked well for data sets from Hochman et

al. (1995) and Hochman et al. (1992) and estimated pHBC with a RMSE of 0.37. It performed poorly with the remaining three data sets where pHBC was underestimated (Figure 31) giving slopes of regression equations of estimated on measured pHBC ranging from 0.29 to 0.35 and an overall RMSE of 2.36. The variance accounted for by these regression equations however ranged from 0.75 to 0.88 suggesting that this pedotransfer function can be used across these five data sets but it needs local calibration prior to use. It should also be noted that ECEC varies with soil pH, (Conyers et al., 2000). Therefore several pedotransfer functions can be expected depending on the pH at which the ECEC measurement was made and the nature of the soil organic matter involved.

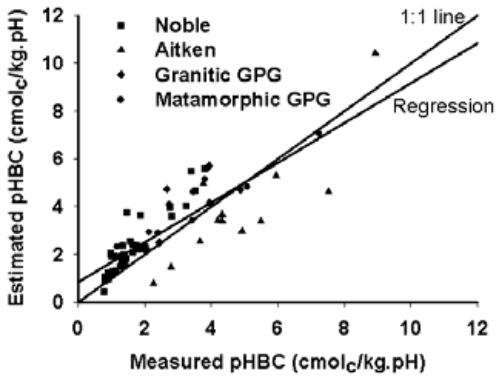


Figure 30: Regression of pHBC estimated from organic matter and clay content (Aitken et al., 1990) on measured pHBC for four data sets. The 1:1 line is shown for comparison.

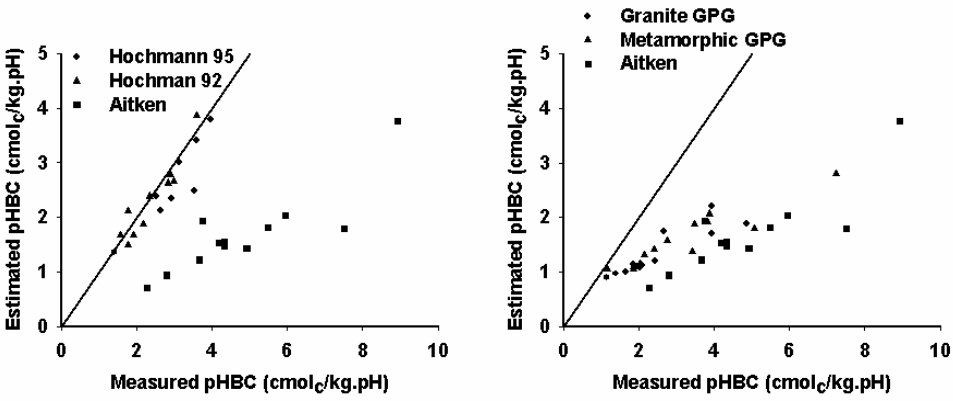


Figure 31: Comparison of pHBC estimated from organic matter and ECEC (Merry, 1997) and measured pHBC for five data sets. The 1:1 lines are shown for comparison.

In addition to the WA data shown in Figure 27b, only the unpublished data from the Dalrymple Shire, North of Queensland referred to by Noble (2001) had the soil organic matter and field texture measurement necessary to test the Merry 2 pedotransfer function. The estimates of pHBC were in good accord with pHBC measured by titration of a 1:5 soil to 0.002 M calcium chloride suspension with HCl or NaOH at 25^{o}C over a period of seven days (Figure 32). The RMSE of the estimate was 0.40. There is currently insufficient data to test

this function more widely. However the implication of the results shown in Figure 27 and Figure 32 is that the Merry 2 pedotransfer function should be used for these kinds of soil.

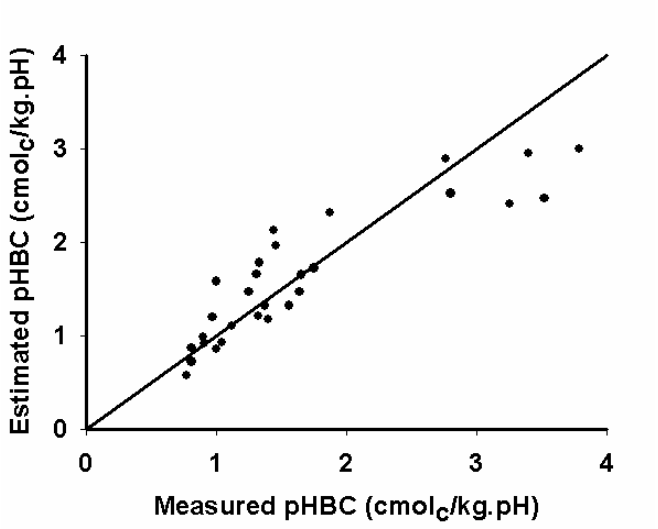


Figure 32: Comparison of pHBC estimated from organic matter and field texture clay (Merry, 1997) and measured pHBC for one data set from the Dalrymple Shire, North of Queensland. The 1:1 line is shown for comparison.

The Hochman et al. (1989) pedotransfer function is based on correlating indices of pHBC (SL_s) with measured pHBC. Values of SL_s could be calculated for the data sets from Hochman et al. (1995), Hochman et al. (1992), Aitken et al. (1998) and two unpublished data sets from Gillman for soils derived from granite and metamorphic rocks. These indices were variously correlated with measured pHBC (Figure 33). The authors of this pedotransfer function suggested using soil organic matter and clay contents to obtain a more widely applicable pedotransfer function. The results shown earlier for the Aitken et al. (1990) pedotransfer function support this view.

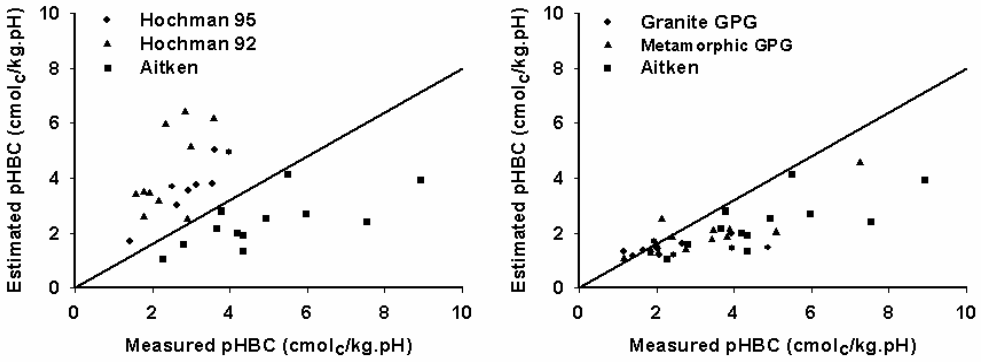


Figure 33: Comparison of pHBC indices (SLs) estimated from soil pH and ECEC (Hochman et al., 1989) and measured pHBC for five data sets. The 1:1 lines are shown for comparison.

The Limeit model (Noble, 2001) takes account of the effect of both SL_s and changes in exchangeable aluminium upon liming on pHBC. This approach yielded estimated of pHBC that mirrored those estimated based on SL_s alone (Figure 34).

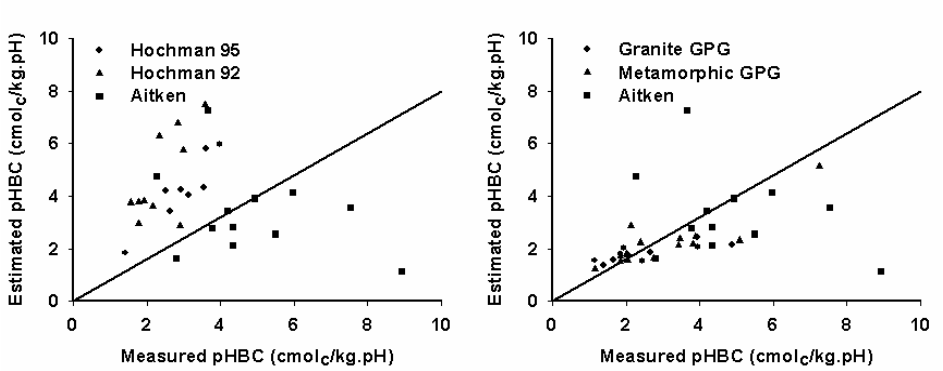


Figure 34: Comparison of pHBC estimated from the Limeit model (Noble, 2001) and measured pHBC for five data sets. The 1:1 lines are shown for comparison.

The pedotransfer function used in Western Australia is the only one that uses only one soil property (organic carbon content) to estimate pHBC (Moore et al., 1998). Measured and estimated pHBC using only soil organic carbon content were linearly related for all available data sets (Figure 35). This suggests that soil organic carbon could be used to estimate pHBC subject to local calibration to take account of differences in properties of soil organic matter in different soils and environments.

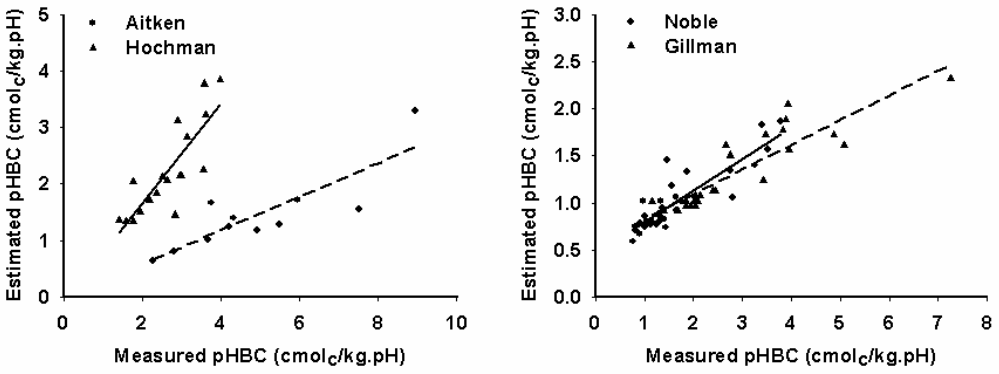


Figure 35: Regressions of pHBC estimated from soil organic carbon content (Moore et al., 1998) on measured pHBC for five data sets (Aitken et al., 1998, Hochman et al., 1995, Hochman et al., 1992, Noble data for Dalrymple Shire, North of Queensland and two unpublished data sets from Gillman for soils derived from granite and metamorphic rocks).

The regression equations relating estimated pHBC ($pHBC_{est}$) to measured pHBC ($pHBC_{meas}$) where only soil organic carbon content was used with the Moore et al. (1998) equation to derive values for $pHBC_{est}$ are given by Equations [19] to [22].

Noble's Dalrymple Shire: $pHBC_{est} = 0.33(pHBC_{meas}) + 0.47 \quad (r^2 = 0.76)$ [19]

Hochman et al. (1992, 1995): $pHBC_{est} = 0.88(pHBC_{meas}) - 0.10 \quad (r^2 = 0.69)$ [20]

Aitken et al. (1998): $pHBC_{est} = 0.30(pHBC_{meas}) - 0.01 \quad (r^2 = 0.72)$ [21]

Gillman granite and metamophic soils: $pHBC_{est} = 0.26(pHBC_{meas}) + 0.57 \quad (r^2 = 0.80)$ [22]

The Moore et al. (1998) equation was able to account for 69 to 80% (or 91% for the WA soils in Figure 28) of the variation in measured pHBC in the data sets examined. The different regression equations obtained with different data sets indicates that a local calibration is required to optimise predictions of pHBC. Differences in the chemical composition of soil organic carbon, especially the content of carboxyl and phenoxy-hydroxyl groups and the allocation of soil organic carbon to different fractions, are expected to result in different contributions to pHBC per unit carbon. This surface chemistry of the soil organic matter needs to be elucidated before a more comprehensively valid pedotransfer function to estimate pHBC can be developed. It is however interesting to note that pHBC measured by titration of the soil suspension at room temperature over a seven day period (Noble and Gillman's two data sets) gave similar regression equations reinforcing the need to agree on a standard method to determine pHBC.

4.3 Net Acid Addition Rate (NAAR)

The chemical reactions and processes that can generate or consume acidity in soils are many and varied (van Breemen et al., 1983). In productive agricultural systems, acidification is dominated by reactions and processes associated with the carbon and nitrogen cycles, the addition of acids and the addition of materials with a neutralising (liming) potential (Helyar and Porter, 1989). NAAR for any given system can be defined according to Equation [23] where OA is organic anions, L is liming materials, H^+ refers to strong acids and the subscripts ac, ex, ad refer to material that is *in situ* accumulation, export to an external sink, and addition from an external source, respectively (Helyar and Porter, 1989).

$$\begin{aligned} \text{NAAR (mol } H^+ \text{ ha}^{-1} \text{ period}^{-1}) = \\ &\left(OA_{ac} + OA_{ex} - OA_{ad} + HCO^-_{3\,ac} + HCO^-_{3\,ex} - HCO^-_{3\,ad}\right) + \\ &\left(NH^+_{4\,ad} - NO^-_{3\,ad} - NH^+_{4\,ac} + NO^-_{3\,ac} + NO^-_{3\,ex} - NH^+_{4\,ad}\right) + \\ &\left(-L_{ad}\right) + \\ &\left(H^+_{ad} - H^+_{ex}\right) \end{aligned} \quad [23]$$

Of these reactions, the most important are the change in organic matter in the soil, the export of organic matter (product), the addition of inorganic nitrogen fertilisers (potential acidification from ammonium based fertiliser and alkalisation from nitrate based fertiliser), the addition of lime, and the leaching loses of nitrate. The effect of the nitrogen cycle on acid generation is shown in Figure 36.

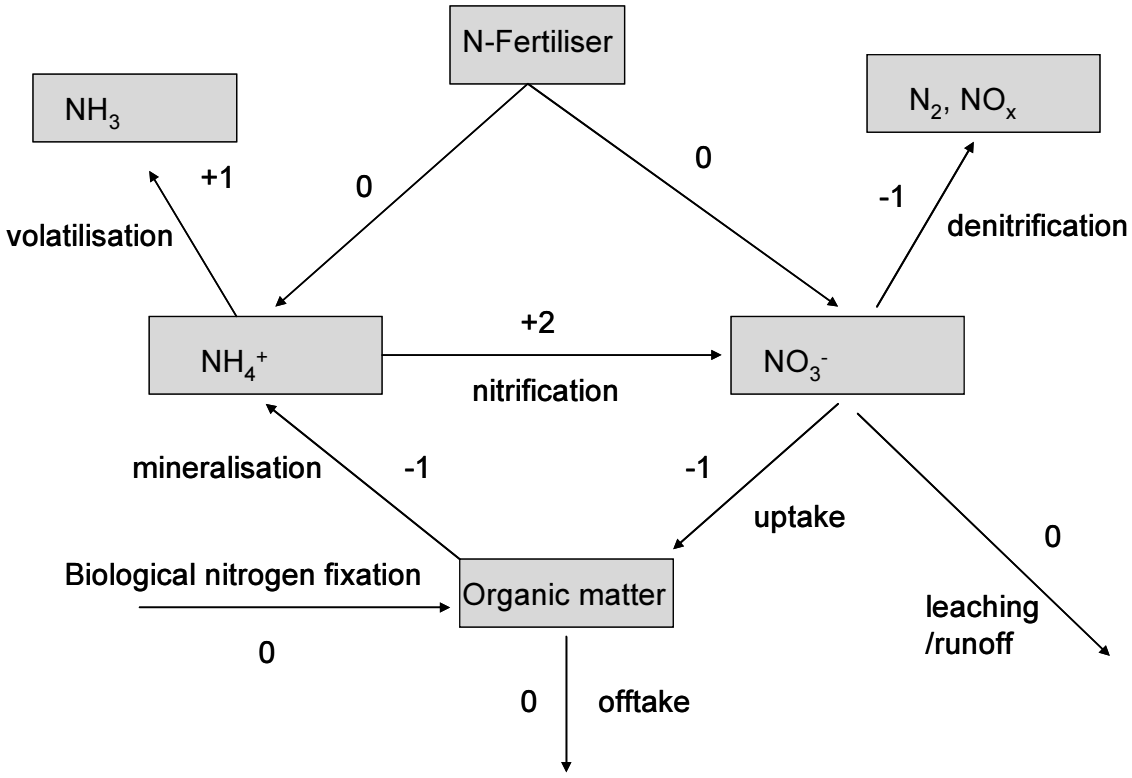


Figure 36: Effect of nitrogen cycle on acid generation. The numbers refer to the number of hydrogen ions produced.

The carbon cycle, because of its association with organic acids, also influences soil acidification. Most organic matter has an excess of inorganic cations, over inorganic anions, with the balance being made up by organic anions. Producing organic anions is an acidifying process. Similarly, because of the excess inorganic cations present, decomposition of organic matter in the soil is an alkalising process. Thus land management practices that induce an increase or decrease in soil organic matter content will influence NAAR. An accumulation of organic matter *in situ* (OA_{ac} in Equation [23]), will acidify while a loss of organic matter will alkalise soil. It is also important to recognise that if an increased addition of organic matter is associated with an equivalent loss of organic matter through decomposition, the overall effect will be neutral.

The production of organic matter via plant growth (crops or native vegetation) also results in an acidification. If all plant residues are returned to the soil, this acidification will be offset by the alkalisation induced during decomposition. However, it is possible that the acidifying and alkalising processes occur in different parts of the soil resulting in both an acidification in one

part of the soil and an alkalisation in another. For example, if the excess cations are taken up by plant roots deep in the soil profile and the majority of organic plant residues are added to the soil surface, acidification will occur at depth and alkalisation will occur near the surface.

Another consideration pertinent to agricultural systems is the export of organic material associated with product removal. If organic plant material is harvested and exported (OA_{ex} in Equation [23]), the acidity generated in the production of that organic matter remains in the soil and is not neutralised. On the other hand, addition of organic matter (OA_{ad} in Equation [23]), imported from offsite reduces acidity in the soil to which it is added, because the alkalinity associated with the organic matter is released during decomposition. With both organic matter export and addition from offsite, the change in acidity will be compensated for in the part of the landscape where the residues were either deposited or removed. Thus a change in land use which results in a change in soil organic matter, amount and alkalinity of product exported, or import of organic material will cause a change in pH simply from the change in organic matter independent of other causes.

There are a number of ways to determine the acid contribution of exporting or accumulating organic matter. The 'ash alkalinity' of exported product (or imported organic matter) can be determined by (a) ashing the product to remove the organic materials leaving the inorganic anions and cations, and then titrating the ash do determine its alkalinity; or (b) by content of the major inorganic cations (K, Mg, Ca, Na) and anions (P, S, Cl), then in both cases, calculating the excess cations in $cmol^{+}\ kg^{-1}$ of product exported or imported. These values for ash alkalinity can then be converted to kg $CaCO_3\ Mg^{-1}$ of organic matter.

For organic matter contained in mineral soil to influence NAAR, a change in soil organic matter content has to occur. If soil organic matter increases, additional organic anions will be present and depending on soil pH and pKa of the organic anions. It is difficult to separate soil organic matter from the rest of the soil and thus neither of the methods for measuring ash alkalinity of pure organic materials are suitable. Instead, organic acids accumulated in the soil can be calculated from the soil organic matter content. Given that the contribution of soil organic matter to acidity (which is dependent on the CEC of the organic matter) varies with soil pH, it can be calculated using Equation [24] where α is the slope of the titration curve for the organic acids. This value varies depending on the nature of the organic matter, but the average value of 32 $cmol^{+}\ kg^{-1}$ OM found by Helling et al. (1964) as the average over a range of organic acids is considered to be representative of the organic matter present in soils (Helyar and Porter, 1989).

$$\text{OM} - \text{CEC}\ (\text{cmol}^{+}\ \text{kg}^{-1}\ \text{OM}) = \alpha\left(\text{pH} - 1.5\right) \qquad [24]$$

The net effect of nitrogen cycling on NAAR is illustrated using three examples presented subsequently: a closed native system in which N enters by biological fixation and all N is internally recycled, an agricultural production system using ammonium-based fertiliser; and an agricultural production system using nitrate-based fertiliser.

Closed native system with N entering by biological N fixation: The process of nitrogen fixation is neutral and results in the formation of organic N in plant material. On decomposition, mineralisation of one mole of organic N results in a consumption of one mole of H^+ and production of one mole of NH_4^+. Subsequent nitrification of NH_4^+ to NO_3^- releases two moles of H^+ for each mole of NH_4^+ nitrified. If the one mole of NO_3^- produced is taken up by plants, one mole of H^+ will be consumed. Thus in a closed system (where no N losses occur) the biological fixation of N and its subsequent movement through the N cycle is a net neutral process. However, if losses of NO_3^- were to occur through leaching, a net acidification would result because the lost NO_3^--N would not be available for uptake by plants and therefore could not completely offset the acidity produced by the process of nitrification (Figure 36).

Ammonium-based fertiliser: If nitrogen is added to an agricultural production system in the form of an ammonium based fertiliser (e.g. ammonium sulphate; but not ammonium nitrate because of the nitrate) the first reaction that occurs is the release NH_4^+ to the soil solution (this step is neutral). If one mole of ammonium based fertiliser NH_4^+-N is nitrified to NO_3^-, 2 moles of H^+ are produced and 1 mole of NO_3^- is present in the soil. If that 1 mole of NO_3^- is taken up by the roots, 1 mole of H^+ ions is consumed, leaving 1 mole of H^+ behind. Thus the immediate effect of adding an ammonium-based fertiliser is acidification irrespective of whether all of the NO_3^- is taken up. However, such tight N cycling does not occur in open agricultural systems. In agricultural systems, NO_3^- can be denitrified or leached and N taken up by plants is removed in harvested products. The result of these N losses is that a portion of the acidity released by nitrification cannot be neutralised because the lost N cannot move completely through the nitrogen cycle. Losses or removal of N from agricultural systems therefore results in a net acidification (Table 5, Figure 36).

Nitrate-based fertiliser: If nitrogen is added to a soil in the form of a nitrate based fertiliser (except ammonium nitrate because of the ammonium), the process of nitrification is avoided. For each mole of fertiliser NO_3^- taken up by plants, one mole of H^+ ions is consumed and the process can be considered as alkalising. Thus nitrate based fertilisers have the potential to neutralise acidifying processes (Table 5).

The acidification rate induced by the nitrogen cycle is greatest when large amounts of acidifying N-fertilisers are applied, nitrate generated is lost via denitrificaiton and leaching and nitrogen exported in the products is high (e.g. hay production). Although the use of nitrate-based fertilisers could reduce acidification rates, they are generally more expensive

than urea or ammonia-based fertilisers. Other fertilisers, such as elemental sulphur are also acidifying (Table 5, Figure 36).

The remaining processes involved in determining NAAR (Equation [23]) include the addition of alkali (L_{ad}) usually in the form of a liming agent (lime, dolomite etc), direct addition of acid (H^+_{ad}) usually in the form of rainfall and acid export (H^+_{ex}) is usually in the form of leaching, runoff, and ground water flow.

Table 5: Lime requirement for different sources of N and S with different leaching patterns.

Fertiliser or source	Lime Requirement* (kg/kg N)		
	No leaching	50% leaching	100% leaching
Ammonium sulphate Mono-ammonium phosphate	3.6	5.4	7.1
Di-ammonium phosphate	1.8	3.6	5.4
Urea Ammonium nitrate Aqueous ammonia Anhydrous ammonia Legume-fixed N	0	1.8	3.6
Sodium nitrate Potassium nitrate Calcium nitrate	-3.6	-1.8	0
Elemental sulphur	3.1	N/A	N/A
Sulphate sulphur	0	N/A	N/A

*Source: Fenton and Helyar (2000); Dolling et al. (2001)

4.3.1 Measuring NAAR based on ΔpH and pHBC

NAAR can be determined by rearranging Equation [1] to solve for NAAR and entering measured values for ΔpH and pHBC (Equation [25]). Since acidity can be generated or consumed by processes operating differentially at a variety of soil depths, to obtain a true estimate of the NAAR at a given location, the change in pH (ΔpH), the pH buffer capacity (pHBC), bulk density (BD) and volume of soil (V) associated with each soil layer need to be defined and summed (Equation [26] where i refers to the individual soil layers). This multi layer approach has the added benefit of aiding in the definition of active processes and where they are occurring in the soil profile as well as the development of appropriate management practices that may alleviate or counter the generation of acidity.

$$\mathrm{NAAR} = \Delta\mathrm{pH} \times \mathrm{pHBC} \times \mathrm{BD} \times \mathrm{V} \qquad [25]$$

$$\mathrm{NAAR} = \sum_{i=1}^{n} \Delta\mathrm{pH}_i \times \mathrm{pHBC}_i \times \mathrm{BD}_i \times \mathrm{V}_i \qquad [26]$$

If the “repeated measurements in time” approach typical of a soil monitoring program is being used, the method requires the determination of pH at different times, sufficiently far apart to

detect a pH difference. This will usually be in the range of years to ten's of years. There is thus the potential for other properties to change. Noble et al. (1998) determined a change in pHBC from 1.8 to 2.2 (cmol H^+ kg^{-1} pH $unit^{-1}$) over a period of 36 years. In addition, land use can affect BD between the time of the original and current measurements. So the question is; which pHBC to use? Helyar and Porter (1989) suggest that it is appropriate to use the pHBC at the end of the time period, and that was the method used by Ridley and Coventry (1995). However, others have taken a different approach. Noble et al. (1998) used the pHBC's measured at both the beginning and at the end of the time period; Lesturgez et al. (2006) used the average of the two measurements; and Slattery et al. (1998) used a pHBC value defined at a time between the determination of the two pH values. In this report we recommend using the pHBC at the end of the period as this is the pHBC that will determine the final pH measured in response to the acid that has been added.

In a monitoring program, it may also be of value to include comparisons of managed and unmanaged or differently managed soils all sampled at a single time. In this "repeated measurements in space" approach, the NAAR method requires the determination of pH at two sites. The question arises as to which of the pHBC values determined should be used (e.g. unmanaged versus managed). Dolling and Porter (1994) showed a change in pHBC from 0.39 to 0.59 (cmol H^+ kg^{-1} pH $unit^{-1}$) when comparing a site which had been cleared for 80 years to an uncleared site. Noble et al. (2003) showed a decrease in pHBC from 2.8 to 1.9 (cmol H^+ kg^{-1} pH $unit^{-1}$) when comparing a site which practised green cane trash blanketing to burning of sugar cane residues. It is also quite likely that BD will differ between the two sites. This form of analysis will not be a major component of a soil monitoring program, but if invoked to compare specific soils, it is suggested that the pHBC and BD should be measured on the most intensively managed site and used with the difference in pH between the sites to determine NAAR.

In spite of the issues with determining NAAR using this approach, it is probably the most reliable for the repeated measurement through time approach used in soil monitoring programs. This method integrates acid addition over many years and relies on few assumptions. Unfortunately, this method requires measurement over many years under a specific well documented land use. Thus while it is useful, it cannot be used to predict acidification rates under new systems or systems under which no measurements have been taken. Additionally, it does not provide insight into the magnitude of the particular processes that may have led to an acidification of a soil and thus, the development of effective ameliorative management practices or interventions will be difficult.

4.3.2 Measuring NAAR based on carbon and nitrogen cycling and direct additions of acid and alkali

The formula from Helyar and Porter (1989) (Equation [23]) which shows the dependence of NAAR on carbon and nitrogen cycling and direct additions of acid and alkali can be used to calculate NAAR if the various component are known, can be estimated, or are negligible.

In the carbon cycle components, the bicarbonate reactions are either deemed negligible in acid soils or estimated from Table III in Helyar and Porter (1989). OA_{ad} and OA_{ex} can be calculated from farm records of organic amendments and crop off-take and the ash alkalinity of the material. Ash alkalinities of a number of products (Jarvis and Robson, 1983a,b; Slattery et al., 1991; Fenton and Helyar, 2000) or leaf litter (Noble and Randall, 1998) have been determined. Ash alkalinities calculated from cation excess for a number of crops have also been determined (Hyland et al., 1995; International Fertilizer Industry Association, 1992; International Plant Nutrition Institute, 2008; Javis and Robson, 1983a,b. see Appendix 5). Not all cations and anions were analysed for each crop so there may be some overestimations and some underestimations. However, K and P were analysed on all and these represent the two dominant nutrients. A selection of crops and pastures from the above sources and relevant to Australian agriculture is presented in Table 6. The OA_{ac} component of the NAAR calculation is usually estimated from changes in organic matter content of the soil (which may be negative) over the period of the study. The contribution of OA_{ac} to acidity is difficult to determine experimentally; however, Equation [24] with α=32 $cmol^{+}\ kg^{-1}$ OM can be used to provide an estimate.

For the nitrogen cycle, $NH_4^+{}_{ad}$ and $NO_3^-{}_{ad}$ can be obtained from fertiliser records; $NH_4^+{}_{ac}$ and $NO_3^-{}_{ac}$ can be assessed from appropriate soil analysis; however, $NH_4^+{}_{ex}$ and $NO_3^-{}_{ex}$ (i.e. leaching and runoff losses) are difficult to measure. Generally, $NH_4^+{}_{ac}$ is assumed to be negligible in most agricultural soils as any added NH_4^+ is rapidly converted to NO_3^-. Thus $NH_4^+{}_{ex}$ is also assumed to be negligible. This then leaves $NO_3^-{}_{ex}$ to be estimated, and some authors have done so (Ridley et al., 2001, 2003, 2004; and John Armour et al., unpublished). However, as it is difficult to measure, some authors (e.g. Ridley et al., 1990; Dolling et al., 1994; Moody and Aitken, 1997) have used NAAR values established from ΔpH and pHBC, and partial NAAR values from the carbon and nitrogen cycle to estimate the difference, which is attributed $NO_3^-{}_{ex}$ for that particular system of land use and management. In some cases, $NO_3^-{}_{ex}$ is ignored (Noble et al., 1998) or the 'official value' (Adams, 1984) of the nitrogen applied is used ("Vineyard Soil Acidity and Sodicity Calculator 2-1" by Richard Merry).

The lime additions should be known from farm records and this, with the neutralising value of the product, will determine the value of L_{ad}.

The acid additions refer to acid added in rainfall or lost by leaching and run off. Typically they are either ignored or calculated from Table IV in Helyar and Porter (1989). In regions that receive acid rain, ignoring these terms would not be sensible.

Table 6: Ash alkalinities associated with crops and pastures grown in Australia.

Crop	Component	Ash Alkalinity (kg $CaCO_3$ Mg^{-1} product)	Reference	Method
Wheat	grain	9	4	Ash
Oats	grain	3	1,5,6	KP, KCaMgPS, Ash
Barley	grain	8	4	Ash
Sorghum	grain	4	6	Ash
Maize	grain	3	6	Ash
Millet	grain			Ash
Rice	grain	3	1,2	KCaMgPS
Triticale	grain	7	4	Ash
Mung Bean	grain	15	5	KCaMgP
Cotton	lint	18	6	Ash
Cotton	seed	10	6	Ash
Lupin	grain	20	4	Ash
Oil poppies				
Peanut	grain	10	1,2	KCaMgP, KCaMgPS
Field Pea	grain	16	1,5	KCaMgP, KCaMgPS
Chick Pea	grain	34	1,5	KCaMgPS
Canola	grain	-5	5	KCaMgPS
Sugarcane	stem	13	3,6	Ash
Sunflower	grain	29	1	KCaMgP
Vetch				
Lentil	grain	4	5	KCaMgPS
Faba bean	grain	10	5	KCaMgPS
				Ash
Phalaris		28	4	Ash
Cocksfoot		26	4	Ash
Subterranean clover	whole plant	41	4	Ash
	stems	45	4	Ash
	leaves	49	4	Ash
Sorrel		39	4	Ash
Lucerne		60	4	Ash
Mixed grasses		30	4	Ash
Tropical grass/legume	20% legume	41	1	KCaMgPS
Fodder legumes		56	1	KCaMgPS
Forage grasses		35	6	Ash
Medic		44	5	KCaPS

Reference code

1 International Fertilizer Industry Association (1992)
2 International Plant Nutrition Institute (2008)
3 Richard Merry (unpublished)
4 Slattery et al. (1991)
5 Hyland et al. (1973)
6 Pierre and Banwart (1973)

4.3.3 Summary of NAAR measurement methods

Both methods of calculating NAAR (Equation [26] and Equation [23]) have issues of concern. The ΔpH and pHBC method assumes a constant NAAR and linear relationship of pH change with time. But this need not be the case. A number of researchers have shown that rate of pH change diminishes with time, especially after lime incorporation which induces an initial flush of mineralisation and acidification. Again, while it is not possible to account for this with historical data, any future monitoring should be tailored to allow for the determination of any non linearity and avoid the assumption above that NAAR is constant over the monitoring period. The Carbon and Nitrogen cycle method relies on good records of yield and product; ash alkalinity of product; amount and type of fertiliser use; and probably the most difficult, an estimate of nitrate leaching. Accurate estimate of nitrate leaching is important as it is estimated to contribute about 3 times more acidity to cereal based cropping systems than the combined contributions of product removal and fertiliser use (Fisher et al., 2003). This quantification of contributions to acidity is not possible by the ΔpH and pHBC method.

4.4 Lime requirement for liming to a desired soil pH

Lime requirement (LR) is the amount of lime required to raise pH of a soil layer to the desired value. Liming is effective in ameliorating acidity; however, due to practical and economic constraints is mostly used to ameliorate topsoil acidity. Liming is less effective in ameliorating subsoil acidity because of its costs associated with its deep placement and its slow mobility down the soil profile (Whitten et al., 2000). Ameliorating topsoil acidity, however, benefits the subsoil as failure to ameliorate topsoil acidity may result in accelerated subsoil acidification (Sumner and Noble, 2003). A target pH that the soil should be limed to is more difficult to define as this depends on the objective of liming and the crop grown as different crops have different pH values at which crop production is maximised (Edmeades and Ridley, 2003). A primary objective of liming is to control Al phytotoxicity. Aluminium becomes soluble at phytotoxic concentrations to sensitive species at pH_{water} below ~5.0-5.2. To remove Al phytotoxicity, liming should be designed to raising soil pH_{water} to 5.5 or higher. Increasing pH to values >5.5 may provide benefits to nutrient availability and therefore enhance productivity

Calcitic lime (composed mostly of calcium carbonate) is the most common form of lime used to raise soil pH. Dolomitic lime (calcium and magnesium carbonates) is also used, particularly when a source of magnesium is required in addition to the requirement of neutralising acidification. Other sources of lime include calcium hydroxide and various industrial by-products. Typically the liming potential of all products is converted to its $CaCO_3$

equivalent. To calculate lime requirement (LR) in Mg $CaCO_3$ ha^{-1} we need an equation that performs the following functions:

- Converts pHBC from its measured units of cmol kg^{-1} pH^{-1} to units of Mg $CaCO_3$ t^{-1} pH^{-1}
- Calculates the weight (t ha^{-1}) of soil being limed based on a liming depth
- Calculates the amount of lime required to increase soil pH from its current to its target values

These requirements are met by Equation [27] in which pHBC is given in cmol kg^{-1} pH^{-1}, depth refers to the liming depth given in m, and bulk density (BD) is given in Mg soil m^{-3} soil. Since most sources of lime are not pure, a correction to reflect the neutralising value (NV) expressed as $\%CaCO_3$ of the lime source is required. A final correction can be made to account for the percentage of coarse fractions such as gravels in soil (Equation [28]).

$$\text{LR}\left(\text{Mg Lime ha}^{-1}\right) = \left(\text{pHBC} \times 5 \times \text{depth} \times \text{BD}\right) \times \left(\text{pH}_{\text{Target}} - \text{pH}_{\text{Current}}\right) \quad [27]$$

The factor 5 in Equations [27] and [28] converts LR from the pHBC unit of cmol(H+) kg^{-1} pH^{-1} to the LR unit of Mg lime/ha. A $cmol_c$ of $CaCO_3$ is 0.5 g.

$$\text{LR}\left(\text{Mg Lime ha}^{-1}\right) = \left(\text{pHBC} \times 5 \times \text{depth} \times \text{BD}\right) \times \left(\text{pH}_{\text{Target}} - \text{pH}_{\text{Current}}\right) \times \left(\frac{100}{\text{NV}}\right) \times \left(1 - \frac{\text{CF}}{100}\right) \quad [28]$$

Once a soil has been limed to achieve a desired pH, it is then important to define how much lime is required to maintain this pH. This is equivalent to the amount of lime required to offset NAAR and is referred to as the maintenance lime requirement (MLR). When NAAR is expressed in units of kg $CaCO_3$ ha^{-1} y^{-1}, MLR (kg $CaCO_3$ ha^{-1} y^{-1}) can be calculated according to Equation [29] where NV is the neutralising value of the lime source expressed as $\%CaCO_3$.

$$\text{MLR (Mg lime ha}^{-1}\text{ y}^{-1}) = \frac{\text{NAAR}}{10 \times \text{NV}} \quad [29]$$

4.5 pH, Buffer capacity and NAAR protocols for a soil monitoring program

To allow for changes in laboratories or staff completing the analyses and for small changes over time, a number of reference soils should be prepared and stored in various locations around the country. A large quantity of each should be mixed and subsampled into individual containers according to Australian Standard “AS 4433.2-1997 Guide to the sampling of particulate materials - Preparation of samples”.

These samples will provide a reference over time and should be included in every batch of samples analysed.

If there is a need for change in laboratory, method, or staff, samples and reference samples should be analysed under both conditions for long enough to establish a relationship between the new and old conditions.

4.5.1 Measuring soil pH in a national soil monitoring program

As with most soil measurements, values obtained for soil pH are method-dependent. Soil pH is commonly measured as a 1:5 suspension in water or in dilute calcium chloride. The measured values vary with both the soil to solution ratio and the concentration of solution used to suspend the soil. Soil pH measured in dilute calcium chloride is normally lower than in water. It is desirable that a standard method of pH measurement is adopted to facilitate comparison of results spatially and temporally. We recommend measuring soil pH as a 1:5 air-dried soil to solution suspension in 10 mM calcium chloride (Rayment and Higginson, 1992). This method is less susceptible to seasonal changes in soil solution composition due to rainfall and fertiliser use.

4.5.2 Measuring pHBC in a national soil monitoring program

The current poor availability of pHBC data is exacerbated by lack of a nationally agreed method to measure soil pHBC. As a result, the 8 sets of pHBC data available to test pedotransfer functions were measured by 5 different methods which differed in factors such as reaction time, laboratory or field conditions, incubation or titration, valance of counter ion and ionic strength. This diversity of methods will give different results and limit comparisons between soils and undermine pHBC-based assessment of NAAR, lime requirement and time to critical pH. Consistent adoption and use of a reliable and quick method of pHBC measurement will be a requirement of a nationally coordinated soil monitoring program.

Titration is a reliable method of determining pHBC and lime requirement (Aitken and Moody, 1994, Aitken et al., 1990a, Helyar and Porter 1989, van Breemen, 1991). The titration method is relatively rapid and yield results similar to those of more time consuming moist incubation of soil with lime (Aitken et al., 1990a, Alabi et al., 1986, McLean et al., 1977). The soil suspension (1:5 in 0.002 M $CaCl_2$) is treated with incremental amounts NaOH or HCl and equilibrated over a period of 7 days at 25°C (Merry, 1997). Values of pHBC measured in NaOH and HCl were not significantly different for the majority of soil studied in Australia (Aitken and Moody, 1994). Toluene can be added to each soil sample to suppress microbial growth and the in situ production of acidity during the warm equilibration period. The use of chloroform as a microbial inhibitor should be avoided as it reacts with NaOH. The use of

0.002 M $CaCl_2$ ensures that the main counter ion valence and ionic strength are similar to those likely to be present under field conditions over the pH range of 4.0 to 6.5 (Aitken and Moody, 1994).

The pHBC of soil samples examined varied by a factor of ~15 depending on organic carbon and clay content. This poses a problem in determining how much NaOH and/or HC1 to apply to achieve the desired range of pH values during the titration assessment. A rapid measurement of soil pH in a single buffer provides an effective method to determine how much acid or alkali to add to the soil to achieve a successful titration analysis. The Mehlich (1976) single buffer discussed earlier is linear over the pH range 3.8 to 6.6 and has a buffer capacity of 0.004 $cmolH^+ ml^{-1} pH^{-1}$. Soil pH in Mehlich buffer is measured by first wetting 10 g soil with 10 g of water and then equilibrating with 10 ml of the buffer solution for 1 hr before measuring soil pH (Aitken et al., 1990). The total amount of soil acidity that reacted with the Mehlich buffer (initial pH 6.6) is determined from the soil pH in buffer (MpH) according to Equations [30] and [31].

$$\text{Total acidity } \left(\text{cmol } H^+ \text{ kg}^{-1} \text{ soil}\right) = \left(6.6 - \text{MpH}\right) \times 0.04 \times 100 \quad [30]$$

$$\text{Total acidity } \left(\text{g } CaCO_3 \text{ kg}^{-1} \text{ soil}\right) = \left(6.6 - \text{MpH}\right) \times 2 \quad [31]$$

Total acidity that reacted with the Mehlich buffer is well correlated to the reported lime requirement to pH 5.5 obtained by moist incubation of soil with lime (Figure 26) (Aitken et al., 1990). All soils used by Aitken et al. (1990) had a pH_{CaCl2} <5.5. The Mehlich buffer therefore did not react with any soil acidity in the pH 5.5 to 6.5 range and the lime requirement to shift soil pH to 6.5 could not be calculated from change in buffer pH. Typically this requirement is up to ~2 times larger than lime requirement to reach pH 5.5. We therefore propose that the amounts of alkali needed in soil titrations to expand the pH range to ~6.5 should be up to 2 times the total acidity measured by the Mehlich single buffer method. With subsequent testing and correlation analysis it is possible that the use of a one hour Mehlich single buffer method may be able to replace the 7-day titration method of determining pHBC. It is proposed that all samples to be collected and analysed within a national soil monitoring program are analysed using both the titration and Mehlich single buffer methodologies initially and then a protocol established to define the nature of subsequent measurements taken through time. A more detailed presentation of the methodologies associated with these measurements is given in Appendix 3.

4.5.3 Measuring NAAR in a national soil monitoring program

During the monitoring project, NAAR can also be determined from the change in pH and the measured pHBC. If the pHBC changes during the measurement period, the most recent pHBC should be used. Alternatively, but more complicated, both the pHBCs can be used if

the concept of a ‘nominal’ NAAR is used as described in Appendix 3. If paired sites are used to obtain historical acidification rates, the pHBC from the site being estimated (usually the developed site) should be used

To complement this and gain a better mechanistic understanding of the processes involved, estimates of carbon, nitrogen and acid/alkalinity cycles should be obtained. This will reveal the causes of acidification and thus guide management decisions. When calculating ash alkalinity (part of carbon cycle) of the product removed, the preference is for the ashing method rather than a calculation based on cation/anion balance.

Ash alkalinity should be expressed in terms of product removed. For example if wheat grain has 12% moisture, then the ash alkalinity should be expressed on that weight basis. This makes it simpler to convert weight of product removed to an alkalinity removed. Similarly, ash alkalinity should be based on the actual product removed, not just the part consumed or used. For example, if whole corn cobs (including husks) are exported from the farm then the ash alkalinity should be determined on the whole cob and husks, not just the kernels.

Often the acid addition by any incoming water is ignored. However, this may be important if irrigation water is used or rain in the area is known to be acid.

When using NAAR in a predictive way to estimate time to critical pH, the ‘root distribution’ function of Bloesch et al. (2006) should be used if the actual distribution of roots through the profile is not known.

5 DATA MANAGEMENT, REPORTING AND INSTITUTIONAL ARRANGEMENTS

5.1 Data capture and storage

All data collected within the proposed soil monitoring system will be housed within CSIRO's NatSoil relational database (see McKenzie, 2000b). A site is the core element of NatSoil which translates to the Monitoring Site described in this report. At each site there may be several observations of the soil profile depending on the level of bulking of soil samples performed. For each profile (single core or bulked cores) there will be soil layers each of which can have a variety of soil attributes (measured values) stored in a number of tables.

Several deficiencies identified in the use of NatSoil to house data from the proposed monitoring program include the absence of a structure to handle the proposed monitoring program hierarchy (monitoring regions, monitoring units and monitoring sites), an inability to document meta data associated with observations and no ability to record temporal changes.

To deal with the hierarchy issue, sample identification codes could be altered by adding prefixes and/or suffixes linked through new database tables to the monitoring program hierarchy (e.g. Table 7 where the site identification code is linked through to monitoring region, unit and site identification strata). Such a variation in NatSoil would not alter the underlying structure but would make partitioning and aggregation of data on the basis of spatial elements of the monitoring program hierarchy more efficient. Similar modifications could be incorporated into NatSoil to allow collection of temporal data from individual sites. The new measurement methodologies included in the monitoring program can be accommodated through the entry of a series of new method codes. In summary, with minor alteration, NatSoil would provide an effective means of housing and working with soil data collected in the monitoring program. A similar approach could be used to accommodate entry of data from wind and water erosion monitoring.

Table 7: Examples of proposed Monitoring Site identification in NatSoil sites table. The form of the sample identification shown in this table is a recommendation only.

Site Identification Number	Monitoring Region	Monitoring Unit	Monitoring Site	Description
AY001	Avon	YDS	001	Master Site
AY001C1	Avon	YDS	001	Characterisation 1
AY001C2	Avon	YDS	001	Characterisation 2
AR002	Avon	Rocky	001	Master Site
AR002A	Avon	Rocky	001	Individual A, shallow
AR002AC	Avon	Rocky	001	A Characterisation 1
AR002B	Avon	Rocky	001	Individual B, deep
AR002BC	Avon	Rocky	001	B Characterisation 1

Building ability to record critical events that occur between observations would also be beneficial. For example, defining the date that a conversion from one vegetation type to another took place. A new table (e.g. Table 8), linked to the sites table, that includes a date field and a text field into which a categorised description of the event could be entered would meet the required need.

Table 8: Proposed table to record critical events between soil collections.

Site identification number	Date of event	Event description
AY001	28/04/2010	Soil cultivated to allow sowing of crop into previous grass pasture
AY001	15/03/2011	Soil limed with 20 t $CaCO_3$ ha^{-1} having a neutralising value of 78%
AY002	3/3/2010	Site was deep ripped to a depth of 40 cm on a 6m interval
AY055	18/07/2011	A horizon lost from 80% of the site due to significant overland flow erosion in response to a 320mm rainfall event..

5.2 Primary data collection

Table 9 provides an example of the primary data to be collected from the monitoring sites. Primary data is used in this context to refer to measured values (not estimated, interpolated or recalculated data). The variation in these primary data over monitoring sites could be used to statistically define the temporal change across a monitoring unit. In line with the question, "*How much has the value of variable 'A' changed and what is the probability that the change is real*?" each monitoring unit should be considered separately. Analysing pooled data across monitoring units can help clarify the question *Are the changes consistent in different environments*? However, this pooling does not increase the statistical power of the analysis.

5.3 Secondary data

From the primary monitoring data such as pH and organic carbon, a range of secondary values can be calculated for the monitoring sites and the monitoring units. Values for these data will be defined through the application of queries run on the database tables and thus do not need data tables. However, formulation of a table that defines the calculations used and justification within the database would be useful. An example of secondary data would be the amount of organic carbon contained in the 0-30 cm soil layer expressed in units of Mg C ha^{-1} which requires use of carbon content, bulk density and soil layer thickness primary

data for each of the individual soil layers collected within the 0-30 cm layer. Another example would be the calculation of net acid addition rate (NAAR) from soil pH and pHBC primary data.

Table 9: Example of primary pH and organic carbon data to be collected at a monitoring site.

				Date				
			units	surf	0-10	10-20	20-30	0-30
Layer thickness			m		0.1	0.1	0.1	0.3
Bulk Density			g/m3		1.42	1.49	1.51	
Layer soil mass			tonnes/ha		1420	1490	1510	4420
coarse fragments			%		0	0	0	
clay			%		4	6	8	
pH (CaCl2)					5.21	4.92	4.74	
pH Buffer Capacity		pHBC	cmol H^+ kg^{-1} pH^{-1}		x	y	z	w

Organic Carbon:								
Surface Plant Residues	OM mass	SPR	t/ha	0.7				
	OC	SPRC	%	45				
	OC mass		t/ha	0.32				
Buried Plant Residues	OC	BPRC	%		0.5	0.01	0	0.16
	OC mass		t/ha		7.1	0.15	0	7.25
Particulate	OC	POC	%		0.65	0.25	0.1	0.33
	OC mass		t/ha		9.23	3.73	1.51	14.5
Humus	OC	HUM	%		0.35	0.15	0.05	0.18
	OC mass		t/ha		4.97	2.24	0.76	7.96
Recalcitrant	OC	ROC	%		0.01	0	0	0
	OC mass		t/ha		0.14	0	0	0.14
Total Soil	OC	TOC	%		1.01	0.4	0.15	0.51
	OC mass		t/ha		14.3	5.96	2.27	22.6
Mineralisable carbon			% of TOC		4.2	2.1	1.0	
Mineralisable nitrogen			% of TN		3.6	1.5	.8	

5.4 Reporting

The measurement protocols specified in this report have been defined to quantify temporal responses of soil carbon and acidification in response to imposed land management practices. However, the selection of regions considered vulnerable to change renders the results region specific. Aggregation of data should not progress beyond the monitoring region within which it was collected and statements pertaining to the implications of land management on soil properties should not be extended beyond the regions within which the soils were collected.

5.5 Institutional Arrangements

The proposed national monitoring program will be a collaborative initiative between CSIRO, the Federal Government and relevant state and territory agencies. It will thus extend current arrangements under the Australian Collaborative Land Evaluation Program (ACLEP)

overseen by the National Committee on Soil and Terrain. It is envisaged that a sub-committee of the NCST will oversee the operations of the program – but these governance and accompanying technical arrangements will need to be developed at the start of the operational phase.

It will be a requirement of a national program that the information is stored in the Australian Soil Resource Information System and is accessible from the system. Most state and territory agencies will have their own version of the information embedded in the overall soil information system.

The details of these institutional arrangements and any legal or contractual issues need to be identified and resolved prior to the national program starting.

Recommendation: That ACLEP with relevant State Agencies and BRS develop and agree to support a long-term system to assess, and record land use and land management practices as an integral part of the national monitoring scheme

Recommendation: That ACLEP in conjunction with key database officers in State Agencies amend the NatSoil database to accommodate soil condition indicator monitoring data including expanded land use/management options consistent with ALUM codes and develop a field / laboratory database with storing, reporting and analysis tools for pH, OC and related soil indicators

Recommendation: That ACLEP with relevant State Agencies develop confidentiality protocols to ensure that monitoring data acquired for individual paddocks/farms cannot be traced back to individual farmers in any reporting within ASRIS

Recommendation: That the National Committee on Soil and Terrain (NCST) be invited to recommend on governance guidelines for the conduct of the National Soil Condition Monitoring Program, an overview committee and processes for day to day management.

6 REFERENCES

Adams F 1984. Crop responses to lime in the southern United States. `Adams F, Editor. Soil acidity and liming. Second ed. Madison: American Society of Agronomy, Inc/Crop Science Society of America, Inc/Soil Science Society of America, Inc; 1984; pp. 211-265.

Aitken R L, P W Moody and P G McKinley 1990. Lime requirement of acidic Queensland soils. 1. Relationship between soil properties and pH buffer capacity. Australian Journal of Soil Research 28, 695-701.

Aitken R L, P W Moody and P G McKinley 1990a. Lime requirement of acidic Queensland soils. II. Comparison of methods for predicting lime requirement. Australian Journal of Soil Research 28, 703-715.

Aitken R L, P W Moody and T Dickson 1998. Field amelioration of acidic soils in south-east Queensland. 1. Effect of amendments on soil properties. Australian Journal of Soil Research 49, 627-637.

Aitken RL and Moody PW 1994. The effect of valence and ionic strength on the measurement of pH buffer capacity. Australian Journal of Soil Research 32, 975-984.

Alabi K E, R C Sorensen, D Knudsen and G W Rehm 1986. Comparison of several lime requirement methods of coarse textured soils of north eastern Nebraska. Soil Science Society of America Journal 50, 937-941.

Amelung, W., Bol, R., Friedrich, C. 1999. Natural ^{13}C abundance: a tool to trace the incorporation of dung-derived carbon into soil particle-size fractions. Rapid Communications in Mass Spectroscopy 13, 1291-1294.

Anderson, D.W., Paul, E.A. 1984. Organo-mineral complexes and their study by radiocarbon dating. Soil Science Society of America Journal 48, 298-301.

Anderson, J.P.E., Domsch, K.H. 1978. A physiological method for the quantitative measurement of microbial biomass in soils. Soil Biology & Biochemistry 10, 215-221.

Angers, D.A., Edwards, L.M., Sanderson, J.B., Bissonnette, N. 1999. Soil organic matter quality and aggregate stability under eight potato cropping sequences in a fine sandy loam of Prince Edward Island. Canadian Journal of Soil Science 79, 411–417.

Appuhn, A., Joergensen, R.G. Raubuch, M., Scheller, E., Wilke, B. 2004. The automated determination of glucosamine, galactosamine, muramic acid, and mannosamine in soil and root hydrolysates by HPLC. Journal of Plant Nutrition and Soil Science 167, 17-21.

Bache B W 1988. Measurement and mechanisms in acid soils. Communications in Soil Science and Plant Analysis, 19, 775-92.

Baisden, W.T., Amundson, R., Cook, A.C., Brenner, D.L. 2002. Turnover and storage of C and N in five density fractions from California annual grassland surface soils. Global Biogeochemistry Cycles 16, 11-17.

Baldock, J.A. 2007. Composition and cycling of organic carbon in soils. *In* P. Marschner et al. (Eds). Nutrient Cycling in Terrestrial Ecosystems. Soil Biology. Volume 10. Springer Berlin Heidelberg pp. 1-35.

Baldock, J.A., Masiello, C.A., Gélinas, Y., Hedges, J.I. 2004. Cycling and composition of organic matter in terrestrial and marine ecosystems. Marine Chemistry 92, 39-64.

Baldock, J.A., Nelson, P.N. 1999. Soil Organic Matter. *In* M.E. Sumner (Ed). Handbook of Soil Science. pp. B25-B84. (CRC Press: Boca Raton, USA.)

Baldock, J.A., Oades, J.M., Waters, A.G., Peng, X., Vassallo, A.M., Wilson, M.A. 1992. Aspects of the chemical structure of soil organic materials as revealed by solid-state ^{13}C NMR spectroscopy. Biogeochemistry 16, 1-42.

Baldock, J.A., Skjemstad, J.O. 1999. Soil organic carbon/soil organic matter. *In* K.I. Peverill et al. (Eds). Soil Analysis: An Interpretation Manual. pp. 159-170. (CSIRO Publishing: Collingwood.)

Baldock, J.A., Skjemstad, J.O. 2000. Role of the soil matrix and minerals in protecting natural organic materials against biological attack. Organic Geochemistry 31, 697-710.

Baldock, J.A., Smernik, R.J. 2002. Chemical composition and bioavailability of thermally altered *Pinus resinosa* (Red pine) wood. Organic Geochemistry 33, 1093-1109.

Barrow N J and V C Cox, 1990. A quick and simple method for determining the titration curve and estimating the lime requirement of soil. Australian Journal of Soil Research 28, 685-694.

Bauhus, J., Khanna, P.K., Raison, R.J. 1993. The effect of fire on carbon and nitrogen mineralisation and nitrification in an Australian forest soil. Soil Biology & Biochemistry 31, 621-639.

Beavis, J., Mott, C.J.B. 1996. Effects of land use on the amino acid composition of soils: 1. Manured and unmanured soils from the Broadbalk continuous wheat experiment, Rothamsted, England. Geoderma 72, 259-270.

Beavis, J., Mott, C.J.B. 1999. Effects of land use on the amino acid composition of soils: 2. Soils from the Park Grass experiment and Broadbalk wilderness, Rothamsted, England. Geoderma 91, 173-190.

Bell, M.J., Moody, P.W., Connolly, R.D., Bridge, B.J. 1998. The role of active fractions of soil organic matter in physical and chemical fertility of Ferrosols. Australian Journal of Soil Research 36, 809-819.

Benzing-Purdie, L.M., Nikiforuk, J.H. 1989. Carbohydrate composition of hay and maize soils and their possible importance to soil structure. Journal of Soil Science 40, 125-130.

Blair, G.J., Lefroy, R.D.B., Lisle, L. 1995. Soil carbon fractions based on their degree of oxidation, and the development of a carbon management index for agricultural systems. Australian Journal of Agricultural Research 46, 1459-1466.

Bloesch P, Le Grand J, Moody P, Moss J, and Searle, R (2006). *Soil erosion and soil condition hazard maps for Great Barrier Reef Catchments of Queensland*. Natural Resources, Mines & Water, Brisbane, Australia, QNRM06214

Bonde, T.A., Christensen, B.T., Cerri, C.C. 1992. Dynamics of soil organic matter as reflected by natural C-13 abundance in particle-size fraction of forested and cultivated Oxisols. Soil Biology & Biochemistry 24, 275-277.

Bromfield SM, Cumming RW, David DJ, Williams CH 1983. Change in soil pH, manganese and aluminium under subterranean clover pasture. Australian Journal of Experimental Agriculture and Animal Husbandry 23:181-91.

Brookes, P.C. 1995. The use of microbial parameters in monitoring soil pollution by heavy metals. Biology and Fertility of Soils 19, 269-279.

Broos, K., Macdonald, L.M., Warne, M.St.J., Heemsbergen, D.A., Barnes, M.B., Bell, M., McLaughlin, M.J. 2007. Limitations of soil microbial biomass carbon as an indicator of soil pollution in the field. Soil Biology & Biochemistry 39, 2693-2695.

Bureau of Rural Sciences, 2006, 'Guidelines for land use mapping in Australia: principles, procedures and definitions', Edition 3, Bureau of Rural Sciences, Canberra

Cambardella, C.A. 1998. Experimental verification of simulated soil organic matter pools. *In* R. Lal et al. (Eds). Soil processes and the carbon cycle. Lewis Publishers; Boca Raton, FL. pp. 519-526.

Cambardella, C.A., Elliott, E.T. 1992. Particulate soil organic matter changes across a grassland cultivation sequence. Soil Science Society of America Journal 56, 777-783.

Campbell, C.A., Biederbeck, V.O., Zentner, R.P., Lafond, G.P. 1991. Effect of crop rotations and cultural practices on soil organic matter, microbial biomass and respiration in a thin Black Chernozem. Canadian Journal of Soil Science 71, 363-376.

Cayley JWD, McCaskill MR, Kearney GA 2002. Changes in pH and organic carbon were minimal in a long term field trial study in Western District of Victoria. Australian Journal of Agricultural Research 53:115-26.

Chan, K.Y., Heenan, D.P., Oates, A. 2002. Soil carbon fractions and relationship to soil quality under different tillage and stubble management. Soil & Tillage Research 63, 133-139.

Chefetz, B., Salloum, M.J., Deshmukh, A.P., Hatcher, P.G. 2002. Structural components of humic acids as determined by chemical modifications and carbon-13 NMR, pyrolysis, and thermochemolysis-gas chromatography/mass spectrometry. Soil Science Society of America Journal 66, 11-59.

Christensen, B.T. 1996a. Carbon in primary and secondary organomineral complexes. *In* M.R. Carter and B.A. Stewart (Eds). Advances in soil science – structure and organic matter storage in agricultural soils. CRC Lewis. Boca Raton. pp. 97-165.

Christensen, B.T. 1996b. Matching measurable soil organic matter fractions with conceptual pools in simulation models of carbon turnover: revision of model structure. *In* D.S. Powlson et al. (Eds). Evaluation of soil organic matter models using existing long-term datasets. NATO ASI Series I: Global Environmental Change, vol 38. Springer-Verlag, Berlin Heidelberg New York, pp. 143-159.

Christensen, B.T. 2001. Physical fractionation of soil and structural and functional complexity in organic matter turnover. European Journal of Soil Science 52, 345-353.

Coleman N T and G W Thomas 1964. Buffer curves of acid clays as affected by the presence of ferric iron and aluminium. Soil Science Society of America proceeding 28, 187-190.

Conteh, A., Blair, G.J., Rochester, I.J. 1998. Soil organic carbon fractions in a vertisol under irrigated cotton production as affected by burning and incorporating cotton stubble. Australian Journal of Soil Research 53, 655-667.

Conyers M K, K R Helyar and G J Poile 2000. pH buffering: the chemical response of acidic soils to added alkali. Soil Science 165, 560-566.

Conyers MK, Heenan DP, Poile GJ, Cullis BR, Helyar KR 1996. Influence of dryland agricultural management proactices on acidification of a soil profile. Soil & Tillage Research 37:127-41.

Conyers MK, Mullen CL, Scott BJ, Poile GJ, Braysher BD 2003. Long-term benefits of limestone applications to soil properties and to cereal crop yields in southern and central New South Wales. Australian Journal of Experimental Agriculture 43(1):71-8.

Cookson, W.R., Marschner, P., Clark, I.M., Milton, N., Smirk, M.N., Murphy, D.V., Osmon, M., Stockdale, E.A., Hirsh, P.R. 2006. The influence of season, agricultural management, and soil properties on gross nitrogen transformations and bacterial community structure. Australian Journal of Soil Research 44, 453-465.

Coventry DR 1992. Acidification problems of duplex soils used for crop-pasture rotations. Australian Journal of Experimental Agriculture 32(901-914).

Coventry DR, Slattery WJ 1991. Acidification of soil associated with lupins grown in a crop rotation in north-eastern Victoria. Australian Journal of Agricultural Research 42:391-7.

Dalal, R.C. 1998. Soil microbial biomass - what do the numbers really mean? Australian Journal of Experimental Agriculture 38, 649–665.

Dalal, R.C., Harms, B.P., Krull, E., Wang, W.J., Mathers, N.J. 2005. Total soil organic matter and its labile pools following mulga (*Acacia aneura*) clearing for pasture

development and cropping. 2. Total and labile nitrogen. Australian Journal of Soil Research 43, 179-187.

Davidson, E.A., Ackermann, I.L. 1993. Changes in soil carbon inventories following cultivation of previously untilled soils. Biogeochemistry 20, 161-164.

de Gruijter, J,J, Brus, D.J, Birkens, M.F.P. and Knotters, M (2006) *Sampling for Natural Resource Monitoring*. Springer, 332 pp.

De Lanne, R.D., Reddy, C.N., Patrick, W.H. Jr. 1981. Organic matter decomposition in soil as influenced by pH and redox conditions. Soil Biology & Biochemistry 13, 533-534.

Dolling PJ and Porter WM 1994. Acidification rates in the central wheatbelt of Western Australia. 1. On deep yellow sand. Australian Journal of Experimental Agriculture 34:1155-1164.

Dolling PJ, Moody PW, Noble AD, Helyar KR, Hughes B, Reuter DJ and Sparrow L 2001. Soil Acidity and Acidification. (National Land and Water Resources Audit).

Dolling PJ, Porter WM, and Rowland IC 1994. Acidification rates in the central wheatbelt of Western Australia. 2. On a sandy duplex soil. Australian Journal of Experimental Agriculture 34:1165-1172.

Donohue, R., Roderick, M., and McVicar, T. (2007). Correcting Long-Term AVHRR Reflectance Data Using the Vegetation Cover Triangle.CSIRO Land and Water Science Report 26/07. Canberra: CSIRO. http://www.clw.csiro.au/publications/science/2007/sr26-07.pdf

Edmeades DC and Ridley AM 2003. Using lime to ameliorate topsoil and subsoil acidity. In Z. Rangel (ed). Handbook of Soil Acidity. Pp 297-336. Marcel Dekker, NY.

Ellert, B.H., Janzen, H.H., VandenBygaart, A.J., Bremer, E. 2008. Measuring change in soil organic carbon storage. *In* M.R., Carter, E.G., Gregorich (Eds). Soil Sampling and Methods of Analysis, 2nd Edition., CRC Press Taylor & Francis, Boca Raton, FL, USA, pp. 25-38.

Fenton G and Helyar KR 2000. Soil acidification. Charman, PEV and Murphy, BW, Eds. Soils: Their properties and management. 2nd ed. Melbourne: Oxfor University Press; pp. 223-237.

Fisher J Diggle A. and Bowden B 2003. Quantifying the acid balance for broad-acre agricultural systems. Rengel, Z., ed. Handbook of Soil Acidity. New York: Marcel Dekker, Inc.; pp. 117-133.

Franzluebbers, A.J. 1999. Potential C and N mineralisation and microbial biomass from intact and increasingly disturbed soils of varying texture. Soil Biology & Biochemistry 31, 1083-1090.

Franzluebbers, A.J., Hons, F.M., Zuberer, D.A. 1994. Seasonal changes in soil microbial biomass and mineralisable C and N in wheat management systems. Soil Biology & Biochemistry 26, 1469-1475.

Friedel, J.K., Scheller, E. 2002. Composition of hydrolysable amino acids in soil organic matter and soil microbial biomass. Soil Biology & Biochemistry 34, 315-325.

Gilbert MA, Dickinson G, Moody PW, Cooksley D 1995. Soil acidification under nitrogen fertilised pastures in tropical Australia. Date RA, Grundon NJ, Rayment GE, Probert ME, editors. Plant-Soil Interactionsat low pH: Principles and Management. Dordecht: Kluwer Academic Publishers, 785-90.

Gillman GP, Sumpter EA (1986). Surface charge characteristics and lime requirements of soils derived from basaltic, granitic and metamorphic rocks in high-rainfall tropical Queensland. *Australian Journal of Soil Research* **24**, 173-192.

Godsey C B, G M Pierzynski, D B Mengel and R E Lamond 2007. Evaluation of common lime requirement methods. Soil Science Society of America Journal 71, 843-850.

Golchin, A., Oades, J.M., Skjemstad, J.O., Clarke, P. 1994. Study of free and occluded particulate organic matter in soils by solid state ^{13}C CP/MAS NMR spectroscopy and scanning electron microscopy. Australian Journal of Soil Research 32, 285-309.

Gregorich, E.G., Carter, M.R., Doran, J.W., Pankhurst, C.E., Dwyer, L.M. 1997. Biological attributes of soil quality. *In* E.G. Gregorich and M.R. Carter (Eds). Soil Quality for Crop Production and Ecosystem Health. Elsevier, Amsterdam. pp. 81-113.

Hamer, U., Marschner, B., Amelung, W., Brodowski, S. 2004. Interactive priming of black carbon and glucose mineralisation. Organic Geochemistry 35, 823-830.

Hassink, J. 1994. Effect of soil texture on the size of the microbial biomass and on the amount of C and N mineralised per unit of microbial biomass in Dutch grassland soils. Soil Biology & Biochemistry 26, 1573-1581.

Helyar KR, Cullis BR, Furniss K, Kohn GD, Taylor AC 1997. Changes in the acidity and fertility of red earth soil under wheat-annual pasture rotations. Australian Journal of Agricultural Research 48:561-86.

Helyer K R and W M Porter, 1989. Soil acidification, its measurement and the processes involved. In Soil Acidity and Plant Growth. A D Robson (ed). Academic Press, Australia. Pp61-101.

Hochman Z, Godyn D L and B J Scott 1989. The integration of data on lime use by modelling. In A D Robson (ed) Soil acidity and plant growth. Academic Press, Australia. Pp265-301.

Houghton, R.A. 2005. The contemporary carbon cycle. *In* W.H. Schlesinger (Ed). Biogeochemistry. Amsterdam Elsevier Science. pp. 473-513.

Hoyle, F.C., Murphy, D.V., Fillery, I.R.P. 2006. Temperature and stubble management influence microbial CO2-C evolution and gross N transformation rates. Soil Biology & Biochemistry 38, 71–80.

Hyland M 1995. Soil nutrient depletion. Australian Journal of Soil and Water Conservation.; 8(1):28-30.

International Fertiliser Industry Association 1992. IFA World Fertilizer Use Manual. International Fertiliser Industry Association, Paris.

International Plant Nutrition Institute 2008. Planter's Diary 2008, International Plant Nutrition Institute, Singapore.

Janik, L.J., Skjemstad, J.O., Shepherd, K.D., Spouncer, L.R. 2007. The prediction of soil carbon fractions using mid-infrared-partial least square analysis. Australian Journal of Soil Research, 45, 73-81.

Janzen, H.H., Campbell, C.A., Brandt, S.A., Lafond, G.P., Townley-Smith, L. 1992. Light-fraction organic matter in soils from long-term crop rotations. Soil Science Society of America Journal 56, 1799-1806.

Jarvis SC and Robson AD 1983a. The effects of nitrogen nutrition of plants on the development of acidity in Western Australian soils. I. Effects with subterranean clover grown under leaching conditions. Australian Journal of Agricultural Research. 34:341-353.

Jarvis SC and Robson AD 1983b. The effects of nitrogen nutrition of plants on the development of acidity in Western Australian soils. I. Effects of differences in cation/anion balance between plant species grown under non-leaching conditions. Australian Journal of Agricultural Research. 34:355-365.

Jenkinson, D.S. 1977. The soil microbial biomass. New Zealand Soil News 25, 213-218.

Jenkinson, D.S., Hart, P.B.S., Rayner, J.H., Parry, L.C. 1987. Modelling the turnover of organic matter in long-term experiments at Rothamsted. INTECOL Bulletin 15, 1-8.

Jenkinson, D.S., Ladd, J.N. 1981. Microbial biomass in soil: measurement and turnover. *In* Ladd, J.N. (Ed), Soil Biochemistry, vol. 5. Dekker, New York, pp. 415-471.

Jenkinson, D.S., Parry, L.C. 1989. The nitrogen cycle in the Broadbalk wheat experiment: a model for the turnover of nitrogen through the soil microbial biomass. Soil Biology & Biochemistry 21, 535–541.

Jenkinson, D.S., Rayner, J.H. 1977. The turnover of soil organic matter in some of the Rothamsted classical experiments. Soil Science 123, 298–305.

Jenkinson., D.S. 1976. The effects of biocidal treatments on metabolism in soil. IV. The decomposition of fumigated organisms in soil. Soil Biology & Biochemistry 8, 203–208.

Jennings JN, Mabbutt JA (1986) Physiographic outlines and regions. In 'Australia, a geography. Volume 1. The natural environment.' (Ed. DN Jeans) (Sydney University Press: Sydney)

John, B., Yamashita, T., Ludwig, B., Flessa, H. 2005. Storage of organic carbon in aggregate and density fractions of silty soils under different types of land use. Geoderma 128, 63-79.

Kahle, M., Kleber, M., Torn, M.S., Jahn, R. 2003. Carbon storage in coarse and fine clay fractions of illitic soils. Soil Science Society of America Journal 67, 1732-1739.

Kamprath E J 1970. Exchangeable aluminium as a criterion for liming leached mineral soils. Soil Science Society of America proceedings 34, 252-254.

Krull, E.S., Baldock, J.A., Skjemstad, J.O. 2003. Importance of mechanisms and processes of the stabilisation of soil organic matter for modelling carbon turnover. Functional Plant Biology 30, 207-222.

Krull, E.S., Skjemstad, J.O. Baldock, J.A. 2005. Functions of soil organic matter and the effect on soil properties. GRDC report. pp. 1-129 (http://www.grdc.com.au/director/events/grdcpublications?item_id=2E7B554DF7964 6147F64C3704857B3EF&pageNumber=3)

Krull, E.S., Swanston, C.W., Skjemstad, J.O., McGowan, J.A. 2006. Importance of charcoal in determining the age and chemistry of organic carbon in surface soils. Journal of Geophyical Research 111, GO4001.

Ladd, J.N., Oades, J.M., Amato, M. 1981. Microbial biomass formed from ^{14}C, ^{15}N-labelled plant material decomposing in soils in the field. Soil Biology & Biochemistry 13, 119-126.

Lefroy, R.D.B., Blair, G.J., Strong, W.M. 1993. Changes in soil organic matter with cropping as measured by organic carbon fractions and ^{13}C natural isotope abundance. Plant and Soil 156, 399-402

Leifeld, J., Kögel-Knabner, I. 2005. Soil organic matter fractions as early indicators for carbon stock changes under different land-use? Geoderma 124, 143-155.

Lesturgez G, Poss R, Noble AD, Grünberger O, Chintachao W and Tessier D 2006. Soil acidification without pH drop under intensive cropping systems in northeast Thailand. Agriculture, Ecosystems and Environment 114:239-248.

Loss SP, Ritchie GSP, Robson AD 1993. Effect of lupins and pasture on soil acidification and fertility in Western Australia. Australian Journal of Experimental Agriculture 33:457-64.

Lowe, L.E. 1978. Carbohydrates in soil. *In* M. Schnitzer, S.U. Khan (Eds). Soil organic matter. Elsevier Scientific Publishing Company. Amsterdam. pp. 65-93.

Magid, J., Mueller, T., Jansen, L.S., Nielsen, N.E. 1996. Modelling the measurable: interpretation of field-scale CO_2 and N-mineralisation, soil microbial biomass and light fractions as indicators of oilseed rape, maize and barley straw decomposition. *In* G., Cadisch, K.E. Giller (Eds). Driven by nature: plant litter quality and decomposition. CAB International, Wallingford, UK, pp. 349-362.

Malhi, S.S., Harapiak, J.T., Nyborg, M., Gill, K.S., Monreal, C.M., Gregorich, E.G. 2003. Total and light fraction organic C in a thin Black Chernozemic grassland soil as affected

by 27 annual applications of six rates of fertilizer N. Nutrient Cycling in Agroecosystems 66, 33-41.

Mann, L.K. 1986. Changes in soil carbon storage after cultivation. Soil Science 142, 279-288.

Marschner, B., Brodowski, S., Dreves, A., Gleixner, G., Gude, A., Grootes, P.M., Hamer, U., Heim, A., Jandl, G., Ji, R., Kaiser, K., Kalbitz, K., Kramer, C., Leinweber, P., Rethemeyer, J., Schäffer, A., Schmidt, M.W.I., Schwark, L., Wiesenberg, G.L.B. 2008. How relevant is recalcitrance for the stabilization of organic matter in soils? Journal of Plant Nutrition and Soil Science 171, 91-110.

Martens, D.A., Loeffelmann, K.L. 2002. Improved accounting of carbohydrate carbon from plants and soils. Soil Biology & Biochemistry 34, 1393-1399.

Martens, D.A., Loeffelmann, K.L. 2003. Soil amino acid composition quantified by acid hydrolysis and anion chromatography-pulsed amperometry. Journal of Agricultural and Food Chemistry 51, 6521-6529.

Mason MG, Porter W.M., Cox WJ 1994. Effect of an acidifying nitrogen fertiliser and lime on soil pH and wheat yields. 1. Soil effects. Australian Journal of Experimental Agriculture 34:237-46.

McBratney A B, B Minasny, S R Cattle, R W Vervoort 2002. From pedotransfer functions to soil inference systems. Geoderma 109, 41-73.

McCaskill MR , Ridley AM, Okom A, White RE, Andrew MH, Michalk DL, Melland A, Johnston WH and Murphy SR 2003. SGS nutrient theme: environmental assessment of nutrient application to extensive pastures in the high rainfall zone of southern Australia. Australian Journal of Experimental Agriculture 43:927-44.

McCown, R.L., Hammer, G.L., Hargreaves, J.N.G., Holzworth, D.P., Freebairn, D.M. 1996. APSIM: a novel software system fro model development, model testing and simulation in agricultural systems research. Agricultural Systems 50, 255-271.

McDonald RC, Isbell RF, Speight JG, Walker J, Hopkins MS (1990) (Eds), 'Australian soil and land survey handbook – field handbook, 2nd edn.' (Inkata Press: Melbourne).

McKenzie NJ, Henderson B, McDonald WS (2002) Monitoring soil change. Principles and practices for Australian conditions. CSIRO Land and Water Technical Report 18/02, Canberra.

McKenzie NJ, Ryan PJ, Fogarty P, Wood J (2000) 'Sampling, measurement and analytical protocols for carbon estimation in soil, litter and coarse woody debris.' National Carbon Accounting System Technical Report No. 14, Australian Greenhouse Office, Canberra.

McKenzie, N.J. and Dixon, J.C. (2007) (editors) Monitoring soil condition across Australia Recommendations from the Expert Panels Prepared on behalf of the National Committee on Soil and Terrain for the National Land and Water Resources Audit

McLean E O 1973. Testing soils for pH and lime requirement. In L M Walsh and J D Beaton J D (ed) Soil testing and plant analysis. SSSA, Madison, Wisconsin, USA.

McLean E O, D J Eckert, G Y Reddy and J F Trierweiler 1977. An improved SMP soil lime requirement method incorporating double buffer and quick test features. Soil Science Society of America Journal 42, 311-316.

Mehlich A 1976. New buffer method for rapid estimation of exchangeable acidity and lime requirement of soils. Communication in Soil Science and Plant Analysis 7, 637-652.

Mendham, D.S., O'Connell, A.M. Grove, T.S. 2002. Organic matter characteristics under native forest, long-term pasture, and recent conversion to Eucalyptus plantations in Western Australia: microbial biomass, soil respiration, and permanganate oxidation. Australian Journal of Soil Research 40, 859-872.

Merry R H 1997. Estimation of simple lime requirement based on pH buffer capacity measurement and other soil factors. Unpublished report. CSIRO Land and Water.

Merry, R.H., Spouncer, L.R. 1988. The measurement of carbon in soils using a microprocessor-controlled resistance furnace. Communications in Soil Science and Plant Analysis 19, 707-720.

Millennium Ecosystem Assessment (2005). Ecosystems and Human Well-being: Desertification Synthesis. World Resources Institute, Washington, DC.

Miller, A.E., Schimel, J.P., Meixner, T., Sickman, J.O., Melack, J.M. 2005. Episodic rewetting enhances carbon and nitrogen release from chaparral soils. Soil Biology & Biochemistry 37, 2195-2204.

Minasny, B. and McBratney, A.B. 2006 A conditioned Latin hypercube method for sampling in the presence of ancillary information, Computers & Geosciences vol32, pp 1378-88

Moody PW, Aitken RL 1997. Soil acidification under some tropical agricultural systems. 1. Rates of acidification and contributing factors. Australian Journal of Soil Research 35:163-73.

Moody, P.W., Yo, S.A., Aitken, R.L. 1997. Soil organic carbon, permanganate fractions, and the chemical properties of acidic soils. Australian Journal of Soil Research 35, 1301-1308.

Moore G, P Dolling, B Porter and L Leonard 1998. Soil acidity. In Soil Guide. A handbook for understanding and managing agricultural soils. G Moore (ed). Published by DAWA pp127-140.

Muller, P.E. 1887. Studien über die natürlichen Humusformen und deren Einwirkunger auf Vegetation und Boden. Springer, Berlin.

Murphy, D.V., Recous, S., Stockadale, E.A., Fillery, I.R.P., Jensen, L.S., Hatch, D.J., Goulding, K.W.T. 2003. Gross nitrogen fluxes in soil: theory, measurement and application of 15Npool dilution techniques. Advances in Agronomy 79, 69–118.

Noble A D 2001. Assessment of pH buffer capacity. Report to NLWRA Theme 5 Project 4c on Acidic Soils and Acidification. http://www.anra.gov.au/topics/soils/pubs/soil_acid/phbc_report.pdf.

Noble AD and Randall PJ 1998. The impact of trees and fodder shrubs on soil acidification. Canberra: Rural Industies Reasearch and Development Corporation/Land and Water Research and Development Corporation/ Forest and Wood Products Research Development Corporation.

Noble AD, Cannon M, Muller D 1997. Evidence of accelerated soil acidification under *Stylosanthes*-dominated pastures. Australian Journal of Soil Research 35:1309-22.

Noble AD, Moody PW and Berthelsen S 2003. Influence of changed management of sugarcane on some soil chemical properties in the humid wet tropics of north Queensland. Australian Journal of Soil Research 41:1133-1144.

Noble AD, Thompson CH, Jones RJ and Jones RM 1998. The long-term impact of two pasture production systems on soil acidification in southern Queensland. Australian Journal of Experimental Agriculture 38:335-343.

Northcote, K H, G G Beckmann, E Bettenay, H M Churchward, D C van Dijk, G M Dimmock, G D Hubble, R F Isbell, W M McArthur, G G Murtha, K D Nicolls, T R Paton, C H Thompson, A A Webb and M J Wright (1960-68): 'Atlas of Australian Soils, Sheets 1 to 10, with explanatory data'. CSIRO and Melbourne University Press: Melbourne.

Northcote, K.H. 1979. A Factual Key for the Recognition of Australian Soils. 4th Ed. Rellim Press, Glenside, SA, Australia.

Northcote, K.H. (1979) A Factual Key for the recognition of Australian Soils. Rellim Technical Publications, Adelaide. 124 pp.

Northcote, K.H., Bettenay, E, Churchward, H.M. and McArthur, W.M. (1967) Atlas of Australian Soils. Sheet 5. Perth - Albany - Esperance Area, with Explanatory Data. CSIRO - Melbourne University Press, Melbourne, Vic., 55pp, 1 map.

Parton, W.J., Schimel, D.C., Cole, C.V., Ojima, D.S. 1987. Analysis of factors controlling soil organic matter levels in Great Plains grasslands. Soil Science Society of America Journal 51, 1173-1179.

Paustian, K., Andrén, O., Janzen, H.H., Lal, R., Smith, P., Tian, G., Tiessen, H., Van Noordwijk, M., Woomer, P.L. 1997. Agricultural soils as a sink to mitigate CO_2 emissions. Soil Use and Management 13, 230-244.

Peverill, K.I. Sparrow, L.A., Reuter, D.J. 1999. *In* K.I. Peverill et al. (Eds). Soil Analysis: An Interpretation Manual. pp. 1-369. (CSIRO Publishing: Collingwood.)

Pierre WH and Banwart WL 1973. Excess-base and excess-base/nitrogen ratio of various crop species and parts of plants. Agronomy Journal 65:91-96.

Poirier, N., Sohi, S.P., Gaunt, J.L., Mahieu, N., Randall, E.W. Powlson, D.S., Evershed, R.P. 2005. The chemical composition of measurable soil organic matter pools. Organic Geochemistry 36, 1174-1189.

Post, W.M., Izaurralde, R.C., Mann, L.K., Bliss, N. 2001. Monitoring and verifying changes of organic carbon in soil. Climatic Change 51, 73-99.

Poulenard, J., Michel, J.C., Bartoli, F., Portal, J.M., Podwojewski, P. 2004. Water repellency of volcanic ash soils from Ecuadorian páramo: effect of water content and characteristics of hydrophobic organic matter. European Journal of Soil Science 55, 487-496.

Powlson, D.S., Jenkinson, D.S. 1976. The effects of biocidal treatments on metabolism in soil. II. Gamma irradiation, autoclaving, air-drying and fumigation. Soil Biology & Biochemistry 8, 179–188.

Prosser IP, Hailes KJ, Melville MD, Avery RP, Slade CJ 1993. A comparison of soil acidification and aluminium under *Eucalyptus* forest and improved pasture. Australian Journal of Soil Research 31:245-54.

Raison, R.J., Connell, M.J., Khanna, P.K. 1987. Methodology for studying fluxes of soil mineral-N *in situ*. Soil Biology & Biochemistry 29, 1557-1563.

Raupach, MR. Kirby, J.M., Barrett, P.R., Briggs, H. Lu, H. and Zhang, L. (2001)Balances of Water, Carbon, Nitrogen and Phosphorus in Australian Landscapes: (2) Model Formulation and Testing. CSIRO Land and Water Technical Report 41/01

Rayment G. E and Higginson F. R. 1992. Australian laboratory handbook of soil and water chemical methods. Inkata press. Melbourne.

Rethemeyer, J., Kramer, C., Gleixner, G., John, B., Yamashita, T., Flessa, H., Andersen, N., Nadeau, M-J., Grootes, P.M. 2005. Transformation of organic matter in agricultural soils: radiocarbon concentration versus soil depth. Geoderma 128, 94-105.

Ridley AM and Coventry DR 1995. Soil acidification under pastures of north-eastern Victoria five years after liming. Date, R. A.; Grundon, N. J.; Rayment, G. E., and Probert, M. E., editors. Plant-Soil Interactions at Low pH: Principles and Management. Dordrecht: Kluwer Academic; pp. 473-477.

Ridley AM, Avery AL, Oram RN, Hunter J, Shovelton JB, Mahoney GP, and Müller WJ 2002. Long-term persistence of aluminium-tolerant and sensitive *Phalaris* lines on acidic soils and associated changes in soil acidity. Australian Journal of Experimental Agriculture 42(8):1033-1042.

Ridley AM, Christy BP, White RE, McLean T and Green R 2003. North-east Victoria SGS national experiment site: water and nutrient losses from grazing systems on contrasting soil types and levels of inputs . Australian Journal of Experimental Agriculture 43(7-8):799-815.

Ridley AM, Helyar KR, Slattery WJ 1990a. Soil acidification under subterranean clover (*Trifolium subterraneum* L.) pastures in north-eastern Victoria. Australian Journal of Experimental Agriculture 30:195-201.

Ridley AM, Slattery WJ, Helyar KR and Cowling A 1990. The importance of the carbon cycle to acidification of a grazed annual pasture. Australian Journal of Experimental Agriculture . 1990; 30:529-537.

Ridley AM, Slattery WJ, Helyar KR, Cowling A 1990b. Acidification under grazed annual and perennial grass based pastures. Australian Journal of Experimental Agriculture 30:539-44.

Ridley AM, Slattery WJ, Helyar KR, Cowling A 1990c. The importance of the carbon cycle to acidification of a grazed annual pasture. Australian Journal of Experimental Agriculture 30:529-37.

Ridley AM, White RE, Helyar KR, Morrison GR, Heng LK and Fisher R 2001. Nitrate leaching loss under annual and perennial pastures with and without lime on a duplex (texture contrast) soil in humid southeastern Australia. European Journal of Soil Science 52(2):237-252.

Riffaldi, R., Saviozzi, A., Levi-Minzi, R. 1996. Carbon mineralisation kinetics as influence by soil properties. Biology and Fertility of Soils 22, 293-298.

Rovira, P., Vallejo, V.R. 2000. Examination of thermal and acid hydrolysis procedures in characterization of soil organic matter. Communications in Soil and Plant Analysis 31, 81-100.

Rumpel, C., Seraphin, A., Goebel, M-O., Wiesenberg, G., Gonzales-Vila, F., Bachmann, J., Schwaark, L., Michaelis, W., Mariotti, A., Kögel-Knabner I. 2004. Alkyl C and hydrophobicity in B and C horizons of an acid forest soil. Journal of Plant Nutrition and Soil Science 167, 685-692.

Schnitzer, M. 1978. Humic substances: chemistry and reactions. *In* M. Schnitzer, S.U. Khan (Eds). Soil organic matter. Elsevier Scientific Publishing Company. Amsterdam. pp. 65-93.

Schöning, I., Morgenroth, G., Kögel-Knabner I. 2005. O/N-alkyl and alkyl C are stabilised in fine particle size fractions of forest soils. Biogeochemistry 73, 475-497.

Scott BJ, Fenton. I.G., Fanning AG, Schumann WG, Castleman LJC 2007. Surface soil acidity and fertilisty in the eastern Riverina and Western Slopes of southern New South Wales. Australian Journal of Experimental Agriculture 47(8):949-64.

Simard, R.R., N'dayegamiye, A. 1993. Nitrogen-mineralization potential of meadow soils. Canadian Journal of Soil Science 73,27-38.

Singh B, Odeh IOA, McBratney AB 2003. Acid buffering capacity and potential acidification of cotton soils in northern New South Wales. Australian Journal of Soil Research 41:875-88.

Skjemstad, J.O., Clarke, P., Taylor, J.A., Oades, J.M., McClure S.G. 1996. The chemistry and nature of protected carbon in soil. Australian Journal of Soil Research 34, 251-271.

Skjemstad, J.O., Janik, L.J., Taylor, J.A. 1998. Non-living soil organic matter: what do we know about it? Australian Journal of Experimental Agriculture 38, 667-680.

Skjemstad, J.O., Le Feuvre, R.P., Prebble, R.E. 1990. Turnover of soil organic matter under pasture as determined by 13C natural abundance. Australian Journal of Soil Research 28, 267-276.

Skjemstad, J.O., Reicosky, D.C., Wilts, A.R., McGowan, J.A. 2002. Charcoal carbon in US agricultural soils. Soil Science Society of America Journal 66, 1249-1255.

Skjemstad, J.O., Spouncer, L.R. 2003. Integrated soils modeling for the NCAS. National Carbon Accounting System Technical Report No. 36, Australian Greenhouse Office, Canberra.

Skjemstad, J.O., Spouncer, L.R. 2003. Integrated soils modelling for the NCAS. National Carbon Accounting System Technical Report No. 36, Australian Greenhouse Office, Canberra.

Skjemstad, J.O., Spouncer, L.R., Cowie, B., Swift, R.S. 2004. Calibration of the Rothamsted organic carbon turnover model (RothC ver. 26.3), using measurable soil organic carbon pools. Australian Journal of Soil Research 42, 79-88.

Skjemstad, J.O., Swift, R.S., McGowan, J.A. 2006. Comparison of the particulate organic carbon and permanganate oxidation methods for estimating labile soil organic carbon. Australian Journal of Soil Research 44, 255-263.

Skjemstad, J.O., Taylor, J.A., Janik L.J., Marvanek, S.P. 1999a. Soil organic carbon dynamics under long-term sugarcane monoculture. Australian Journal of Soil Research 37, 151-164.

Skjemstad, J.O., Taylor, J.A., Smernik, R.J. 1999b. Estimation of charcoal (char) in soils. Communication in Soil Science and Plant Analysis 30, 2283-2298.

Slattery WJ, Edwards DG, Bell LC, Coventry DR and Helyar KR 1998. Soil acidification and the carbon cycle in a cropping soil of north-eastern Victoria. Australian Journal of Soil Research 36:273-290.

Slattery WJ, Ridley AM and Windsor SM 1991. Ash alkalinity of animal and plant products. Australian Journal of Experimental Agriculture 31:321-324.

Smernick, R.J., Skjemstad, J.O., Oades, J.M. 2000. Virtual fractionation of charcoal from soil organic matter using solid state ^{13}C NMR spectral editing. Australian Journal of Soil Research 38, 665-683.

Smith, J.L., Paul, E.A. 1990. The significance of soil biomass estimations. *In* J.M. Bollag and G. Stotzky (Eds). Soil Biochemistry. Marcel Dekker. New York. pp. 357–396.

Sohi, S.P., Mahieu, N., Arah, J.R.M., Powlson, D.S., Medari, B., Gaunt, J.L. 2001. A procedure for isolating soil organic matter fractions suitable for modelling. Soil Science Society of America Journal 65, 1121-1128.

Sohi, S.P., Mahieu, N., Powlson, D.S., Madari, B., Smittenberg, R.H., Gaunt, J.L. 2005. Investigating the chemical characteristics of soil organic matter fractions suitable for modelling. Soil Science Society of America Journal 69, 1248-1255.

Sollins, P., Spycher, G., Glassman, C.A. 1984. Net nitrogen mineralisation from light-fraction and heavy-fraction forest soil organic matter. Soil Biology & Biochemistry 16, 31-37.

Spain, A.V., Isbell, R.F., Probert, M.E. 1983. Soil organic matter. *In* 'Soils: An Australian Viewpoint'. pp. 551-563. (CSIRO/Academic Press: Melbourne/London, UK.)

Sparling, G.P. 1992. Ratio of microbial biomass carbon to soil organic carbon as a sensitive indicator of changes in soil organic matter. Australian Journal of Soil Research 30, 195-207.

Spycher, G.P., Sollins, P., Rose, S. 1983. Carbon and nitrogen in the light fraction of a forest soil: Vertical distribution and seasonal patterns. Soil Science 135, 79-87.

Stevenson, F.J. 1986. Cycles of Soil: Carbon, nitrogen, phosphorus, sulphur, micronutrients. John Wiley and Sons. New York, NY.

Stevenson, F.J. 1994. Humus Chemistry. Genesis, Composition, Reactions. Second Edition. John Wiley and Sons. New York, NY.

Stockdale, E.A., Brookes, P.C. 2006. Detection and quantification of the soil microbial biomass - impacts on the management of agricultural soils. Journal of Agricultural Science 144, 285–302.

Sumner and Noble, 2003. Soil acidification: The world story. In Z. Rengel (ed). Handbook of Soil Acidity. Pp 1-28. Marcel Dekker, NY.

Swanston, C.W., Torn, M.S., Hanson, P.J., Southon, J.R., Garten, C.T., Hanlon, E.M., Ganio, L. 2005. Initial characterization of processes of soil carbon stabilization using forest stand-level radiocarbon enrichment. Geoderma 128, 52-62.

Swift, R.S. 2001. Sequestration of carbon by soil. Soil Science 166, 858-871.

Thackway, R., Cresswell I. D. 1995 An Interim Biogeographical Regionalisation for Australia: a Framework for Setting Priorities in the National Reserves System Cooperative Program, Australian Nature Conservation Agency, Canberra, ACT.

Thomas B, D Reuter, R Merry and B Robinson 2004, Assessing the pH and pH buffering capacity of Australian viticultural soils. Proceedings of 3rd Australian New Zealand Soils Conference, Sydney, 5-9 Dec 2004. Published on CDROM.

Trumbore, S.E., Zheng, S.H. 1996. Comparison of fractionation methods for soil organic matter ^{14}C analysis. Radiocarbon 38, 219-229.

Tuomela, M., Vikman, M., Hatakka, A., Itävaara, M. 2000. Biodegradation of lignin in a compost environment: a review. Bioresource Technology 72, 169-183.

Turchenek, L.W., Oades, J.M. 1979. Fractionation of organo-mineral complexes by sedimentation and density techniques. Geoderma 21, 311-343.

van Breemen N 1991. Soil acidification and alkalinisation. In Soil Acidity. B Ulrich and M E Sumner (eds). Springer, Berlin, pp 1-7.

Van Breemen N, Mulder J and Driscoll CT 1983. Acidification and alkalisation of soils. Plant and Soil 75: 283-308.

Vance, E.D., Brookes, P.C., Jenkinson, D.S. 1987a. Microbial biomass measurements in forest soils: determination of kc values and tests of hypotheses to explain the failure of the chloroform fumigation-incubation method in acid soils. Soil Biology & Biochemistry 19, 689-696.

Vance, E.D., Brookes, P.C., Jenkinson, D.S. 1987b. An extraction method for measuring soil microbial biomass C. Soil Biology & Biochemistry 19, 703-707.

Wakelin, S.A., Macdonald, L.M., Rogers, S.L., Gregg, A.L., Bolger, T.P., Baldock, J.A. 2008. Habitat selective factors influencing the structural composition and functional capacity of microbial communities in agricultural soils. Soil Biology & Biochemistry 40, 803-813.

Wardle, D.A. 1992. A comparative assessment of factors which influence microbial biomass carbon and nitrogen levels in soil. Biological Reviews 67, 321–358.

Weaver A R, D E Kissel, F Chen, L T West, W Adkins, D Rickman and L C Luvall 2004. Mapping soil pH buffering capacity of selected fields in the coastal plain. Soil Science Society of America journal 68, 662-668.

Whitten M. C, M. T. F. Wong and A. W. Rate 2000. Amelioration of subsurface acidity in the south west of Western Australia: downward movement and mass balance of surface incorporated lime after 2-15 years. *Australian Journal of Soil Research*, **38**, 711-728.

Wiesenberg, G.L.B, Schwark, L., Schmidt, M.W.I. 2004. Improved automated extraction and separation for soil lipid analysis. European Journal of Soil Science 55, 349-356.

Wolbach, W.S., Anders, E. 1989. Elemental carbon in sediments: Determination and isotopic analysis in the presence of kerogen. Geochimica et Cosmochimica Acta 53, 1637-1647.

Wong M. T. F. and Whittwer K. 2009. Positive charge discovered across Western Australian wheatbelt soils challenges key soil and nitrogen management assumptions. *Australian Journal of Soil Research* 47, 127-135.

Zak, D.R., Grigal, D.F., Ohmann, L.F. 1993. Kinetics of microbial respiration and nitrogen mineralization in Great Lakes' forests. Soil Science Society of America Journal 57,1100-1106.

7 APPENDICES

Appendix 1: Classification of soil characteristics within physiographic units of Jennings and Mabbott (1986)

Characterising Biophysical Processes (Classification of Regions)

Objective classification can relate each region to each other region and provide a basis for grouping regions with the intent of providing a framework to select regions. This requires consistent, objective data. It could include a landscape and climate parameters and even remote sensed interpretations. However, despite the effort in compiling the best soil data within ASRIS, there is no recent consistent national soil data set. Classification procedures are particularly vulnerable to inconsistent data.

The only reasonably consistent soil information is from the Atlas of Australian Soils mapping, (e.g. Northcote et al. 1967). In many ways it is not appropriate to use this mapping and the interpretations that have been assigned to the units (McKenzie and Hook, 1992, McKenzie, 2000b). However, it is still the only consistent and complete national dataset.

Thus, the Regions were intersected with the Atlas mapping. The data from these intersections was associated with the interpretations made by McKenzie and Hook, 1992, McKenzie, 2000b. From this the proportion of the region (based on area weighting) in a number of parameter classes were calculated:

- in each soil subdivisions Uc, Uf etc (from principal profile forms)
- in A horizon texture class (sands, sandy loams, loams, clay loams, light clays and medium to heavy clays)
- with alkaline surface (from Factual key, Northcote, 1979)
- with alkaline subsurface (from soil reaction trend, Alkaline)
- with shallow soil (<0.5m)
- with duplex soils (the D soil division)

Soils with coarse fragments (as distinguished by KS and K prefixes of the principal profile forms) were interpreted but discarded as the application of these prefixes appeared to be inconsistent across Australia.

Several different datasets of these soil parameters were compiled and each processed separately using modules of the numerical classification package PATN (Belbin, 1987).

The landscape, climate and satellite imagery data were not used in the classifications. If the exploration of classification of the soil data had not provided a relatively simple result, some of these other parameters would have been employed. Some of these data have been used in interpreting and characterising the regions and classifications.

The results of the analysis using two separate datasets are presented here: the soil subdivisions, and the soil properties (A horizon texture class, alkaline surface and subsurface, duplex soils and shallowness of the soil).

For each dataset, an hierarchical agglomerative classification (UPGMA - Unweighted Pair Group Method with Arithmetic Mean) of the 224 regions was produced. For initial interpretation, the classification was viewed at (arbitrary) 10, 20, 40 and 80 group levels. The results of these classifications were presented as a matrix of regions by attributes to allow the degree of accord of these parameters and the classification to be assessed. The spatial distribution of the classified groups was a major element in the interpretation of these results. Figure 37 and Figure 38 provide the distributions of the 10 group level for soil subdivisions and soil properties classifications, respectively. These classifications were reasonably similar (Table 10). There is closer accord between these at the 20 and 40 group levels.

The congruity of the classification with spatial proximity is a significant result. It is acknowledged that in part this is bound to happen at the finest level of the classification (i.e. with many groups) because adjacent regions are bound to share Atlas units. It is emphasized more in Figure 39 which is the 4 group level of classification from the soil properties. However, the strong regional nature of the classification at, for example, the 4 group level is as much a tribute to the consistency of the contributors of the Atlas as it is a representation of the distribution of fundamental characteristics of Australian soils. An examination of the reasons for these will not be presented here.

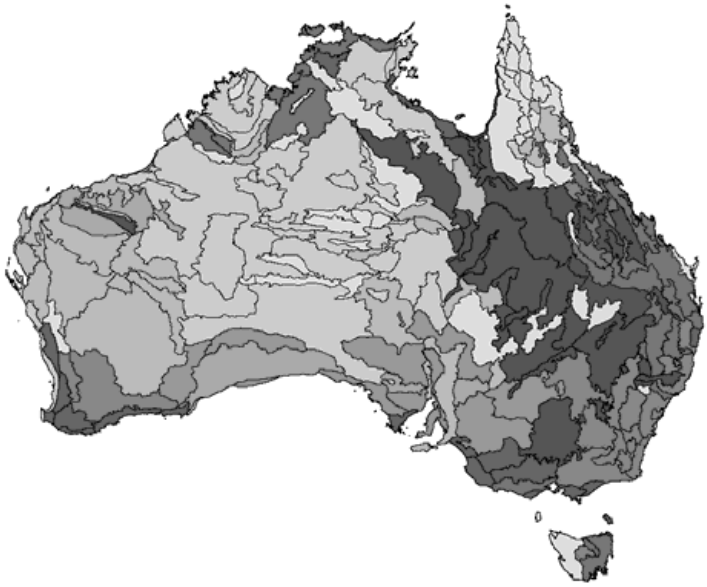


Figure 37: The 10 group classification of Soil subdivisions.

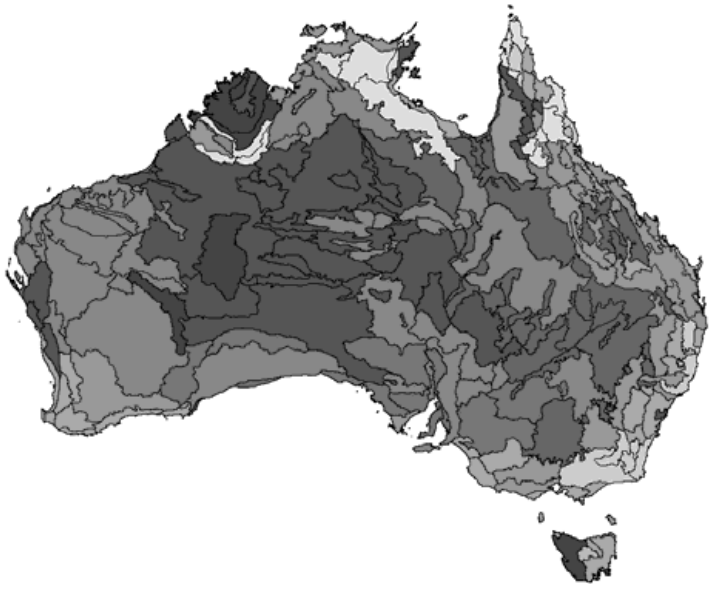


Figure 38: The 10 group classification of Soil properties.

Table 10: Accord between classifications at 10 group level. Rows are the classification groups from the soil parameters.

		Subdivision classification groups									
		1	1	2	2	2	3	3	3	4	4
gp4	gp10	1	2	3	4	5	6	7	8	9	10
1	1	5	4	5					1		
1	2	1					8				
1	3	1					1				
1	4	9	1				5	4	14		
1	5	5					3	11	3	2	
2	6	9		21	5	1	1	2		3	
2	7		1			11					
3	8	3		1	1			1		25	1
4	9	8	24	2			1		1		
4	10	2	3	1							

Which classification and how many groups are useful? To a degree this is not important at this stage. However, from the virtue of comprehension, that based on soil characteristics is recommended. The number of groups is not as important as the relationships. The choice will be integrated with the interpretations of the modifying processes. It is hoped that would be relatively narrow ranges of other biophysical properties in the classification groups. Table 11 provides a summary of the number of regions in classes of valley flatness, slope and Prescott index (related to precipitation). These show a significant relationship with the classification, particularly at the 4 group level.

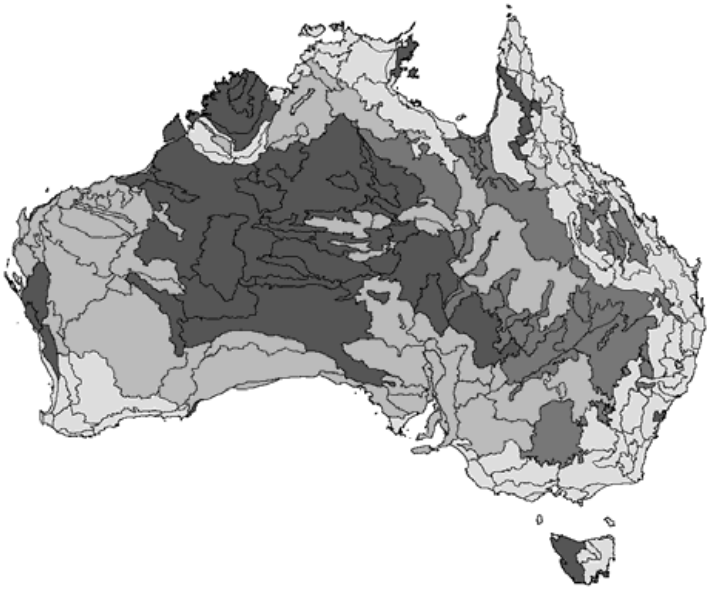


Figure 39: The 4 group classification of Soil properties.

Table 11: Summary of topography and precipitation by classification based on soil properties. Values are numbers of regions in each class.

			Valley flatness							Slope							Prescott				
gp4	gp10	gp20	H	L	LM	M	MH	V		F	FL	L	LM	M	V		L	LM	M	MH	H
1	1	1		2	1						1		1	1							3
1	1	2		11	1						1		8	3				1	10	1	
1	2	3		8	1						1		1	7					2	1	6
1	3	4		2										2							2
1	4	5		20	2		1	1			3		8	13					15	2	7
1	4	6	1	4	2			2			4		4	1					8		1
1	5	7	1	26	5	2		2		1	10		17	7	1				33	1	2
2	6	8		3	4	3		1		2	7	1	1				6		5		
2	6	9		3	8	1		3		1	11		3				11	1	3		
2	6	10		5	2	2	2				6		5				11				
2	6	11	1	4	1					1	2		3				5	1			
2	7	12	3	2	2	1	1	2		2	8	1					9	1	1		
2	7	13		1									1				1				
3	8	14	13	5	3		1	3		2	19		2	2			9		16		
3	8	15	6				1			5	2						4		3		
4	9	16		4	5	1	1			1	5		4	1			6	1	4		
4	9	17	3	5	8	2	2	1		2	15		4				19		2		
4	9	18		1	3						2	1	1				1		3		
4	10	19		2									1	1					1		1
4	10	20		2	1			1			2		1	1			2		2		

Characterising Land Use Pressures

The goal of this element of the study was to develop a representation of intensity of land use from which an inference could be made of the degree to which the land use is likely to be driving change in resource condition. The conceptual land use intensity scale is: native

vegetation, grazing native vegetation, grazing modified pasture, cropping, horticulture and irrigation.

Land use mapping has been conducted by State and Federal agencies over a number of decades and a number of variations of national data interpretations and compilations are available. Inconsistencies abound, despite concerted efforts such as common categories for land uses.

On the face of it the catchment scale interpretations prepared by State agencies should be more accurate since they are based on a combination of images and field observations. However, there are major difficulties with classes such as “grazing natural vegetation” being broadly interpreted by WA and Qld and more narrowly by other states. It includes areas which are not grazed, areas which are grazed and areas which are grossly modified pasture. The boundary between NSW and Qld is a major hiatus, particularly between “grazing natural vegetation” and “grazing modified pastures”. Parts of south western WA are classed as cropping but have not been cropped in decades. Therefore, this dataset is not consistent enough nor differentiated adequately for the required purpose.

The series of 1km classification from 1992 to 2001 (BRS 2006) apparently is a consistent approach although some agencies will disagree about the accuracy. It is derived from a series of rule based classification of satellite imagery. State boundaries are not evident except in so much as it is a reflection of different tenure types. Some of these will be real differences in land use intensity while others not. There are some issues with these data, but for this study it is more about the consistency of the classifications rather than jurisdictions. These are of two forms; correct representation of the land use and temporal consistency.

There is temporal variation; some understandable, some inconsistent. In particular, it is not plausible that land can be being grazing modified pastures in one year and grazing natural vegetation later. Some might be regeneration but much of these differences can only be differences in classification.

As would be hoped, there is a broad accord between the catchment and 1km scale mapping. Both show more or less the same significant regional patterns of land use (Figure 40 and Figure 41). It was concluded that the 1km grid (Figure 41) would provide a useful classification if care is made in interpretation.

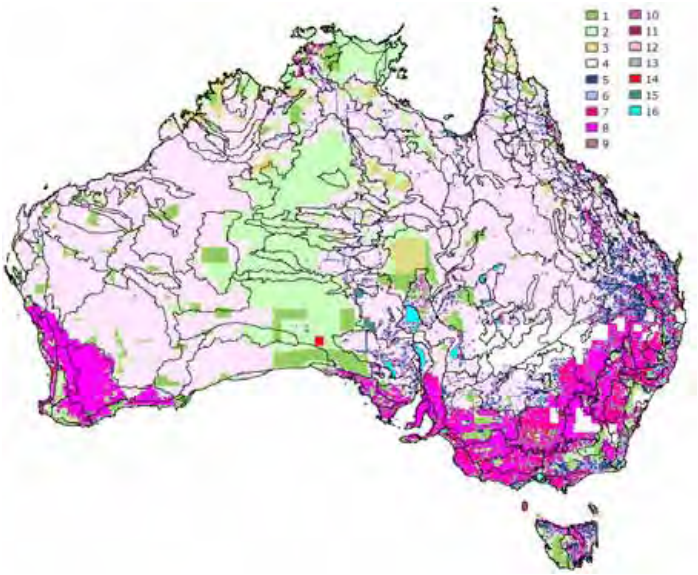


Figure 40: Land Use mapping catchment scale.

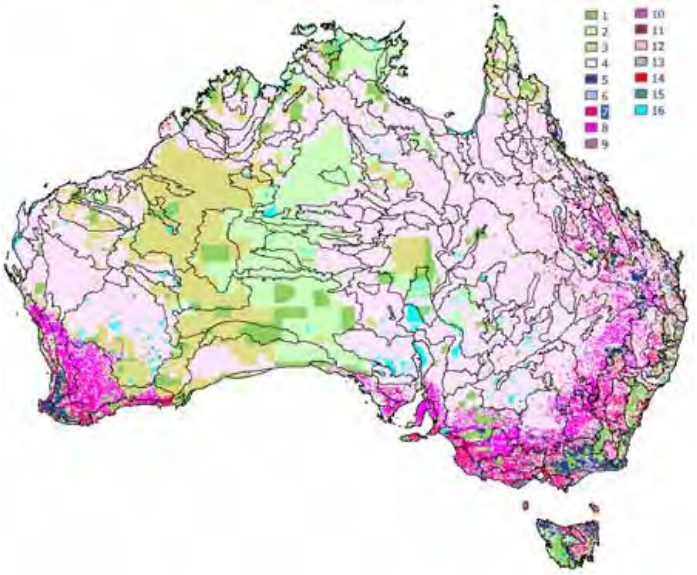


Figure 41: Land Use mapping 1km grid 2001.

The time series of land use was intersected with the physiographic regions and the proportion in each “16 class” converted to a % of the region. These were inspected for consistency between years. Data from 2001 was used for the classification, but some data was drawn from earlier years to overcome temporal inconsistencies. The data was aggregated to the % of agricultural and pastoral use in each region (Figure 42). This is used in priority setting (below).

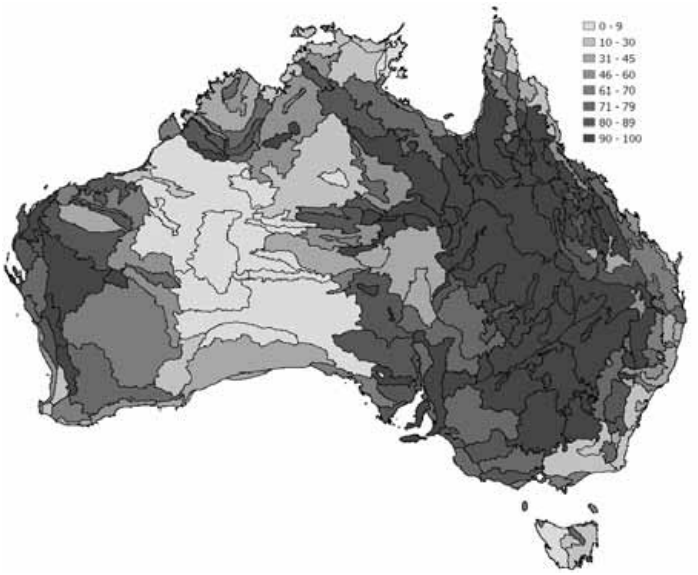


Figure 42: Percent of region in agriculture or pastoral land uses.

The classification was a threshold approach focusing of the preponderance of more intensive land uses first. Table 12 outlines these rules. In a few cases, the classification was adjusted if the amount of cropping and or grazing modified pastures in an earlier year would have meant a more intensive classification from 2001. The Burdekin area of Queensland was affected by this. Figure 43 is a representation of the geographic distribution of these land use classes.

Table 12: Land use classification scheme for physiographic regions.

Rule (in order)	% of Region	Class
Intensive Ag uses (Irrigation etc)	> 39.9	→I1
Intensive Ag uses (Irrigation etc)	> 9.9	
and Dryland cropping >= Grazing modified pastures		→IC
Intensive Ag uses (Irrigation etc)	> 9.9	
and Grazing modified pastures > Dryland cropping		→IP
Grazing natural vegetation	> 89.9	→G1
Dryland cropping	> 39.9	→C1
Dryland cropping	> 19.9	→C2
Grazing modified pastures	> 32.9	→P1
Dryland cropping	> 2.9	→C3
Grazing modified pastures	> 9.9	→P2
else		→G2
(regions with no agriculture or pastoralism)		blank

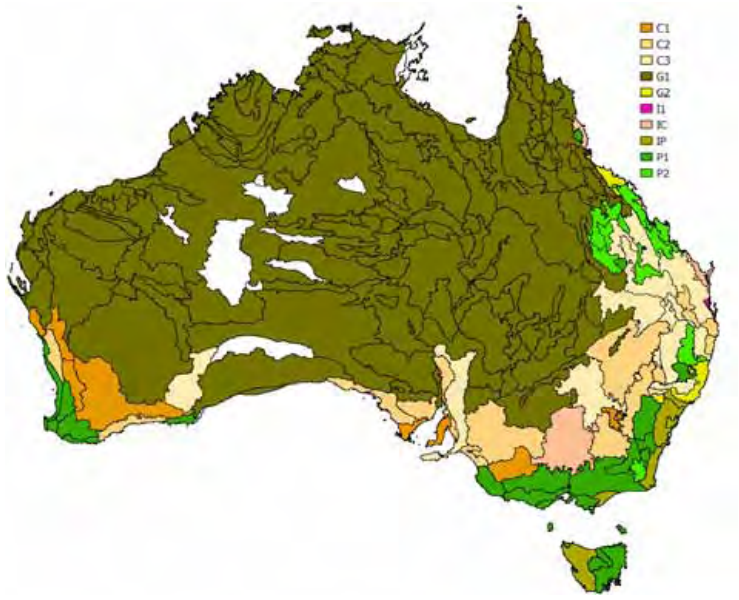


Figure 43: Land use classes for physiographic regions.

While this classification provides a sound general impression of the major land uses of the physiographic regions, the grazing native vegetation class (G1) is extremely broad. In some areas there is almost no grazing, others there is low level browsing, but in others there is grazing of areas to which such as buffel and stylo have been added. Thus, the differences in grazing pressure are not reflected in this classification.

Stock density and profit datasets were interpreted to assist in qualifying the grazing pressure. The stock density (Figure 44) shows the highest densities in the medium to high rainfall margins of Australia. Importantly, it shows a significant regional variation in the stock within the G1 areas. While this is also reflected in the Agricultural profit (Figure 45) there is not a linear relationship with stock. It is concluded that profit is not a reflection of land use intensity. By these interpretations of stock, the G1 area was partitioned into low, low/medium, medium and high intensity. This is represented in Figure 46 by the intensity of shading with increasing intensity corresponding to a darkening of the shading.

From these we have a basis for assessing agricultural intensity. There are not 13 equal steps in an intensity gradient of the 14 classes (combining Figure 43 and Figure 44 plus the "0"). In broad terms no stock is at one end and C1 and I1 are at the other end. These 14 have been grouped into 6 classes of intensity. To demonstrate the process of consolidation, a series of cross tabulations of these classifications with the classification based on the soil properties (Table 13 and Table 14). The regional classifications by soil characters (Figure 38 and Figure 39) are used to represent one aspect of geography.

The geographic distribution of these Land Use intensity classes is shown in Figure 47. This shows quite clearly the main cropping country in the darkest shades with various levels of grazing intensity declining as the shading diminishes. To a certain degree this is over stating

the relative impacts as this is the pressure of the agriculture on the land used for that purpose within each of these regions. The addition of cross hatching in Figure 48 shows those regions with at least 50% agriculture. Thus, Table 14 converts to Table 15 with an agricultural usage class added. In this 22 regions are in the highest intensity class and 41 in the next.

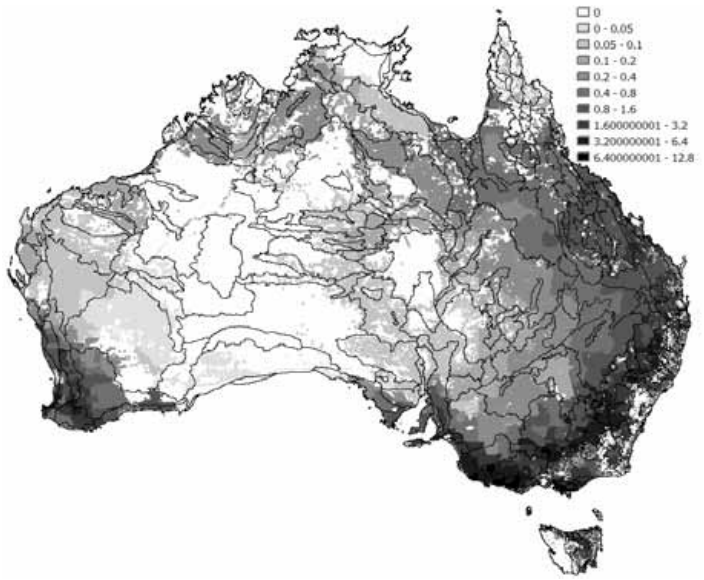


Figure 44: Stock densities.

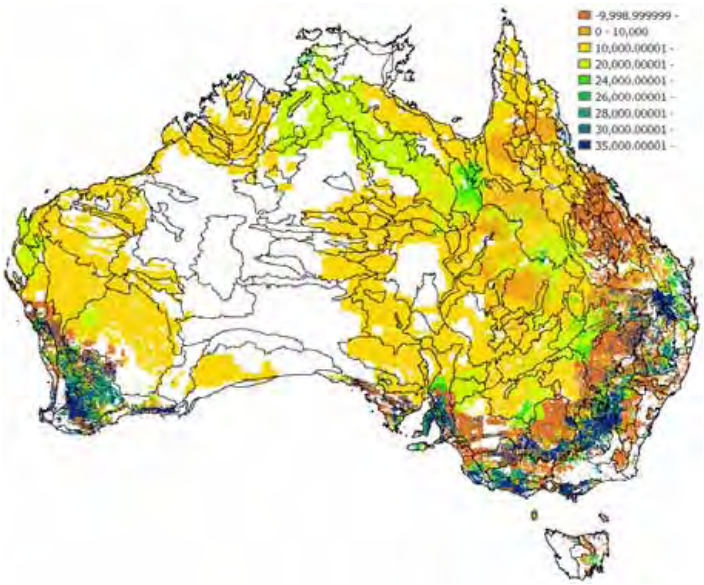


Figure 45: Agricultural profit.

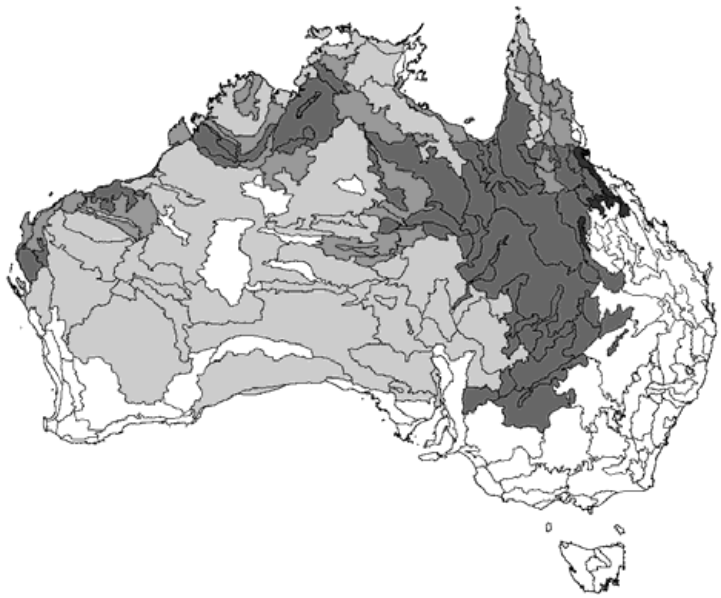


Figure 46: Grazing pressure within G1 class. Note this is based on the stock density within the areas that are used for grazing, not all land in the regions (grazing pressure increases as the shading darkens).

Table 13: Land use classes by soil classification.

		Land Use Class										
gp4	gp10	0	G1	G2	P2	P1	IP	C3	C2	C1	IC	I1
1	1	1	13									1
1	2		1	1	1	3	1	1			1	
1	3					2						
1	4		5	1	2	16	2		3	2	1	1
1	5		14	1	6	3	1	6	3	2		
2	6	1	39					2		1		
2	7	1	5					1	4	1		
3	8		21		1			5	3	1	1	
4	9	8	25				1		1	1		
4	10	1	4				1					
		12	127	3	10	24	6	15	14	8	3	2

Table 14: Land use classes (plus stock classes) by Soil Classification with Land use intensity class. Numbers in bold are # for Intensity class.

		Land Use Intensity															
		1	2	3	4	5							6				
gp4	gp10	0	G1L	G1LM	G1M	G1H	G2	P2	P1	IP	C3		C2	C1	IC	I1	
1	1	**1**	**4**	**6**	**3**											1	**1**
1	2			**1**			1	1	3	1	1	**7**			1		**1**
1	3								2			**2**					
1	4			**4**		1	1	2	16	2		**22**	3	2	1	1	**7**
1	5		**2**		**8**	4	1	6	3	1	6	**21**	3	2			**5**
2	6	**1**	**15**	**8**	**16**						2	**2**		1			**1**
2	7	**1**	**3**		**2**						1	**1**	4	1			**5**
3	8		**2**	**1**	**18**			1			5	**6**	3	1	1		**5**
4	9	**8**	**14**	**8**	**3**					1		**1**	1	1			**2**
4	10	**1**	**2**	**2**						1		**1**					
		12	**42**	**30**	**50**	5	3	10	24	6	15	**63**	14	8	3	2	**27**

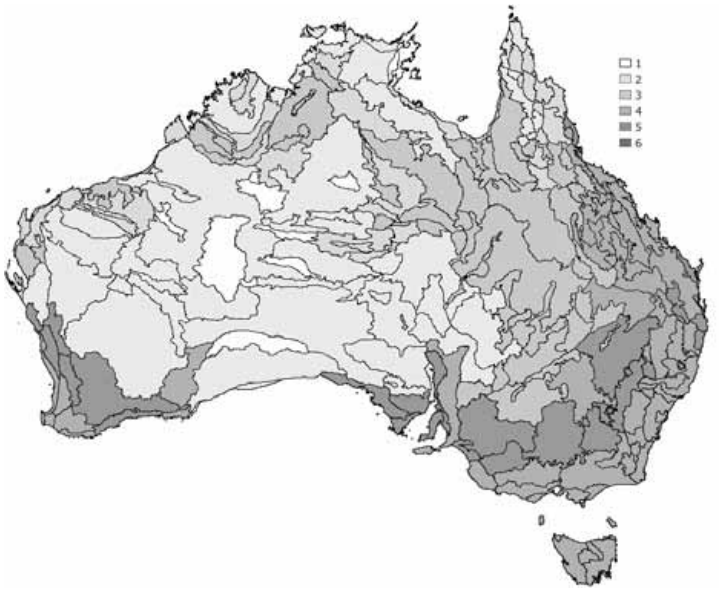


Figure 47. Distribution of Agricultural Land Use Intensity Classes (see Table 14).

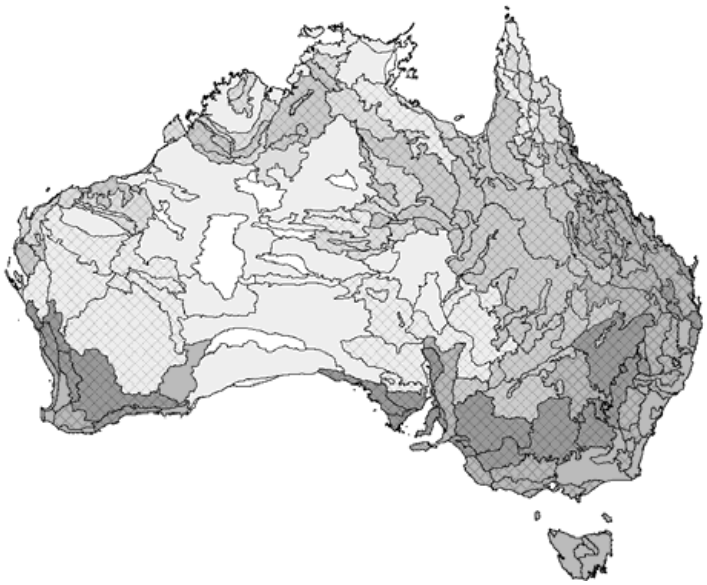


Figure 48: Agricultural Land Use Intensity with hatched regions having at least 50% of the land area under agriculture.

Characterising Resilience

The ability of the soil to resist modifying processes is a function of soil properties. This section is an attempt to utilise the available datasets to inform priority setting.

Soil pH

In the domain of acidity, the pH buffer capacity is a measure developed to characterise this form of resilience. In general terms, this is proportional to the amount of organic carbon and

clay in the soil. Thus, in the absence of measured pH buffer capacity, these surrogates can provide an indication. Alkaline soils also resist acidification by neutralisation.

While consistent national data sets are not available to compute pH buffer capacity, several relevant data sets are outlined independently and are aligned to sandy soils having a low buffer capacity. Thus from this perspective, the regions with low buffer capacity are the darker areas in Figure 49. Sandy loams (Figure 50) will have a low to moderate buffer capacity.

Table 15: Land use Intensity by Agriculture usage by Soil Classification.

		Land Use Intensity Code									
		1	2	2	3	3	4	5	5	6	6
gp4	gp10	* L	L	H	L	H	H	L	**H**	L	**H**
1	1	1	3	1	1	5	3			1	
1	2					1		6	**1**	1	
1	3							2			
1	4				2	2		9	**13**	3	**4**
1	5		1	1			8	2	**19**		**5**
2	6	1	2	13		8	16		**2**		**1**
2	7	1	1	2			2	1			**5**
3	8		1	1	1		18		**6**		**5**
4	9	8	8	6	1	7	3	1			**2**
4	10	1	1	1		2		1			
		12	17	25	5	25	50	22	**41**	5	**22**

*L - low agricultural use in region, H – high agricultural use in region

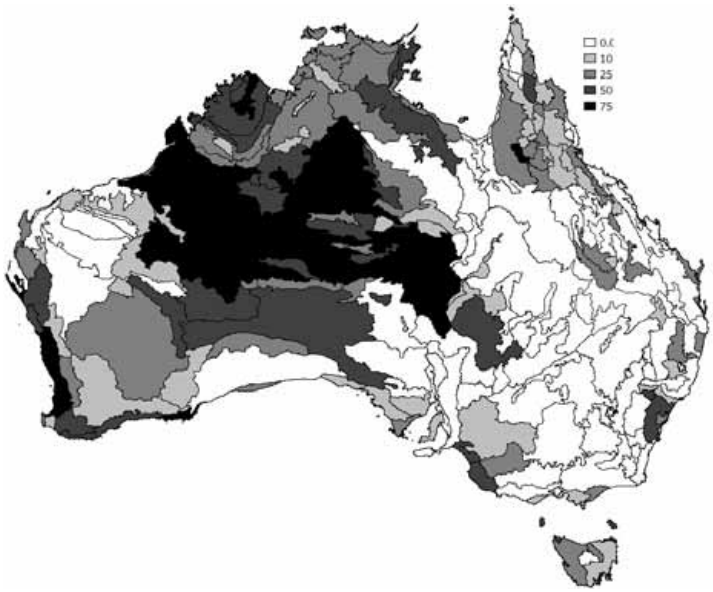


Figure 49: Percentage of region with sandy A horizon. Shading darkens in progressing through the following classes: 0-10%, 10-25%, 25-50%, 50-75% and 75-100%.

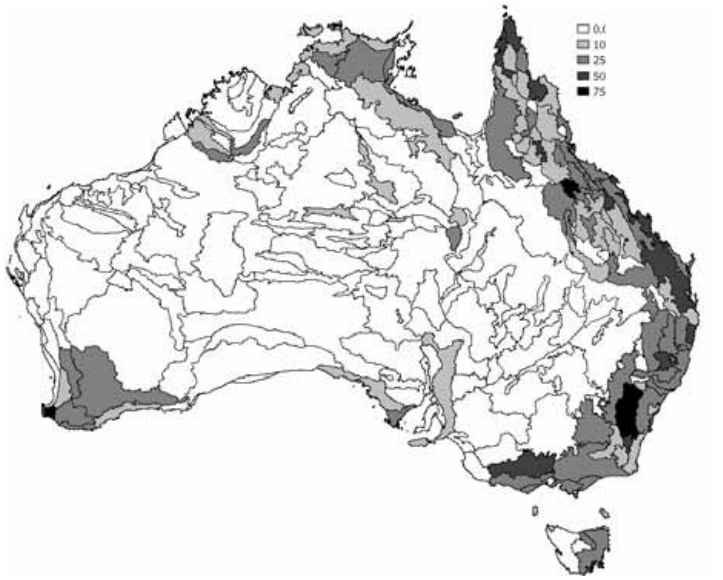


Figure 50: Percentage of region with sandy loam A horizon. Shading darkens in progressing through the following classes: 0-10%, 10-25%, 25-50%, 50-75% and 75-100%.

The level of organic carbon also has a major influence on buffer capacity. Figure 51 is that generated for the Audit (Raupach et al., 2001). This is derived from Net Primary Production (Figure 52) which is based on modelling (e.g. radiation, rainfall, evaporation, soil moisture and nutrients) with limited calibration. These contrast with the Prescott index (Figure 53) which is much higher in the tropics. While rainfall is clearly the major driver, the much higher temperature and evaporation in the tropics has resulted in that area having lower NPP and organic carbon than the southern regions.

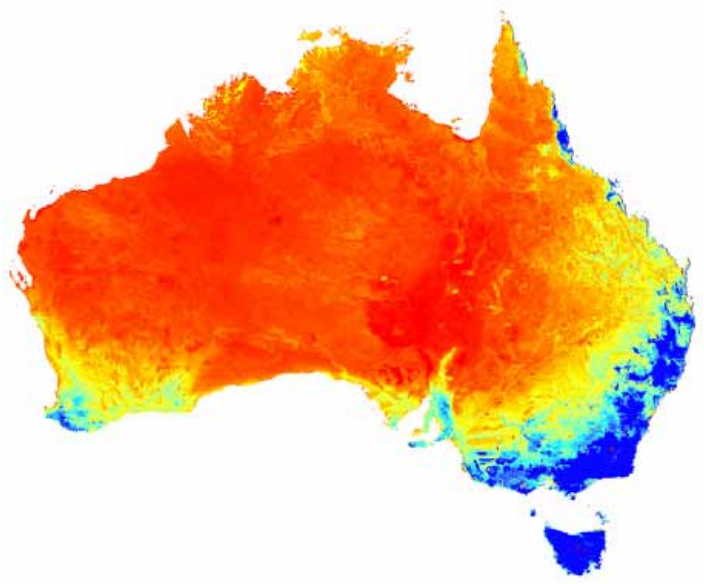


Figure 51: Soil carbon from Raupach et al. (2001) with soil carbon increasing in progressing from red through yellow to blue.

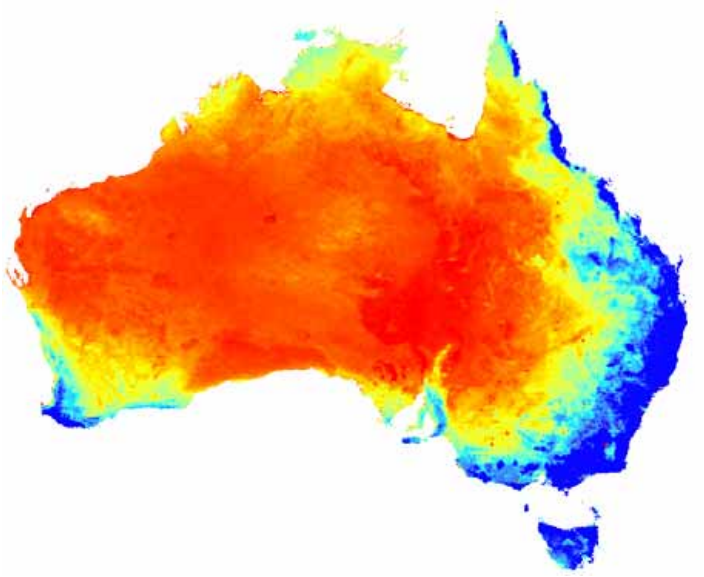


Figure 52: Net Primary Production from Raupach et al. (2001) with net primary productivity increasing in progressing from red through yellow to blue.

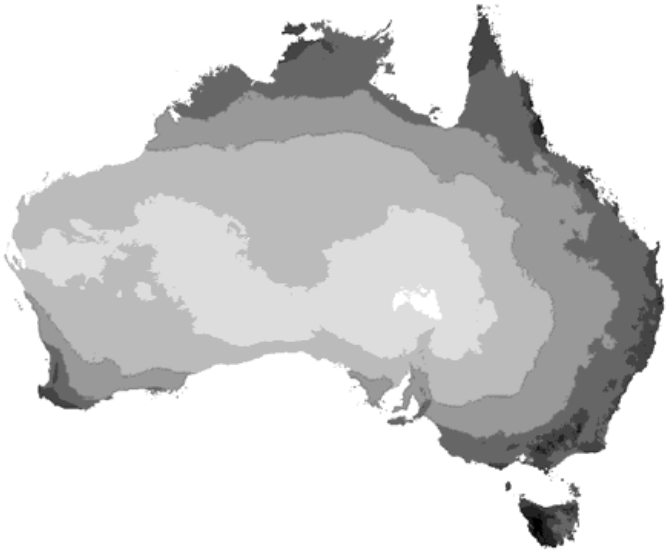


Figure 53: Prescott index (Dr J Gallant CSIRO, personal communication) with the magnitude of the index increasing in progressing from white to black.

At the regional scale, soil type does not appear to have a major influence on soil carbon. However, the Atlas Mapping does contribute significantly at the local scale (Figure 54a, b and c), logically through the soil water and nutrient estimates utilised in the modelling. While, the Prescott index shows broad patterns, it does not have the apparent detail which the soil carbon model clearly derived from the soil mapping (Figure 55a, b and c). Recent interpretations of soil point data (Griffin unpublished data) suggest that climate is more

important determinant of organic carbon than soil classes. However, the aggregation at regional scale reduces this impact.

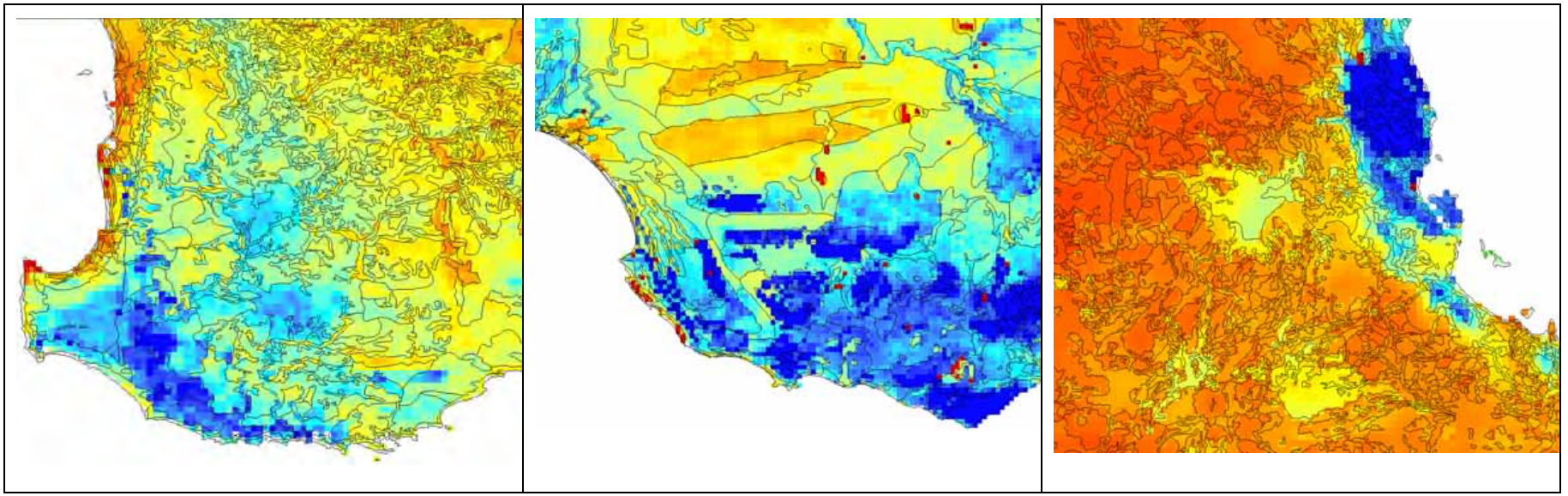


Figure 54: Soil carbon from Raupach et al. (2001) with Atlas mapping (a. south west WA, b. western Vic, c. Cairns, Qld). Soil carbon increases in progressing from red, through yellow to blue.

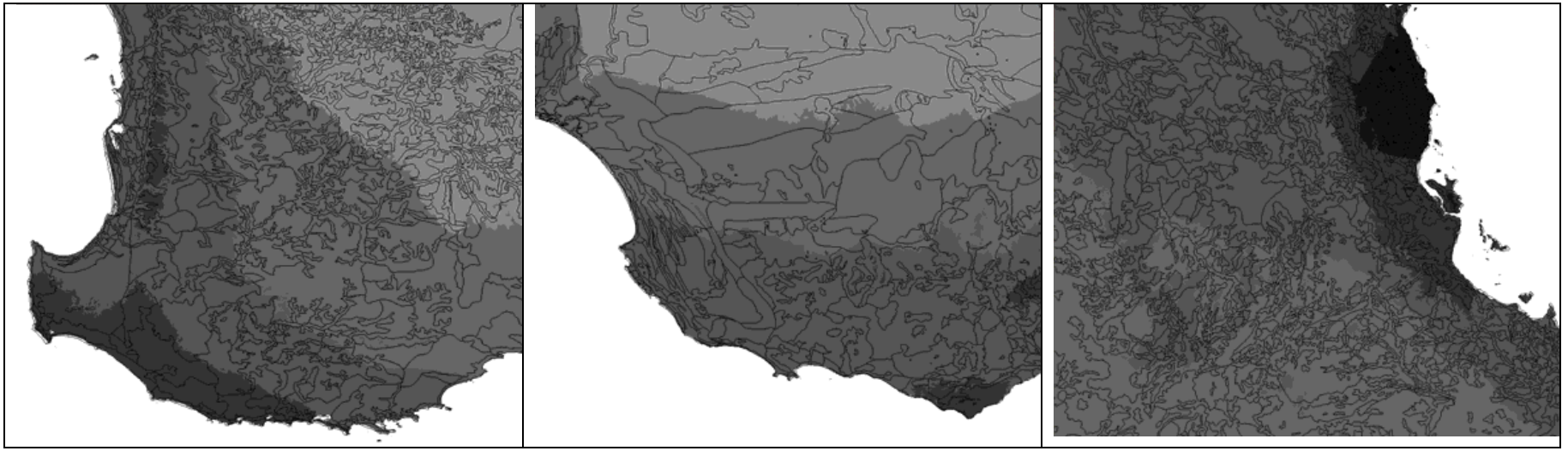


Figure 55: Prescott index with Atlas mapping (a: south west WA, b: western Vic, c: Cairns, Qld) (Dr J Gallant CSIRO personal communication). Values increase in progressing from white to black.

The neutralising value of the soil (free carbonate) has a major influence on the impact of acid addition. Figure 56 represents the likelihood of alkaline surface soils and Figure 57 is the likelihood of alkaline subsoils. In the former case, acid additions from such as agriculture will have negligible effects, and in the latter, there will be limited effects with the depth to the alkaline layer being critical.

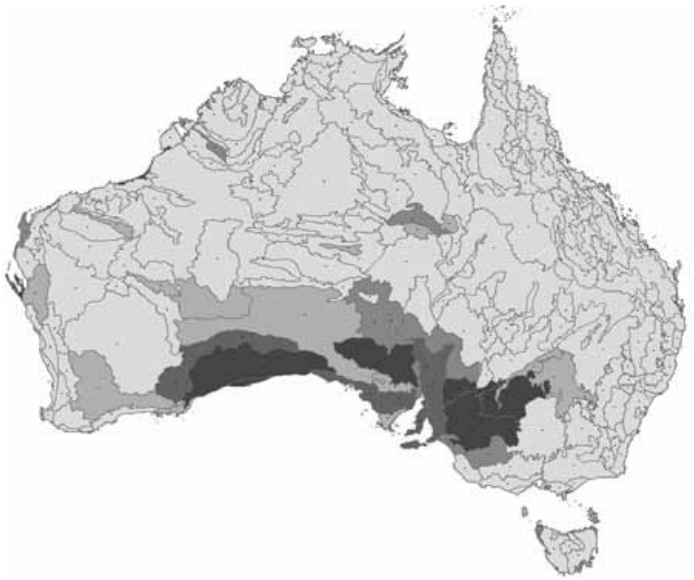


Figure 56: Alkaline surface soils with alkalinity increasing in progressing from light to dark shading.

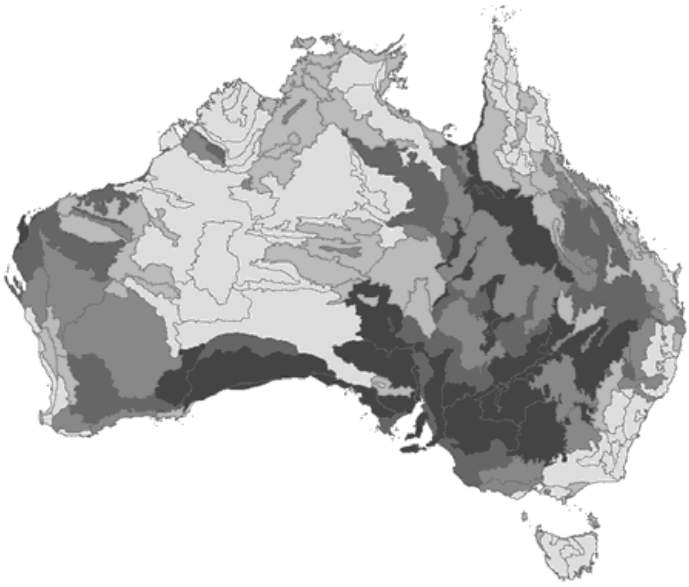


Figure 57 Alkaline subsoils with alkalinity increasing in progressing from light to dark shading.

Estimating pH Resilience

The data available do not permit the estimation of pH buffer capacity per se. However, a scale was developed to sum scores representing the neutralising capacity, the clay buffering and the carbon buffering. Low scores represent areas with low resilience to acidification.

This is presented in Figure 58. To a significant degree this is a reflection of alkalinity of the soils.

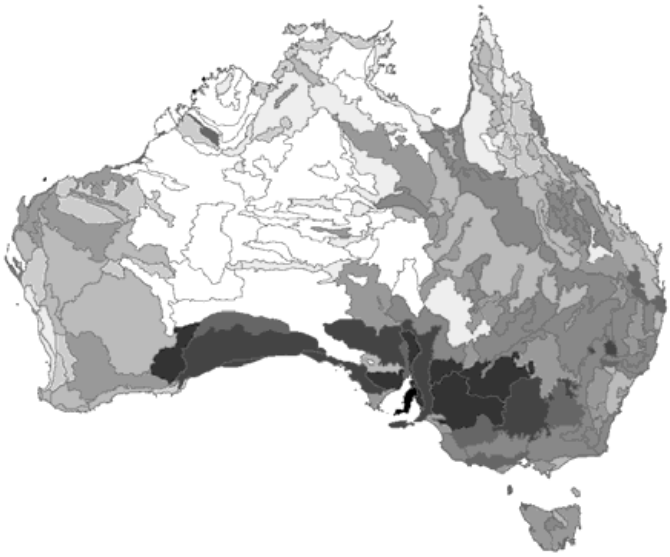


Figure 58: Resilience to pH change with increasing resilianc in progressing from light to dark shading.

Currently acid areas are to a significant degree are buffered, i.e. additional acid is not going to make much difference. The flip side of this is that a small acidification can move the soil into a critical range, while a large change in pH of a neutral soil will be less critical. Figure 59 is a crude indication of currently acid soils through an interpretation of the acid SRT from the Atlas. This generally reflects the higher rainfall and higher organic carbon areas which are intimately linked.

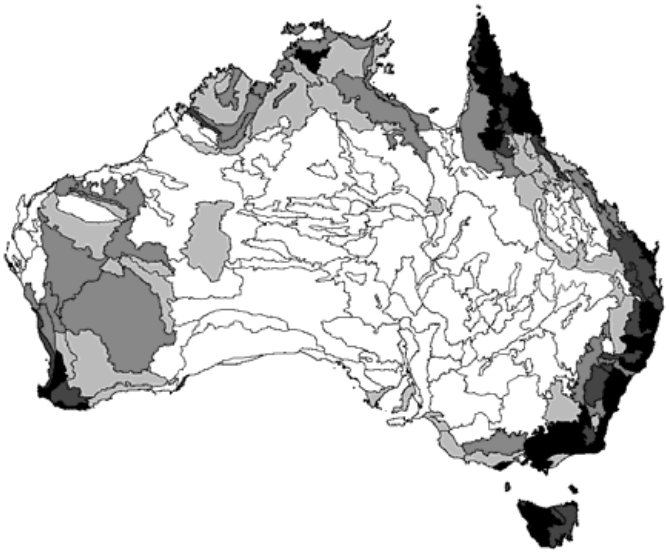


Figure 59: Acid soil reaction trend with acidity increasing in progressing from light to dark shading.

Organic Carbon

The net primary production is a major driver of soil organic carbon. This will be significantly influenced by climate change but that is a separate issue from resilience and is not factored in this assessment, although it merits examination.

Another important issue in resilience to changing soil organic carbon is erosion fluxes: physical removal of surface layers. Surface soil properties are often very significant, but a protective vegetation or mantle cover is critical. So, surface properties can indicate the potential resilience to such losses. Figure 60 and Figure 61 provide estimates of water erosion risk maps (from Audit).

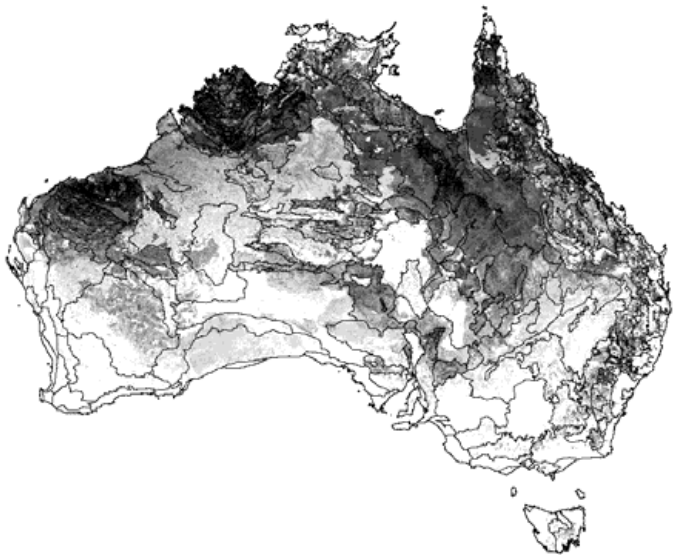


Figure 60: Water erosion risk class from Audit with erosion risk increasing in progressing from light to dark shading.

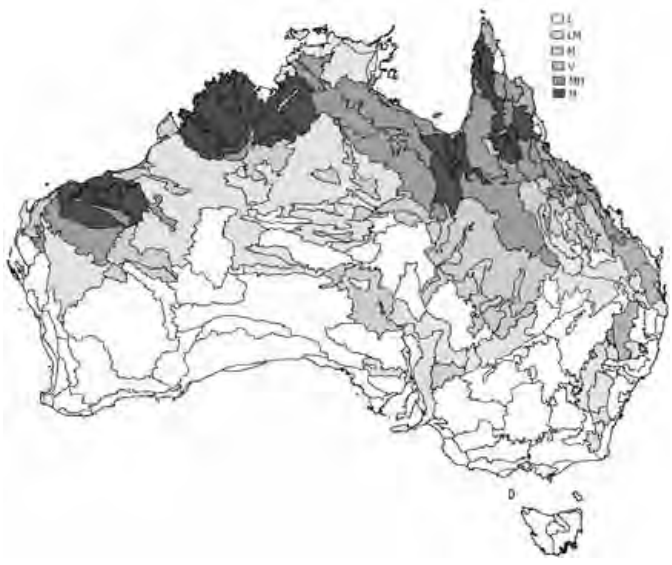


Figure 61: Water erosion risk classes of regions with erosion risk increasing in progressing from light to dark shading.

Areas with significant cover will be more stable. The occurrence of persistent vegetation is a surrogate for a stable cover. Figure 62 and Figure 63 are from Donohue et al. 2007 which is an analysis of a variation of NDVI over many years. This partitioned the signal into persistent and recurrent. These show a significant climate related cover. Thus, combining water erosion with this measure of cover we get Figure 64.

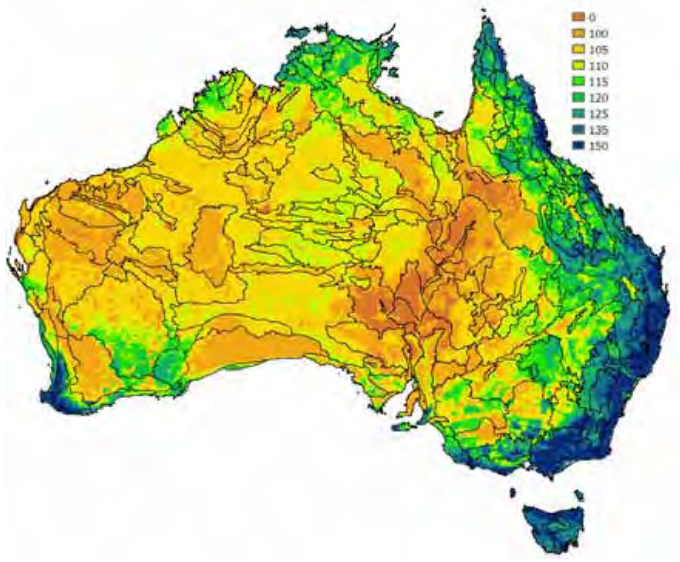


Figure 62: Vegetation persistence with persistence increasing in progressing from brown through yellow to green and then blue.

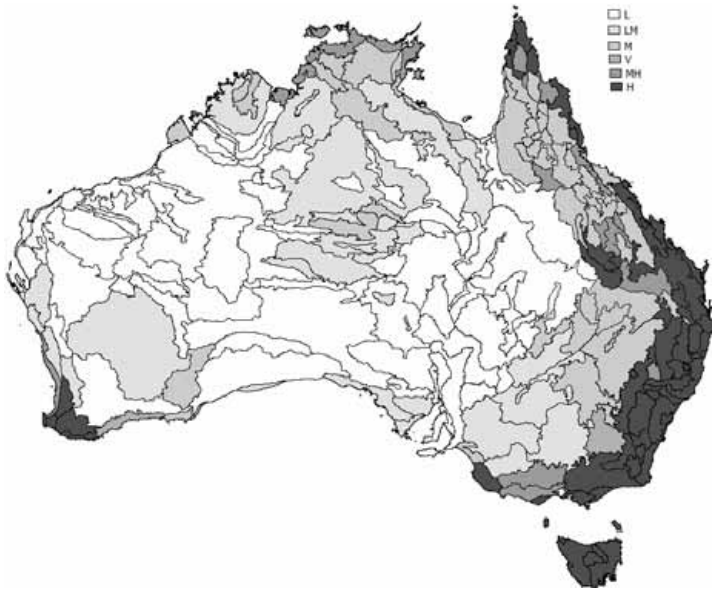


Figure 63: Vegetation persistence cover class of regions with persistence increasing in progressing from light to dark shading.

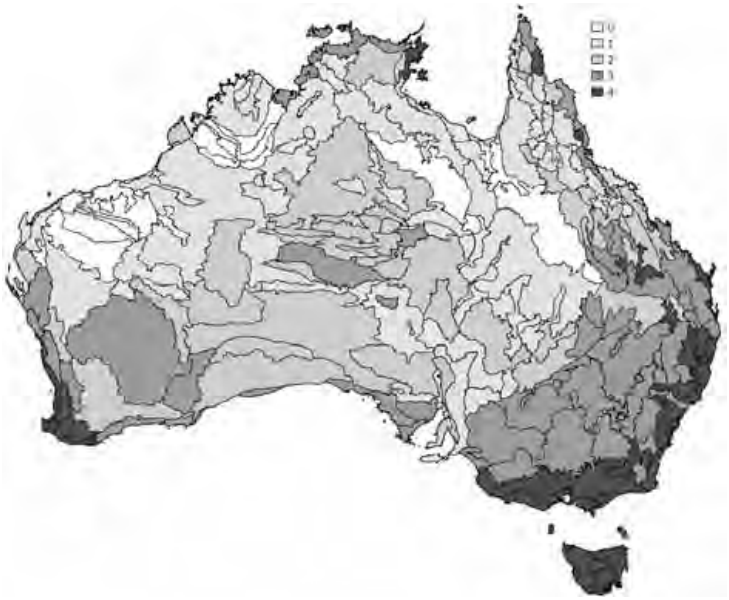


Figure 64: Resilience to water erosion of regions with resilience increasing in progressing from light to dark shading.

The loose sandy surface soils have the greatest potential for wind erosion. Figure 49 represents the areas where sandy soils are predominant. However, any loose soil is highly vulnerable. Finding a surrogate for this was difficult. Areas with significant cover and which are moist will be more stable. Combining surface texture with perennial cover we can get an approximation of wind erosion. Figure 65 is a five class representation of susceptibility to wind erosion. This, however, overlooks the heavier textured soils which have a loose surface. For these, land use intensity is likely to be the main driver.

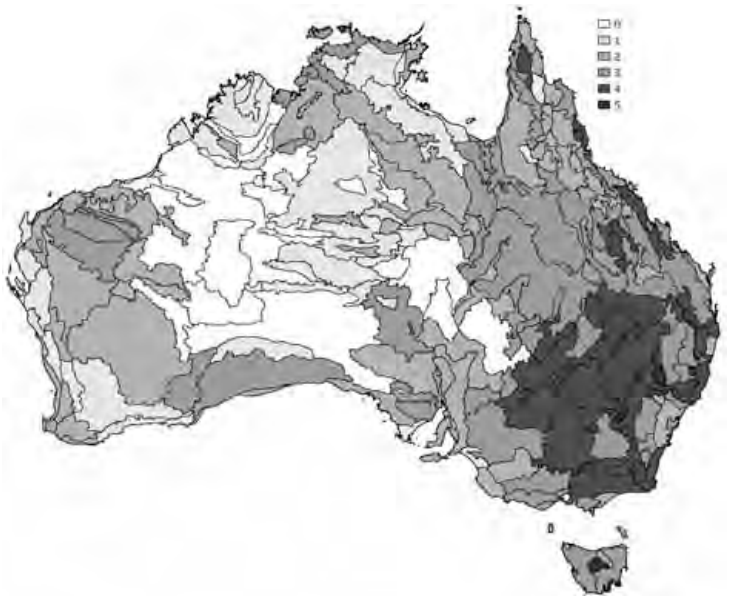


Figure 65: Combining high persistent vegetation with low proportion of sandy surface soils to derive an index of susceptibility to wind erosion with susceptibility decreasing in progressing from light to dark shading.

It was hoped that texture and perennial cover could be combined to define a relative impact on erosion fluxes. This appears to not be reliable, partly because of the incompleteness of a wind erosion risk map.

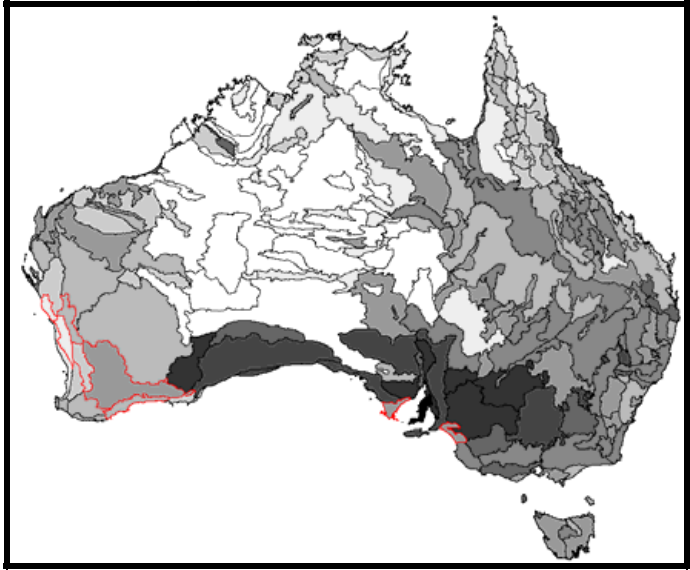
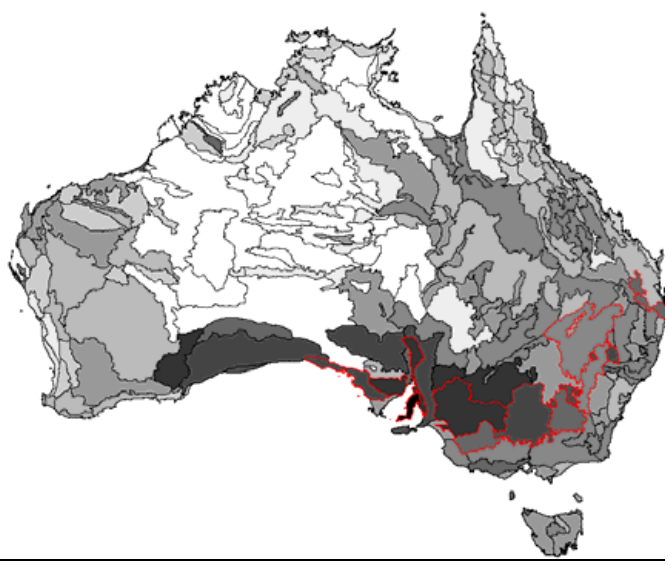
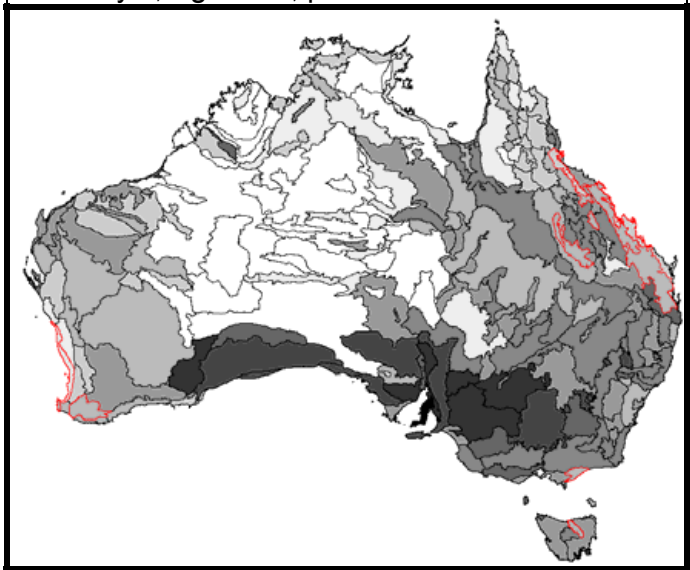
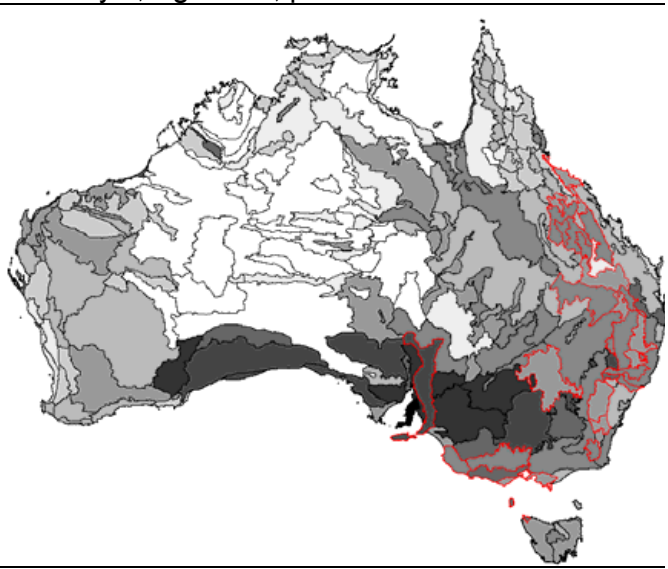
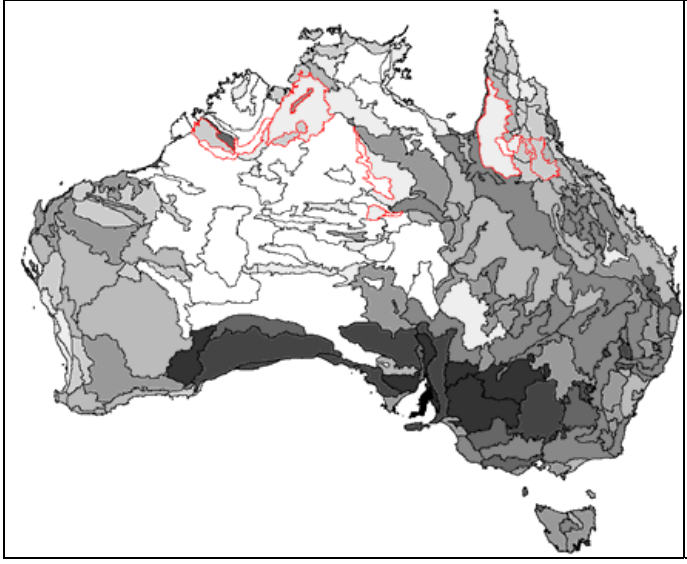
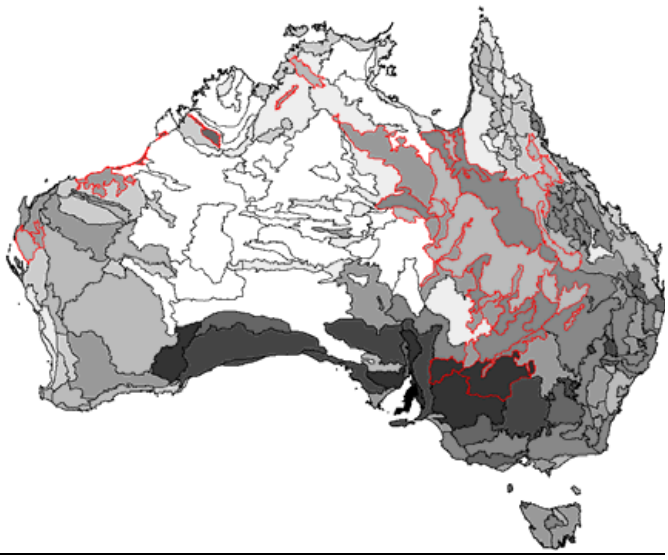
Thus, consistent cover is likely to be the best available measure of resilience to erosion losses. Thus the persistent cover score (Figure 63) is as useful as any attempt to predict erosion and therefore loss of organic carbon.

Combining Classification, Land use and Resilience

Table 15 is a representation of the distribution of the land use intensity classes (Figure 48) by the region classification (Figure 38). An examination of those regions from predominantly agricultural areas (H in Table 15) in relation to resilience to pH change is presented in Table 16. Those highlighted would have the highest priority from acidification perspective as Intensity classes 4, 3 and 2 are different levels of pastoral use with limited fertiliser inputs and agricultural exports. The distributions of these groups are provided in

Table 16: Land Use Intensity classification from soil properties by pH Buffer code. Regions in bold are priority candidates from pH buffer perspective.

Intensity Code	gp10	pH Buffer Class									
		0	1	2	3	4	5	6	7	8	10
6	4			**1**	**1**	**1**		1			
6	5					**2**	1	2			
6	6				**1**						
6	7								1	3	1
6	8						1		4		
6	9		**2**								
5	2						1				
5	4		**1**	**1**	**4**	5	1	1			
5	5			**1**	**7**	5	5	1			
5	6					1			1		
5	8						5	1			
4	1	2	1								
4	5		1	3	4						
4	6		2	1	6	4	1	1		1	
4	7							1		1	
4	8				2	8	8				
4	9	3									
3	1	1	2	2							
3	2				1						
3	4		2								
3	6		2	2	1	3					
3	9	5	1	1							
3	10	1	1								
2	1	1									
2	5			1							
2	6	1		2	4	4	1	1			
2	7						1		1		
2	8					1					
2	9	1	3	1	1						
2	10	1									

Intensity 6, Ag >49%, pH buffer class 0-4	Intensity 6, Ag >49%, pH buffer class 5-10
	
Intensity 5, Ag >49%, pH buffer class 0-3	Intensity 5, Ag >49%, pH buffer class 4-10
	
Intensity 4, Ag >49%, pH buffer class 0-3	Intensity 4, Ag >49%, pH buffer class 3-10
	

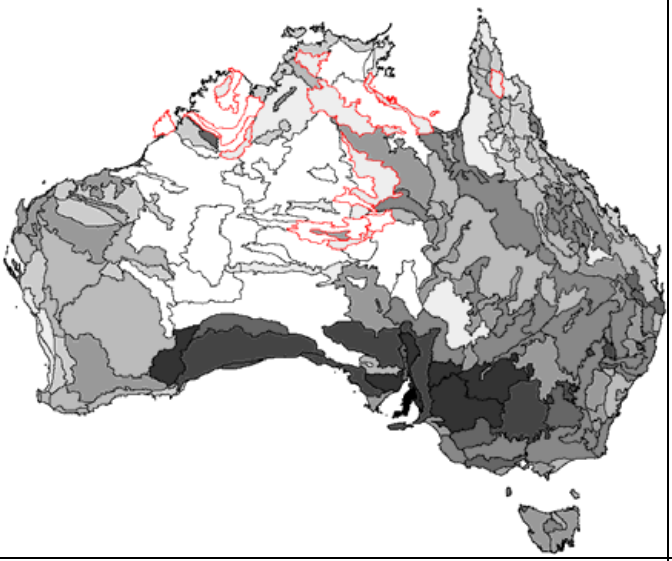
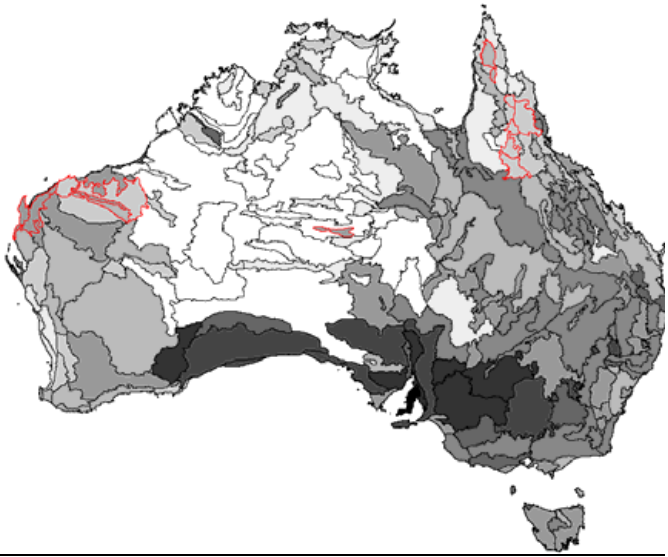
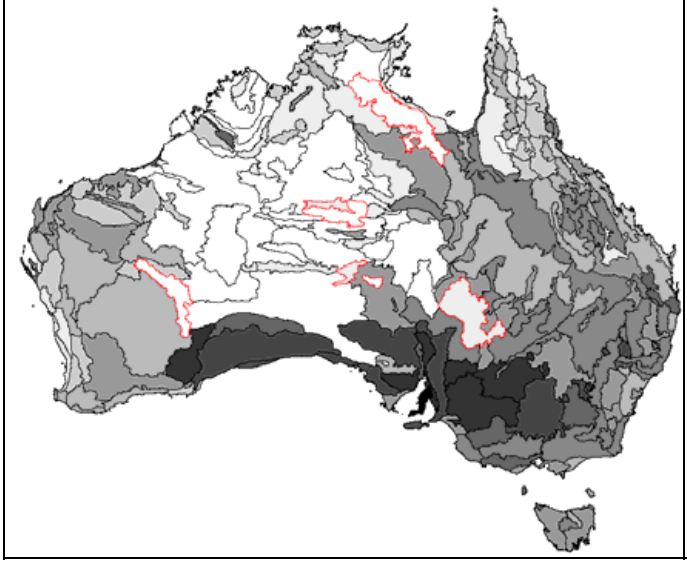
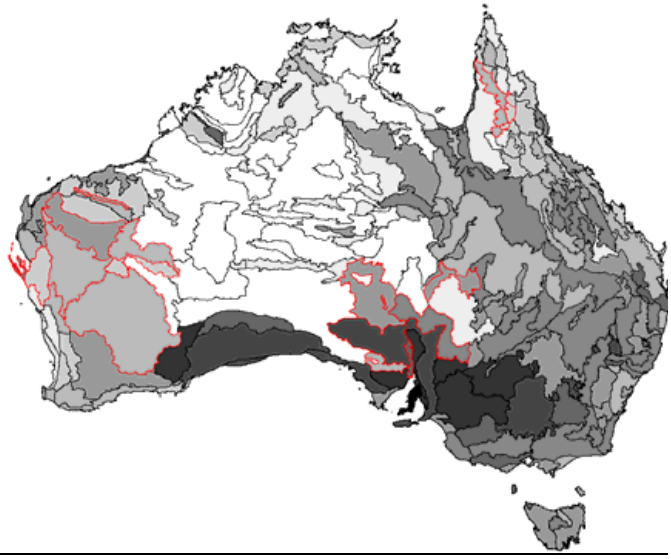
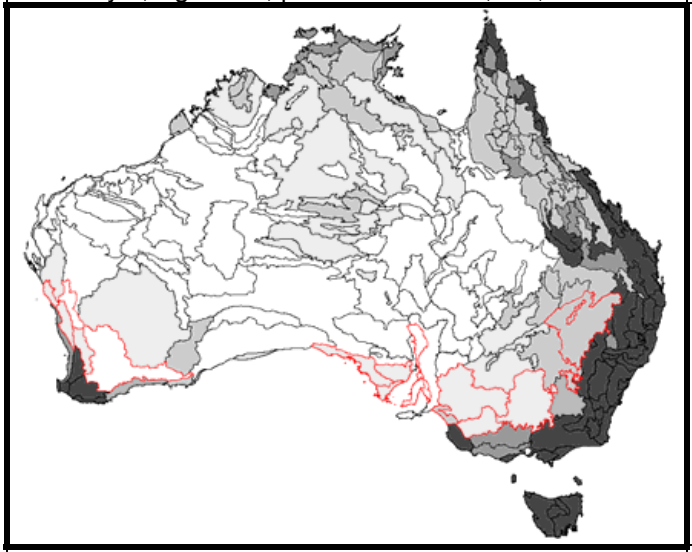
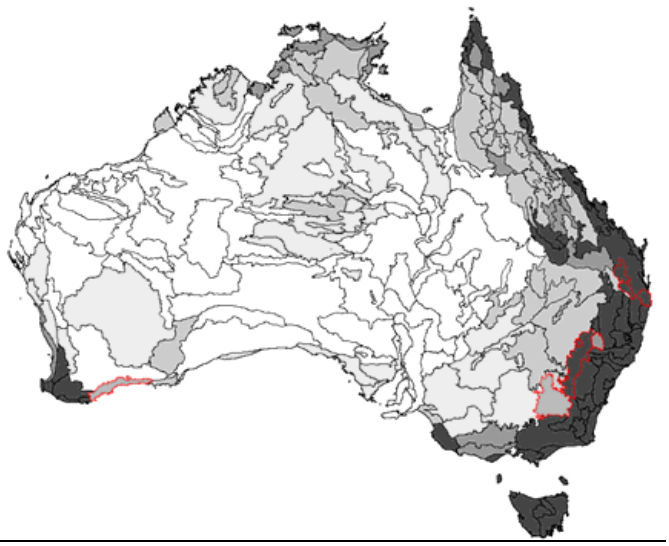
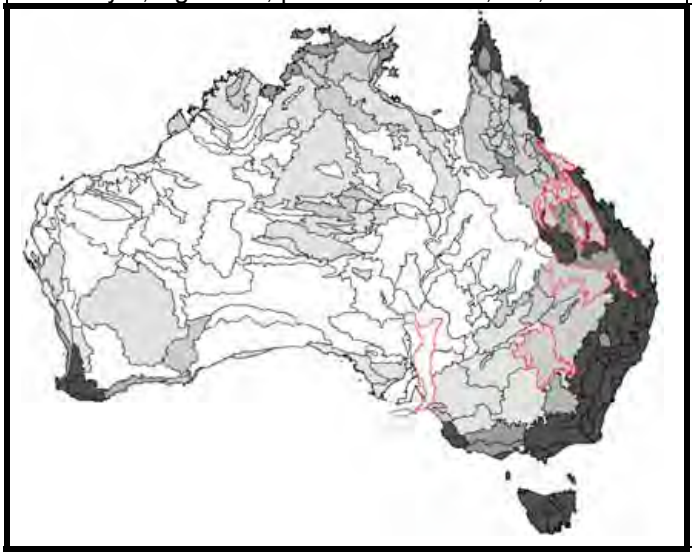
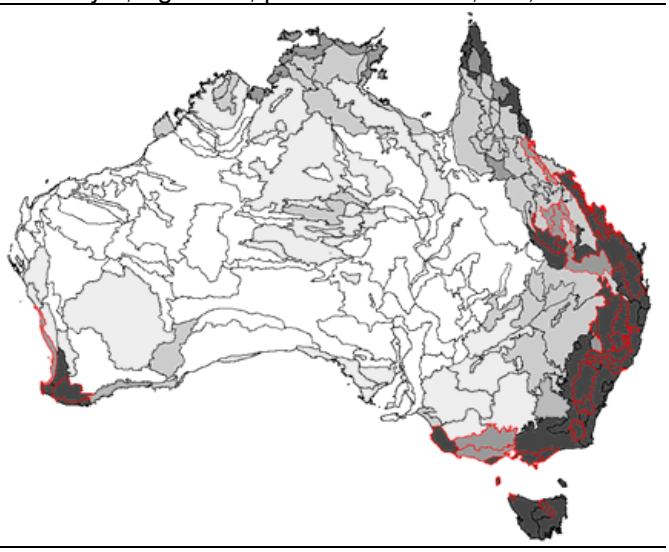
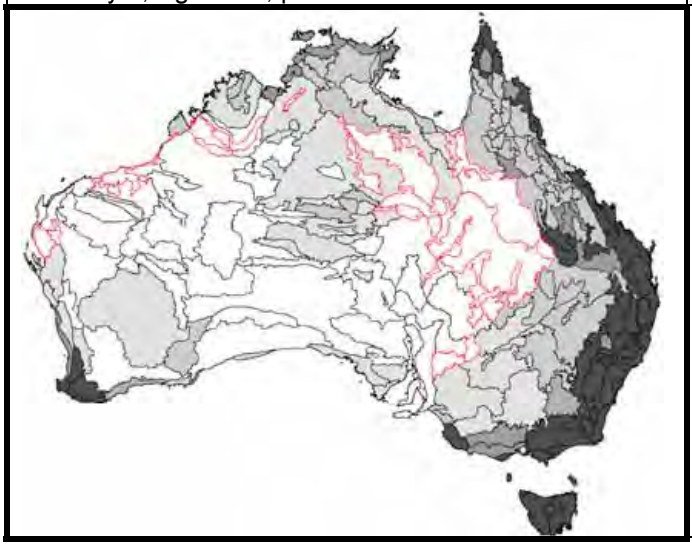
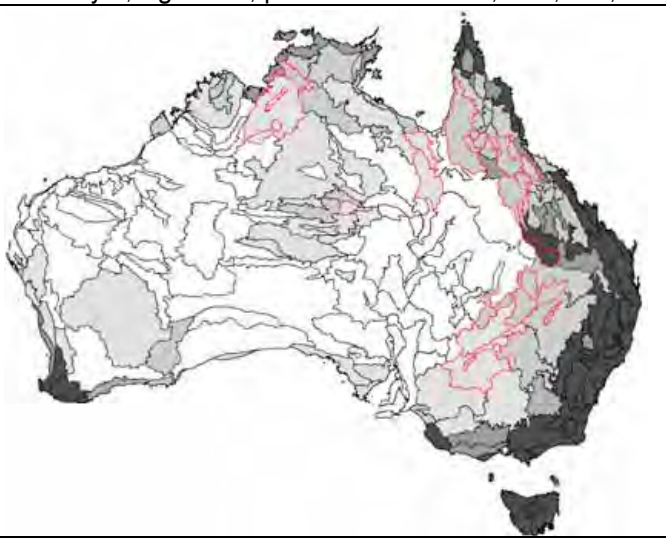
Intensity 3, Ag >49%, pH buffer class 0-1	Intensity 3, Ag >49%, pH buffer class 2-10
	
Intensity 2, Ag >49%, pH buffer class 0-1	Intensity 2, Ag >49%, pH buffer class 2-10
	

Figure 66: Land Use Intensity by pH Buffer class. Red boundary are regions meeting criteria. Base shaded map – pH buffer classes, Figure 58.

Similarly an examination of those from predominantly agricultural areas (H in Table 15) in relation to resilience to erosion change (persistent vegetation cover) is presented in Table 17. Those highlighted would have the highest priority from surface OC loss as Intensity classes 3 and 2 are different levels of pastoral use with limited fertiliser inputs and agricultural exports.

Table 17: Land Use Intensity classification from soil properties by persistent vegetation cover. (Regions in bold are priority candidates from persistent cover perspective.)

		Persistent Vegetation Cover					
Intensity Code	gp10	L	LM	M	V	MH	H
6	4		**2**	**1**	1		
6	5	**1**	**1**		1		2
6	6	**1**					
6	7	**2**	**3**				
6	8		**1**	**2**		1	1
6	9		**2**				
5	2						1
5	4					2	11
5	5			**5**		5	9
5	6	**1**		**1**			
5	8			**3**		1	2
4	1	2		1			
4	5	1		6			1
4	6	11	4	1			
4	7	1	1				
4	8	11	3	4			
4	9	2		1			
3	1	2		3			
3	2					1	
3	4			2			
3	6	4	2	1		1	
3	9		3	4			
3	10	1		1			
2	1		1				
2	5			1			
2	6	11	1	1			
2	7	2					
2	8	1					
2	9	2	3	1			
2	10	1					

Intensity 6, Ag >49%, perennial cover L, LM, M	Intensity 6, Ag >49%, perennial cover V, MH, H
	
Intensity 5, Ag >49%, perennial cover L, LM, M	Intensity 5, Ag >49%, perennial cover V, MH, H
	
Intensity 4, Ag >49%, perennial cover L	Intensity 4, Ag >49%, perennial cover LM, M V, MH, H
	

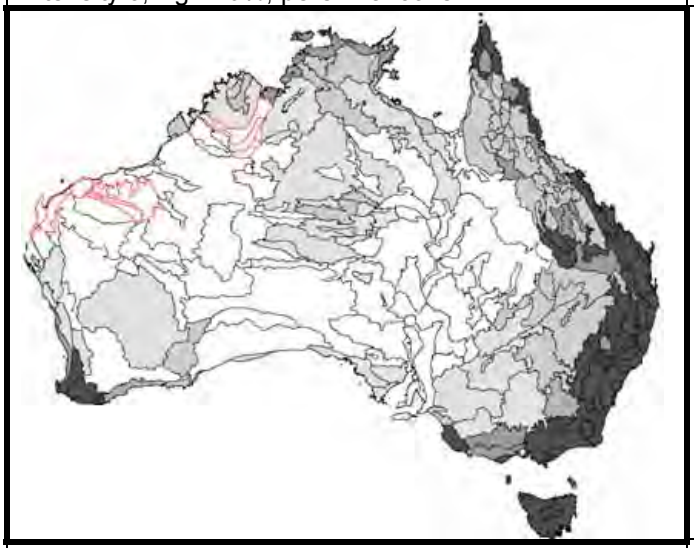
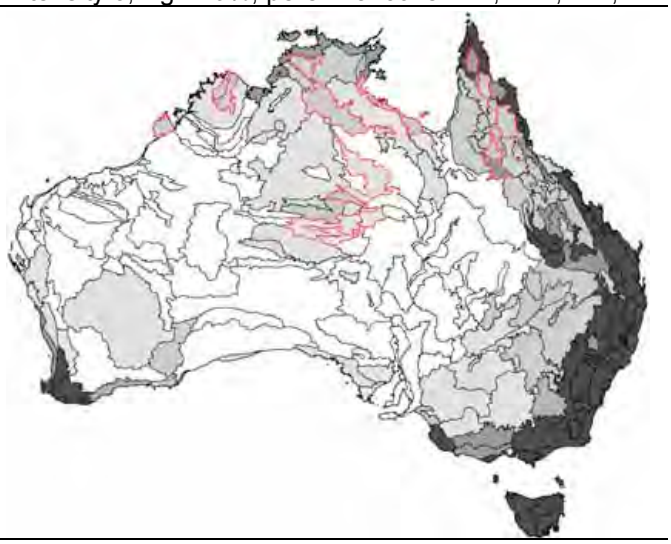
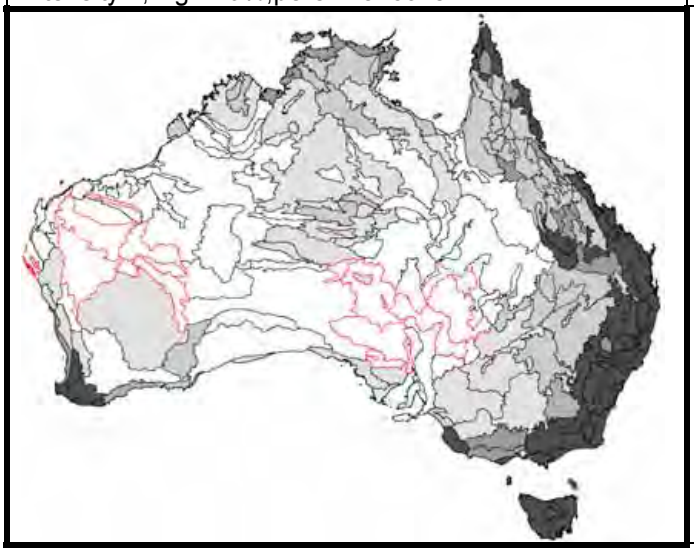
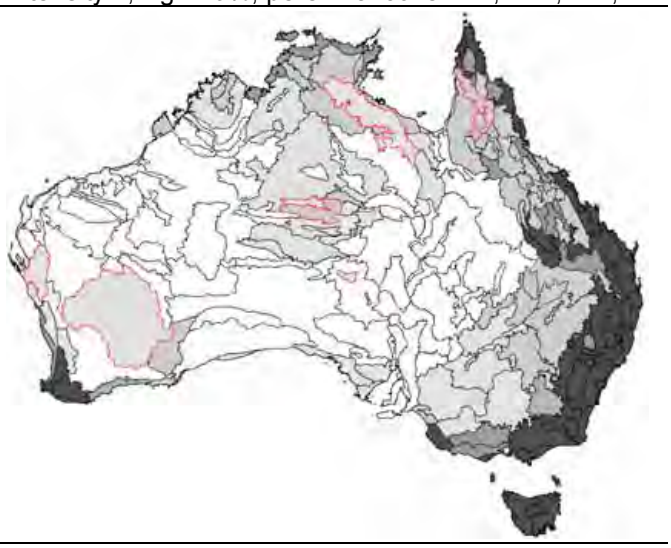
Intensity 3, Ag >49%, perennial cover L	Intensity 3, Ag >49%, perennial cover LM, M V, MH, H
	
Intensity 2, Ag >49%,perennial cover L	Intensity 2, Ag >49%, perennial cover LM, M V, MH, H
	

Figure 67: Intensity combined with perennial cover as a surrogate for erosion potential . Red boundary are regions meeting criteria. Base shaded map – Vegetation Persistent classes, Figure 63.

The distributions of these groups are provided in Figures 66 and 67 (above) are compiled into Figure 68.

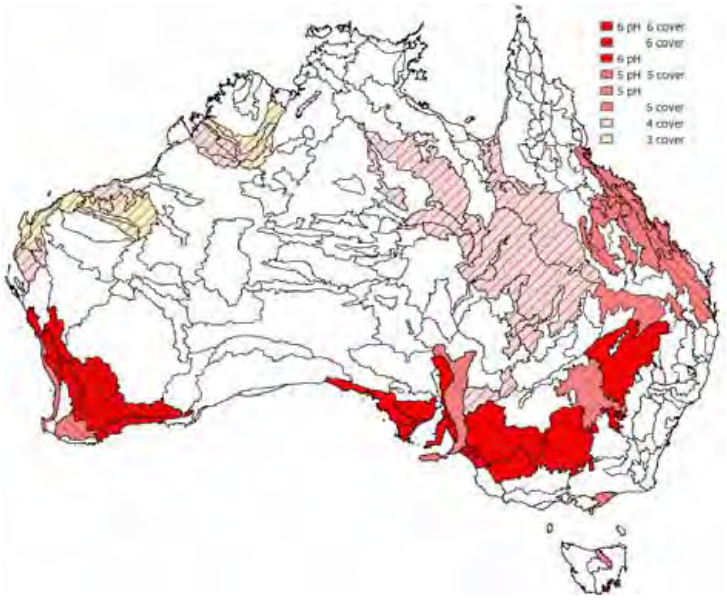


Figure 68: Candidates from Land use intensity and Resilience to pH and Erosion changes. Regions selected from pH hatched to right, regions selected from cover hatched to left.

Seventy four candidate areas were selected (Table 18). In this the candidate regions are represented as a matrix of intensity class by land type classification. Significantly, most of these combinations are represented by at least one candidate region.

By this process, most of the highest land use intensity regions were selected as candidates. This is largely because of these being cropping areas with medium to low permanent vegetation cover and these are by this measure vulnerable to change. The proportion of candidates selected declined as the land use intensity declined.

Most of the different types of land (as represented by the classification, rows in Table 18) have candidate regions. Most of those not represented had largely no agriculture or were in areas of low intensity. Several of the classification groups were represented in several land use intensity classes.

While most classification groups (to 20 group level) with high land use intensity are represented by candidate areas the representation implied by that is not as good as it might seem. Much of this is because of relatively low agricultural activity in some areas (white in Figure 69). Low grazing activities in the rangeland areas have not been selected. Grazing areas in SE Australia have not been selected because these have high perennial cover. This is probably an anomaly in the process as the cover is a value for the whole region and is influenced by the high proportion of forest in these areas.

Table 18: Summary of distribution of candidate regions by soil classification groups.

						Land Use Intensity									
			All	Ag		6		5		4		3		2	
gp4	gp10	gp20	tot	t*	c*	t	c	t	c	t	c	t	c	t	c
1	1	1	3	0	0										
1	1	2	12	9	4					3	2	5	2	1	
1	2	3	9	2	0			1				1			
1	3	4	2	0	0										
1	4	5	24	13	6	1	1	10	5			2			
1	4	6	9	6	4	3	3	3	1						
1	5	7	36	33	14	5	2	19	11	8	1			1	
2	6	8	11	11	3	1	1			4	1	5	1	1	
2	6	9	15	15	8			1	1	7	5	2	2	5	
2	6	10	11	11	5					4	4	1	1	6	
2	6	11	6	3	2			1	1	1	1			1	
2	7	12	11	8	6	5	5			2	1			1	
2	7	13	1	1	0									1	
3	8	14	25	24	11	5	3	6	3	12	5			1	
3	8	15	7	6	6					6	6				
4	9	16	11	7	2	2	2					2		3	
4	9	17	21	9	2					3	2	3		3	
4	9	18	4	2	0							2			
4	10	19	2	1	0							1			
4	10	20	4	2	1							1	1	1	
			224	163	74	22	17	41	22	50	28	25	7	25	0

t* - total in class where %Ag >49, c* - candidates

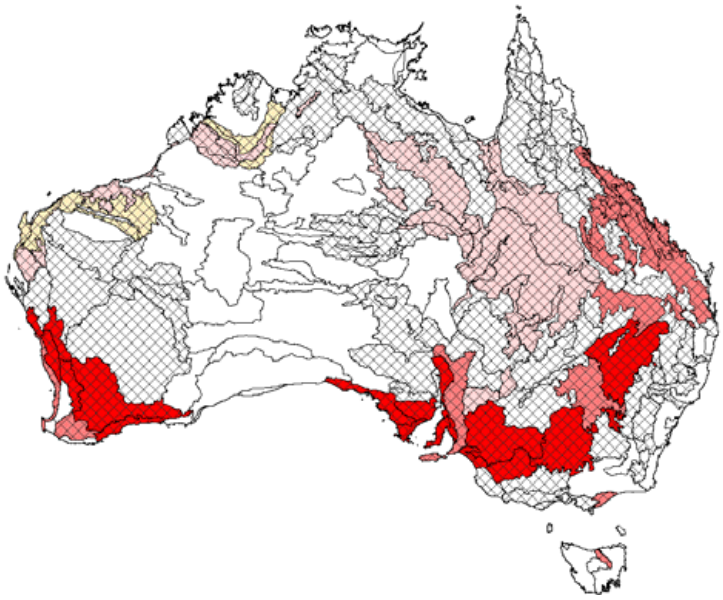


Figure 69: Candidate areas (as per Figure 68) with regions of high agricultural activity cross hatched.

The area of SE Australia had few candidates in the 7, 10, 14, 15 and 16 at the 40 group level classifications (Figure 70 and Figure 71). As just two of these from SE Australia were selected, this type of country is not well represented by the selection process. It was concluded that several of these ought to be added to the final selection.

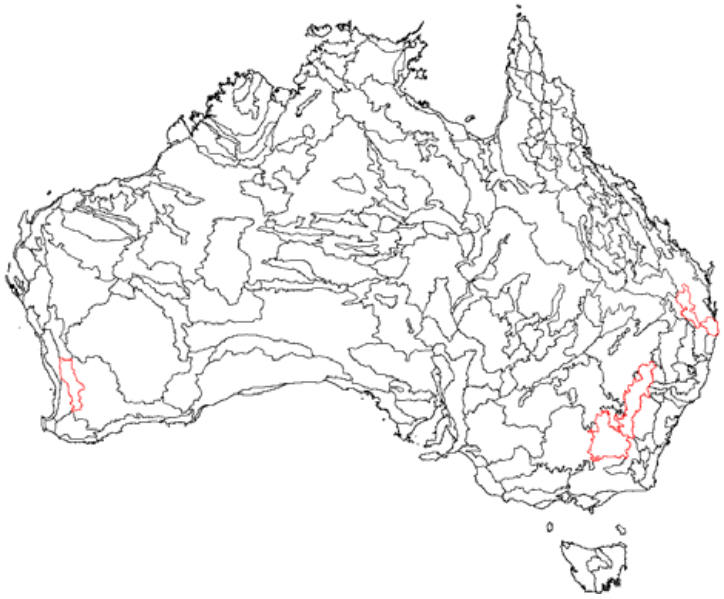


Figure 70: Intensity class 6 with Ag >49.9 from 7, 10, 14, 15 and 16 at the 40 group level.

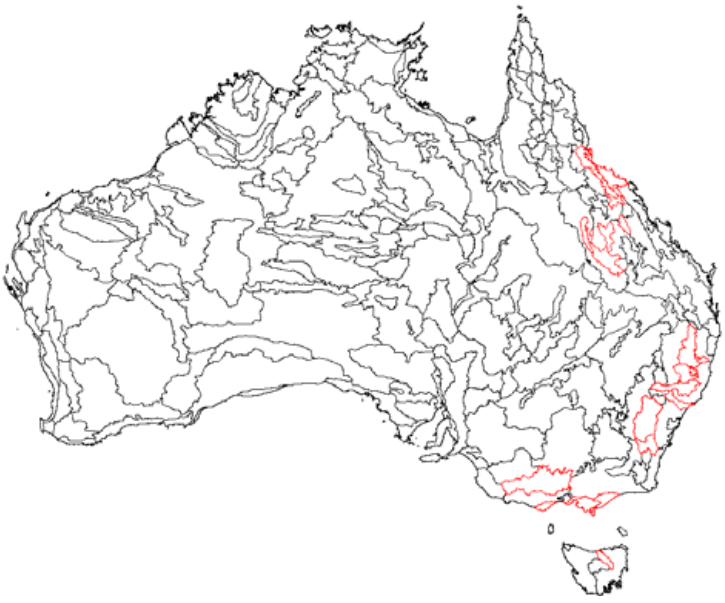


Figure 71: Intensity class 5 with Ag >49.9 from 7, 10, 14, 15 and 16 at the 40 group level.

Appendix 2: Methods for soil carbon analysis

Method 2.1: Total carbon analysis

The analysis given below is generic in nature. Operators must become familiar with the particular instrument being used to complete the analyses and the requirements associated with the instrument in order to obtain a valid result.

1. Prior to analysis all samples must be dried and homogenised. Where required, in particular for soil samples, determine the gravimetric water content (θ_m, mass of water/mass of soil particles) of the samples. This will be used to correct the mass of sample used in the analysis for the presence of water in order that all carbon values can be expressed on a per unit mass of dry soil basis.
2. For soils, check the sample for the presence of carbonate-C by placing a drop of 1M HCl directly on to an aliquot of the sample and checking for any effervescence. If no effervescence is noted, proceed with the total carbon analysis and assume that measuring total carbon will provide a measure of the amount of organic carbon present. Where effervescence is observed, pretreat the sample as per the instructions in the "Sample pretreatment to remove carbonate carbon" method presented in this appendix.
3. Calibration of the carbon analyser is essential. Calibration should be completed using material similar in nature to sample being analysed (e.g. sucrose for plant material, SPR, BPR and POC and a standard soil or carbonate for total SOC and HUM fractions). Once calibration is complete, run an additional calibration sample and ensure that the result obtained is within 2% of the known mean value for the calibration material. Do not initiate analysis of the samples until the instrument is adequately calibrated.
4. Weigh an appropriate mass of dried sample, with a known water content, into sample containers suitable for the instrument being used and initiate sample analyses. Be sure to run a calibration sample every 10-15 samples to confirm that the initial calibration is maintained. If the calibration sample is not within 2% of the known mean value, recalibrate the instrument and rerun some of the previous samples. If acceptable calibration is then obtained carry on with the analyses of the next set of samples.
5. Upon completion of the analyses, recalculate the carbon content data obtained to correct for the presence of water using Equation [32] in which θ_m is the gravimetric water content measured for the sample.

6. Convert corrected SOC contents in units of g C kg^{-1} into amounts of carbon per unit land area (t C ha^{-1}) using Equation [33].

$$\text{Corrected SOC content (g C/kg)} = \frac{\text{Measured SOC content (g C/kg)}}{\left(1+\theta_m\right)} \quad [32]$$

$$\text{SOC content } \left(\text{t C ha}^{-1}\right) = \text{Corrected SOC content } \left(\text{g C kg}^{-1}\right) \times \text{Soil layer thickness (cm)} \times \rho_b \quad [33]$$

Method 2.2: Sample pretreatment to remove carbonate carbon

Prior to the analysis of soil samples on a dry combustion analyser, check for the presence of carbonate carbon. This can be done by sub-sampling a small amount of sample with a spatula and placing it into a plastic well (make sure you record which sample's fizz more than others) place a drop of 1M HCl directly on the sample and observe for any effervescence. If the sample gave a positive effervescence test all carbonate carbon must be removed before a total carbon analysis can be performed. The following procedure is recommended to remove carbonate-C from a soil sample when a LECO C-144 carbon analyser. If an alternative analyser is being used the pretreatment process will need to be modified.

1. Weigh out approximately 1g of soil into a ceramic LECO C-144 analysis boat containing a nickel liner.
2. Transferred to a hot plate and add approximately 1ml of H_2SO_3 to the sample (which subsequently fizzes). Turn the hot plate on to 100°C. When the residual soil dries, add a further 1ml of H_2SO_3 to the sample and leave the sample to dry again. This process is repeated until the sample stops fizzing.
3. Turn the hot plate off and leave the sample to cool on the plate overnight.
4. The samples are now ready to be analysed as described by the "Total carbon analysis" method described in this Appendix with the exception that a wad of zinc wool is to be placed in the top of the analyser's water trap to remove any sulphur that may corrode the system.

Method 2.3: Fractionation of soil organic carbon – direct measurement

The fractionation procedure follows the scheme presented in Figure 25.

SPR-C fraction: The amount of organic carbon associated with the surface plant residue fraction (SPR) is determined by collecting all plant residues (excluding living plant components) residing on the soil surface within a 0.1 m^2 quadrate. Collection of the litter within a 0.1 m^2 quadrate is to be completed at each location where a soil sample will be collected. This collection serves as the first step in the soil collection process (removal of the

loose litter from the area of soil surface from where a soil sample will be collected). The collected litter is to be dried at 60°C to constant mass. The mass of material collected and its total organic carbon content are determined and used to calculate the amount of SPR-C in this fraction in units of t C/ha (Equation [34]).

$$\text{SPR-C (tC ha}^{-1}) = \frac{\text{total mass of SPR collected (g)}}{\text{number of SPR samples collected}} \times \left(\frac{\text{g SPR C}}{\text{kg SPR mass}} \right) \times 0.1 \quad [34]$$

Soil collection and preparation: After collecting the SPR material, a soil sample is then collected from the required soil depth layers within the sampled 0.1 m^2 area. The soil samples must be collected in a manner that allows calculation of accurate bulk density values. This requires measurement of both the volume of soil extracted and its associated equivalent oven dry mass. Typically, the total mass of soil collected will be defined after air drying the sample, measuring its total mass and correcting for the presence of any water remaining in the soil after air drying. It is recommended that the air drying is completed using a fan forced oven set to 50°C. The procedure use to calculate the volume of soil sampled will depend on the sampling process. If push tubes are used to collect a core, the diameter of the soil core and the total depth of soil sampled can be used to calculate the sampled volume. Irrespective of the measurement method, it is important that care is taken to ensure that the volume is defined accurately and no soil mass is lost during the collection and drying processes.

BPR-C: The amount of carbon present in the buried plant residue (BPR) fraction is determined by passing the air dried soil through a 2 mm sieve making sure that no aggregations of primary soil particles are retained on the sieve. All material >2 mm is then quantitatively removed from the sieve and weighed. This material will consist of gravel and pieces of plant residues. The carbon (t C/ha) contained in the plant residues in the BPR-C fraction can be determined by measuring the carbon content of the >2 mm portion of the soil and using the proportion of soil mass in the >2 mm material, the measured bulk density (ρ_b) and the thickness in centimetres of the layer sampled according to Equation [35].

$$\text{BPR-C (tC ha}^{-1}) = \frac{\text{>2 mm mass(g)}}{\text{total soil mass (g)}} \times \frac{\text{g >2mm C}}{\text{kg >2mm material}} \times \rho_b \times \frac{\text{Soil layer}}{\text{thickness}} \text{ (cm)} \times 0.1 \quad [35]$$

POC, HUM and ROC fractions: All of these SOC fractions are contained within the <2 mm soil material. The following procedure is used to quantify the allocation of carbon to each fraction:

1. Weigh 50 g of soil sample into a plastic 250 ml acid resistant centrifuge container. If the soil is calcareous it will require treatment with sulfurous acid (H_2SO_3). If no carbonate is present go directly to step 5.
2. Carbonate removal. In a fume hood add 50 ml of sulfurous acid and stir with glass rod making sure all soil is in contact with acid. Wash any soil stuck to glass rod back into centrifuge tube. Wait for effervescence to become less vigorous and add another 50 ml of sulfurous acid. Place the lid on container a shake/vortex. Release any gas produced for this in the fume hood. Centrifuge samples at 2000 RPM for 15 minutes and pour off supernatant into separate container collecting any buoyant material. Ensure that all material is flocculated and settles (clear supernatant). If dispersion occurs at any stage over steps 2 - 4, add enough $CaCl_2$ or $AlCl_3$ to ensure complete flocculation and minimise any loss soil material.
3. Add 200 ml of De-Ionized water to each sulphurous acid treated sample and shake/vortex. Again centrifuge samples at 2000 RPM for 15 minutes and pour off clear soil free supernatant into container collecting any buoyant material.
4. Wash with 200 ml of de-Ionized water three times spinning at 2000 RPM for 15 minutes each time discarding the clear soil free supernatant.
5. Add 200ml of Sodium Hexametaphosphate, $Na(PO_3)_6$, at 5g L^{-1} and shake overnight.
6. Spin samples at 2000 RPM for 15 min, pour off and collect the supernatant.
7. Set up sieve apparatus with 250 µm sieve on top then 53 µm sieve then funnel and finally 4 litre beaker. Note that steps 8 and 9 should be completed over the 4 Litre beaker and all solution running through the sieves needs to be collected in this beaker.
8. Pour the dispersed sample through the 250 µm sieve (rinsing with water) as well as all buoyant materials collected from the sulphurous acid treatment (if completed). Gently rub and wash the soil until no particles flow through 250 µm sieve. Check sample is free from aggregates (completely dispersed) by examining under microscope. Wash the >250 µm material remaining on the sieve (POM + sand) into a container.
9. Apply the same process to the 53 µm sieve gently rubbing and washing the soil until no particles flow through and water runs through clear. Wash the material collected on the 53 µm sieve into the same container as was used in step 8.
10. Take the 53-2000 µm fractions and freeze dry if possible. If freeze drying is not possible dry at 40°C in an oven. The material remaining after drying is the (POC + ROC_{POC}) fraction. Determine the mass and carbon content of the material collected.

11. Reduce the pH of the <53 µm material collected in the beaker to pH 4 using 1M HCl and add 5 ml saturated $Al_2(SO_4)_2$ to assist flocculation and wait for material to flocculate and settle (may take several hours or overnight until supernatant is free of soil particles).

12. Draw off supernatant using a U-tube, take care not to draw off any of the soil. Pour the remaining and pour into clean 1000 ml centrifuge bottle spin @ 2000 RPM 10 min. Repeat this process using MQ or RO water 2-3 times to remove excess salts but do not allow the sample to disperse.

13. Pour off the final supernatant into suitable containers to allow freeze drying. The material remaining after freeze drying is the (Humus + ROC_{HUM}) material. Weigh this fraction and determine its carbon content.

14. The proportion of resistant organic carbon (ROC) associated with the POC fraction (ROC_{POC}) and Humus fraction (ROC_{HUM}) can then be determined using solid-state ^{13}C NMR and a molecular mixing model as described by Baldock et al. (2004).

15. The calculations used to obtain the values for POC, HUM and ROC in tC ha^{-1} are accomplished using the mass recovery of material collected in each fraction, its carbon content, soil bulk density and soil layer thickness according to Equations [36] to [38].

$$\text{POC (tC ha}^{-1}) = \frac{\text{53-2000µm mass(g)}}{\text{total soil mass (g)}} \times \frac{\text{g 53-2000 µm C}}{\text{kg 53-2000µm material}} \times \left(1 - \text{ROC}_{\text{POC}}\right) \times \rho_b \times \text{Soil layer thickness (cm)} \times 0.1 \quad [36]$$

$$\text{HUM (tC ha}^{-1}) = \frac{\text{<53µm mass(g)}}{\text{total soil mass (g)}} \times \frac{\text{g <53 µm C}}{\text{kg <53µm material}} \times \left(1 - \text{ROC}_{\text{HUM}}\right) \times \rho_b \times \text{Soil layer thickness (cm)} \times 0.1 \quad [37]$$

$$\text{ROC (tC ha}^{-1}) = \left(\left(\frac{\text{53-2000µm mass(g)}}{\text{total soil mass (g)}} \times \frac{\text{g 53-2000 µm C}}{\text{kg 53-2000µm material}} \times \text{ROC}_{\text{POC}} \right) + \left(\frac{\text{<53µm mass(g)}}{\text{total soil mass (g)}} \times \frac{\text{g <53 µm C}}{\text{kg <53µm material}} \times \text{ROC}_{\text{HUM}} \right) \right) \times \rho_b \times \text{Soil layer thickness (cm)} \times 0.1 \quad [38]$$

Method 2.4: Fractionation of soil organic carbon – indirect measurement by mid infrared spectroscopy

Previous work has demonstrated the ability of mid-infrared spectroscopy to predict the allocation of SOC to its component fractions (Janik et al. 2008). This methodology provides a more rapid and less expensive means of generating estimates for the allocation of SOC to the particulate, humus and charcoal carbon fractions.

1. Grind air-dried (dry @ 40°C to constant mass) to a particle size <5 µm.
2. Place an aliquot of ground soil into the autosampler wheel or the sample individual sample holder and scan using a diffuse reflectance accessory installed in a rapid scanning Fourier Transform infrared spectrometer scanning at 1 scan/s with an extended range KBr beamsplitter and DTGS detector over a spectral range of 8300 – 470 cm^{-1} at 8 cm^{-1} resolution.
3. Using the portion of the acquired mid-infrared spectrum between 4000-500 cm^{-1} and calibrations previously defined using a partial least squares approach, the contents of total, particulate, humus and charcoal organic carbon are predicted.
4. A subset of samples encompassing the range of predicted values obtained in the previous step are analysed by the direct fractionation method and used as a validation set of samples. If good agreement between the measured values and predicted values are obtained for the validation set, all predicted values for the set of samples being analysed are accepted. If agreement is poor, a new calibration relationship is derived the data acquired for the validation set of samples. If the new calibration relationship provides a better fit between measured and MIR predicted values, it is used to predict revised data for each sample. If the relationship is no better or poorer than that derived from the original calibrations, then the original predicted values are retained.

Method 2.5: Determination of mineralisable C and N

In this analysis the objective will be to incubate soils under a set of constant environmental conditions and measure the rates and amounts of carbon and nitrogen mineralised over a 28 day period.

1. Pack approximately 16.7g (oven dry equivalent) of <2mm sieved soil to a bulk density of 1.4 Mg m^{-3} in an incubation container with an internal diameter of 39 mm. This will give a total sample thickness of approximately 10 mm. The base of the incubation container is not solid, but rather covered with a 20 µm nylon mesh cloth so that air can enter the soil from the top and bottom of the core.

2. Wet the soil to 70% water filled pore space by the slow addition of water being sure to distribute the water evenly over the soil surface and place the core into a sealed glass jar equipped with a septa for sampling the headspace.
3. Incubate the core for 28 days. Measure the CO_2-C emission repeatedly over this period using a handheld Servomex CO_2 headspace analyser with infrared detection of CO_2. Refresh the headspace with ambient air after every CO_2 measurement.
4. Plot the CO_2-C emission data as cumulative CO_2-C through time and fit the data to a single and double exponential emission function. Record the values of the fitted rate constants and size of the pools of mineralisable C.
5. At the end of the incubation remove the soil sample from the incubation container, extract it with 2 M KCl and measure the concentration of inorganic N (ammonium + nitrate) in the sample. Calculate the content of extractable inorganic N in units of kg N per ha using the values of bulk density and soil depth. Subtract the value of extractable inorganic N measured for an unincubated sample of the same soil to define the net N mineralisation over the 28 day period. The net N mineralisation value will be used as an indicator of nutrient supply capacity of the soil.

Appendix 3: Methods for soil acidification analysis

All methods presented below assume that a representative soil sample has been collected, air dried and sieved to <2 mm.

Method 3.1: Soil pH in Calcium chloride

This method measures soil pH in 0.010 M calcium chloride using a 1:5 soil/solution suspension.

1. Prepare a 0.010 M calcium chloride solution by dissolving 1.4702 g calcium chloride dehydrate ($CaCl_2.2H_2O$) in 1.0 l deionised water.

2. Prepare 1:5 soil:calcium chloride suspensions of the soil samples being measured. For example, for each sample, weigh 20.0 g air-dry soil into a suitable container and add 100 ml of 0.010 M calcium chloride. Close the container and shake mechanically for 1 h and then allow the suspension to settle for 20-30 min.

3. Standardise and test the pH meter according to the manufacturer's instruction using commercial standard buffer solutions.

4. Thoroughly wash electrodes between measurements. Immerse electrodes in the unstirred supernatant and record pH value when the reading appears steady.

5. Report pH (pH_{CaCl2}) on an air-dry basis.

Method 3.2: pH Buffering Capacity by Mehlich Buffer Method

Preparation of Mehlich buffer

Prepare two litres of Mehlich buffer as follows:

1. Mix and dissolve the following materials in a 2 l volumetric flask:

- 1500 ml of distilled water,
- 5.0 ml of glacial acetic acid,
- 18.0 ml of 1:1 triethanolamine mixture in water
- 86 g NH_4Cl
- 40 g $BaCl_2$•2H2O

2. Dissolve 36 g of sodium glycerophosphate in 400 ml of distilled water in a separate container.

3. Add sodium glycerophosphate solution to the 2 l volumetric flask. Mix, allow to cool and then fill to volume with distilled water.

4. Check the pH of the buffer reagent. Mix 10 ml of buffer solution with 10 mL distilled water. The pH should be 6.6 ±0.04. If the pH is greater than 6.64, add drops of acetic acid to the original buffer solution and mix. Retest the pH until it is 6.6. If the pH is less than 6.56, add drops of 1:1 aqueous TEA to the original buffer solution. Retest the pH, and repeat the process until the desired pH is achieved.

5. Finally, test the quality of the buffer by reacting it with a known amount of acid and measuring the resulting pH: mix 10 ml of buffer, 10 ml of distilled water and 10 ml of 0.1 M H^+ acid. Prepare the acid solution by dissolving 4.024 g $AlCl_3$. $6H_20$ in 1000 ml of 0.05 M HCl. The capacity of the linear portion of the Mehlich buffer is 0.004 cmolH^+ ml^{-1} pH^{-1}. Addition of 0.1 cmol of H^+ (10 ml of 0.1 M H^+) should decrease the buffer pH by 0.1/(0.004*10 ml buffer) or by 2.5 pH units. The pH of the acid plus buffer mixture should therefore be (6.6-2.5) = 4.1. If the measured pH is not within 4.1±0.05, reject the buffer and check preparation of the buffer reagents to make sure all ingredients were added.

Measurement of soil pH in Mehlich buffer

- Place 10 g of the sieved soil (<2mm) in a 50 ml container
- Add 10 ml of water, mix and allow to equilibrate for 30 mins
- Add 10 ml of Mehlich buffer solution and shake for 10 mins and allow to equilibrate for a further 50 min
- Measure the pH of the soil- Mehlich buffer mix (MpH)
- Calculate the total amount of soil acidity that reacted with the buffer:

$$\text{Total acidity } \left(\text{cmol } H^+ \text{ kg}^{-1} \text{ soil}\right) = \left(6.6 - \text{MpH}\right) \times 0.04 \times 100 \quad [39]$$

$$\text{Total acidity } \left(\text{g } CaCO_3 \text{ kg}^{-1} \text{ soil}\right) = \left(6.6 - \text{MpH}\right) \times 2 = 13.2 - 2\text{MpH} \quad [40]$$

Method 3.3: pH Buffering Capacity by Titration

Calculation of how much NaOH and/or HCl to use during titration

The maximum amount of OH^- (x) needed to titrate the soil to pH~6.5 is assumed to be up to 2 times the total acidity measured by the buffer method (Figure 26). Therefore, 8 g soil commonly used in titration will need up to (x/1000*8) = 0.008x (cmol OH^-) to reach pH~6.5. Assuming that this is supplied by adding a solution of y M NaOH, then the volume of y M NaOH needed to supply 0.008x (cmol OH^-) is:

$$\text{Volume of y M NaOH needed } (\text{ml}) \;=\; 0.08 \times \frac{x}{y} \qquad [41]$$

For example, if a soil has a total acidity calculated from change in Mehlich buffer pH of 7.5 cmol H^+/kg soil, then x = 15.0 cmol OH^-/kg soil. Assuming that we are titrating the soil suspension with 0.05 M NaOH (y = 0.05), then the maximum volume of 0.05 M NaOH needed is (0.08*15.0/0.05) = 24 ml. The manner in which the titration volumes are increased to this maximum value (v = 24 ml) should depend on the soil pH.

- For soil with 3.8 < pH < 4.5, we recommend adding incremental amounts of 0, 0.0625, 0.125, 0.25, 0.5, 0.75 and 1.0 v.
- For soil with 4.5 < pH < 5.5: There is less difference in lime requirement calculated from soil pH in Mehlich buffer and by regression in this pH range (Figure 37), we recommend adding incremental amounts of 0, 0.125, 0.25 and 0.5 v and 0.0625, 0.125, 0.25 and 0.5 v of the same concentration of HCl.
- For soil with 5.5 < pH < 7.0, (some outside the working range of the Mehlich buffer). These soils do not need lime. We recommend a preliminary test adding increments of 0, 5, 10, 15 and 20 ml of 0.05 M HCl to 8 g soil suspension (final ratio 1:5) to determine the maximum volume of HCl required to achieve the lowest titration pH ~ 4.0. The titration volumes of HCl are then apportioned as 0, 0.0625, 0.125, 0.25, 0.5, 0.75 and 1.0 v as before.

Soil titrations

- Prepare the desired HCl and NaOH solutions in 0.010 M $CaCl_2$ containing toluene to suppress microbial growth. Standardise solutions immediately before use.
- Weigh 8 g air-dry sieved (<2 mm) into pre-weighed 60 ml polythene tubes
- Add predetermined amounts of NaOH/HCl solutions in 0.010 M $CaCl_2$ containing toluene.
- Weigh again and top up weight of solution to 40 g (assumed equal to 40 ml) with 0.010 M $CaCl_2$ containing toluene.
- Equilibrate the suspensions for 24 h at 25^0C on an end-over-end shaker (~30 rpm)
- Remove the suspensions from the shaker and leave to equilibrate for a further 6 days at 25^0C.
- Shake the suspensions for 2 min each day to resuspend the soil and measure soil pH at the end of the 7-day equilibration period.

Calculation and reporting

- Calculate the amounts of H^+/OH^- (cmol kg^{-1} soil) added to each soil as follows:

$$\text{Amount added} = \text{vol}\ (\text{ml}) \times \text{conc}\ (\text{M}) \times \frac{1000}{8\text{g} \times 10} \quad [42]$$

- Plot amount added (y) against soil pH at the end of the 7-day equilibration period (x)
- Calculate the regression equation of amount added (y) on soil pH (x) for the linear portion of the graph.
- Record pHBC of the soil (cmol kg^{-1} pH^{-1} soil) as the slope of the regression equation
- Report pHBC along with soil pH in Mehlich buffer

Method 3.4: Lime requirement for liming to critical pH

Calcitic lime (composed mostly of calcium carbonate) is the most common form of lime used to raise soil pH but dolomite lime (calcium and magnesium carbonates) is also used to provide a source of magnesium in addition to increased pH in soils low in magnesium. To calculate lime requirement (LR) as t $CaCO_3$ ha^{-1} we need an equation that performs the following functions:

- Converts pHBC from its measured unit of cmol kg^{-1} pH^{-1} to unit of kg $CaCO_3$ t^{-1} pH^{-1} by multiplying by 0.5.
- Calculates the weight (t ha^{-1}) of soil being limed from the liming depth (m, the unit used to store soil depth data in ASRIS)) and bulk density (Mg m^{-3}):

$$\text{Weight} = 10000 * \text{Depth} * \text{BD} \quad [43]$$

- The amount of lime required (LR) in Mg ha^{-1} to increase soil pH by one unit is therefore:

$$\text{LR} = \frac{\text{pHBC} \times 0.5 \times 10000 \times \text{Depth} \times \text{BD}}{1000} \quad [44]$$

- The equation for LR to increase soil pH from its current to its target value (assumed to be 5.5) is therefore:

$$\text{LR} = \left(\frac{\text{pHBC} \times 0.5 \times 10000 \times \text{Depth} \times \text{BD}}{1000} \right) \times \left(\text{pH}_{\text{Target}} - \text{pH}_{\text{current}} \right) \quad [45]$$

- The LR calculated using the equation above needs to be corrected to reflect the neutralising value (NV) of the liming material used. NV is expressed as % $CaCO_3$. The LR of the actual liming material being used is therefore:

$$LR = (pHBC \times 5 \times depth \times BD) \times (pH_{Target} - pH_{current}) \times \left(\frac{NV}{100}\right) \quad [46]$$

There is an additional requirement to stop soil limed to their optimum pH from becoming more acid. Lime is supplied at the maintenance rate to neutralise the effect of NAAR for the site and sustain soil quality.

$$\text{Maintenance lime requirement} = NAAR \times \frac{NV}{100} \quad [47]$$

NAAR is sometimes expressed as kg lime ha^{-1} y^{-1} and this gives a direct estimate of maintenance lime requirement after correcting for the NV of the material being used. It is sometimes expressed as k mol H^+ ha^{-1} y^{-1}. This unit can be converted to kg lime ha^{-1} y^{-1} by multiplying by 50. Maintenance lime requirement can then be calculated as before.

Method 3.5: Estimating NAAR by ΔpH and pHBC

If pH and pHBC are measured as planned every five years, then the average annual NAAR for that five year period can be calculated according to the formula:

$$NAAR = \frac{\sum_{i=1}^{n} \Delta pH_i \times pHBC_i \times BD_i \times V_i}{\text{period}} \quad [48]$$

Where ΔpH is the change in pH over a specified period (pH unit); pHBC is the pH buffering capacity of the soil (kg $CaCO_3$.kg $soil^{-1}$.pH $unit^{-1}$); BD is the bulk density of the soil (kg $soil.m^{-3}$); V is the volume of the soil being affected ($m^3.ha^{-1}$); period is the time in years (yr); and *i* refers to the particular soil layer. Thus NAAR, summed over all soil layers, is the net acid addition rate for a particular land use (kg $CaCO_3.ha^{-1}.yr^{-1}$).

The technique will be quite robust as long as:

- the sampling is done at the same seasonal event (such as break of season or after harvest) each year to take account of within-year variation,
- the same methods, and quality control of analytical results through use of reference samples and repeated analysis of some samples from a previous batch are employed. This allows assessment of accuracy and precision across the monitoring period.
- the bulk density of the soil is taken into account by sampling to a given mass of soil, and
- there has been no erosion losses or deposition gains.

If the BD is known to have changed before sampling has occurred, the sampling depth of that layer should be adjusted so that the same 'weight' of soil is collected for that layer (Figure 14).

If a change in BD was discovered only after sampling, there would the option to either resample or adjust the calculation. The calculation can be adjusted by calculating a nominal acidification for the start and the end of the time period by comparing with some arbitrary 'starting' pH. If we assume that the BD only increased in the surface sample (say 0-5) and it increased by 20%, then we would have to adjust the thickness of the lower layer in the start time sample to ensure that we are comparing samples on equal weight.

This is demonstrated in Figure 15; the lower layer for the start sample is 'increased' to 16 cm thick because the initial sampling strategy of 1-5, 5-15, 15-30 was followed without knowing that the soil surface was lower because of compaction. Of course this increase can only be done in a mathematical sense at it must be assumed that this 'new' bit soil had similar properties to that above it.

To calculate the NAAR, we need to calculate a nominal NAAR at the start and a nominal NAAR at the end and calculate the difference. We do this by comparing the pH at each layer to an arbitrary value (e.g. .pH 7.0). The equation above becomes two equations; one for the start and one for the end.

$$NAAR_{start} = \frac{\sum_{i=1}^{n}(7 - pH_i) \times pHBC_i \times BD_i \times V_i}{period} \quad [49]$$

where the layers are 0-5; 5-15; and 15-31 and the BD for layer top layer is 1

$$NAAR_{end} = \frac{\sum_{i=1}^{n}(7 - pH_i) \times pHBC_i \times BD_i \times V_i}{period} \quad [50]$$

where the layers are 0-5; 5-15; and 15-30 and the BD of the top layer is 1.2.

The NAAR is now calculated by difference.

$$NAAR = NAAR_{end} - NAAR_{start} \quad [51]$$

Alternatively, the lower layer at the end sampling could have been mathematically reduced to 14 cm thick, but then this would have to be remembered for the rest of the monitoring period.

If there has been erosion/deposition, there is not much that can be done unless the depth of the erosion/deposition is known. In this case the thickness of the top layer might be reduced/increased by that amount in subsequent samplings.

Method 3.6: Estimating NAAR by carbon and nitrogen cycles

In addition to the monitoring NAAR through direct measurement, supplementary approaches could be used to corroborate measured values. These approaches include the collection of information to predict NAAR through the effects of the C and N cycles operating at a given location.

Land use: conservation forests

It would be difficult to capture acidification in forests through nitrogen and carbon cycles. Thus it will be necessary to rely on pH and pHBC measurements (but see van Breemen et al., 1983).

Land use: production forests (plantation and natural)

There is usually little fertiliser use in plantation forestry except at or soon after planting, so acidification due to nitrate leaching from fertilisers is probably minimal compared to product removal. However, nitrate loss from biologically fixed nitrogen could be significant in high rainfall areas with open forests. However this would be quite difficult to estimate. Product removal, on the other hand, should be easy to monitor at harvest time and is simply a sampling exercise. With harvesting by clear felling, substantial amounts of debris are left behind on site; such as branches and leaves etc. Some components, such as leaves, would decay rapidly releasing nutrients. In particular, organic N, would be mineralised and nitrified to nitrate with the production of one H^+ ion. In wet tropical climates, this would be quite rapid and probably before any significant regrowth of vegetation to capture the nitrate. Thus, this would most like be leached contributing to increased acidification. If this scenario is likely, biomass and N concentration of any green debris should be assessed.

With selective felling, the N from the return of green debris would probably be taken up and thus be acid neutral because of the presence of other live plants.

Land use: pasture

There are a number of approaches which could be used. The main issue which needs to be addressed is the redistribution of N and C within a paddock.

One approach is to estimate off-take. Off-take and ash alkalinity of products is not difficult to address and has been done already to some extent (Slattery et al., 1991). What is more difficult is the assessment of alkalinity movement in urine and faeces.

Another approach is the consumption of pasture. There are techniques to estimate standing biomass and predict pasture growth. These combined may give an indication of pasture consumed. Coupled with measurement of alkalinity, and indication of acidification could be obtained.

Land use: crops (including tree crops and hay production)

This strategy is for any produce that is a plant product and exported from the property.

To estimate NAAR, the best possible data on product export and fertiliser use is needed.

Thus it will necessary to obtain:

Crop yields at harvest for every crop

- Ash alkalinity of crop at harvest (from titration and cation/anion balance). This should be on the total crop exported, not just the portion used (e.g. if corn cobs are exported from the farm, then the analysis should be on the whole cobs, not just the kernel). The ash alkalinity should be expressed in the same terms as the yield. This would usually be in fresh weight. If so, then it is necessary to determine the FW/DW ratio as the ash alkalinity will, in practice, be determined on a DW basis.
- quantity and type of fertiliser used on each crop
- lime equivalent of any irrigation water
- lime equivalent of rain water – especially if acidified by nearby industry.
- quantity and ash alkalinity of any material that is being imported to the property (e.g. lime, bagass etc)
- estimate of root distribution with depth

Which NAAR value to use to predict time to critical pH?

If the NAAR for a particular land use / soil type / region is not known then the following is a guide to where information can be obtained.

Forestry

Use value from NLWRA (Appendix 4)

Pasture/grazing

Use values from NLWRA audit and new data from this project (Appendix 4)

Rotations

Use values from NLWRA audit and new data from this project (Appendix 4)

Crops

Either use data from NLWRA audit and new data from this project (Appendix 4)

or

1. Use lookup table for ash alkalinity of product (in kg $CaCO_3$ per tonne product) (Table 6, Appendix 5).

2. Use rainfall data for SLA for growing season to calculate yield using French-Schultze (tonnes per ha) and then adjust yield by a reduction factor (eg 0.75)

3. Multiply 1 by 2 to get NAAR of product

4. Get actual nitrogen use for an SLA or use the recommended rate of nitrogen use for that crop (kg N/ha)

5. Assume that the nitrogen fertiliser is urea if not known.

6. Use the Official Rate (Adams, 1984) as an indication of acidity left behind. For urea this is 1.8 kg $CaCO_3$ / kg N

7. Multiply N application rate (kg N/ha) by the official value of the fertiliser (kg $CaCO_3$ / kg N) to get NAAR due to fertiliser N.

8. Add 3 to 7 to get NAAR for the cropping system

Appendix 4: NAAR for differing land uses. A tick in the column "NLWRA" indicates that this value is from the original audit document (Dolling et al., 2001)

Audit Commodity Classification	Agroecological region	System	NAAR mean	NAAR range	Reference	Comment	NLWRA
			kg $CaCO_3$/ha/yr				
Agroforestry	9, Temperate highlands	Eucalypt forest	45		Prosser et al. (1993)	Forest compared with unimproved pasture	√
Cereals excluding rice	9, Temperate highlands	Continuous wheat + N	125	45-230	Slattery et al. (1998); Conyers et al. (1996)	Mean of 2 experiments. Rotation expt. Same expt as Coventry and Slattery (1991) but deeper sampling and longer term. Acidification calculated from 2 sampling dates. Rotation expt of Conyers et al. (1996) cont wheat with or without N treatment, 0-20 cm. 12	√
Cereals excluding rice	10, Temperate slopes and plains	Continuous wheat (fertilised with N and P)	60	20-120	Mason et al. (1994); Dolling et al. (1994)	Unlimed treatments. 3 sites of Mason et al (1994) and 1 treatment of Dolling et al. (1994)	√
Cereals excluding rice	10, Temperate slopes and plains	cereal cropping		50-250	Conyers et al. (2003)	Dubbo: pHBC from pH before after (1 yr) lime; delta pH	
Cereals excluding rice	10, Temperate slopes and plains	cereal cropping		150-450	Conyers et al. (2003)	Wagga Wagga: Varies with staring pH (pH7 = 500; pH4.5 = 10)	

Audit Commodity Classification	Agroecological region	System	NAAR mean	NAAR range	Reference	Comment	NLWRA
			kg $CaCO_3$/ha/yr				
Cereals excluding rice	10, Temperate slopes and plains	cereal cropping		50-350	Conyers et al. (2003)	Albury	
Cereals excluding rice		Cereals	105		Bloesch et al. (2006)		
Cereals excluding rice		Sorghum	70		Bloesch et al. (2006)		
Cereals excluding rice		maize	150		Bloesch et al. (2006)		
Crop	10, Temperate slopes and plains	Continuous crop, or mainly so	232	179-320	Merry et al. (unpub)	Mid N, SA; N central Vic; W Vic; 3 sites	√
Crop/legume		maize-soy	205		Bloesch et al. (2006)		
Legumes	9, Temperate highlands	Continuous lupin	625		Slattery et al. (1998)	0-60 cm, 17 yr.	√
Legumes		Chickpeas, mungbeans,legumes	265		Bloesch et al. (2006)		
legumes		peanut	265		Bloesch et al. (2006)		
legumes		legumes	265		Bloesch et al. (2006)		
Other non-cereal crops	3, NE wet/dry tropics	Tobacco monoculture	-120	-260 - -25	Moody and Aitken (1997)	Mean of 3 sites	√
Other non-cereal crops	6, Subtropical slopes and plains	cotton		85-250	Singh et al. (2003)	Northern NSW	
Other non-cereal crops		Cotton	95		Bloesch et al. (2006)		

Audit Commodity Classification	Agroecological region	System	NAAR mean	NAAR range	Reference	Comment	NLWRA
			kg $CaCO_3$/ha/yr				
Sugarcane	4, Wet tropical coast and 7, Wet subtropical coast	Monoculture	170	140-235	Moody and Aitken (1997)	Mean of 3 sites	√
sugarcane	4, Wet tropical coast	continuous cane		69	Noble et al. (2003)	Tully	
sugarcane/fallow	4, Wet tropical coast	fallow		44	Noble et al. (2003)	Tully	
Sugarcane/pasture	4, Wet tropical coast	grass ley		191	Noble et al. (2003)	Tully	
Plantation fruit		Avacado	20		Bloesch et al. (2006)		
Plantation fruit		Fodder cropping and tropical fruit	1710		Bloesch et al. (2006)		
Plantation fruit		cashew	20		Bloesch et al. (2006)		
Plantation fruit		citrus	240		Bloesch et al. (2006)		
Plantation fruit		lychee	20		Bloesch et al. (2006)		
Plantation fruit		macadamia	65		Bloesch et al. (2006)		
Plantation fruit		mango	20		Bloesch et al. (2006)		
Plantation fruit		melon	20		Bloesch et al. (2006)		
Plantation fruit		passionfruit	1710		Bloesch et al. (2006)		
Plantation fruit		papaw	1710		Bloesch et al. (2006)		
Plantation fruit		pineapples	240		Bloesch et al. (2006)		
Plantation fruit	4, Wet tropical coast	Banana monoculture	1710	1400-2000	Moody and Aitken (1997)	Mean of 5 sites	√
Grapes		grape	95		Bloesch et al. (2006)		
Grapes	6, Subtropical slopes and plains	Monoculture	95	65-125	Moody and Aitken (1997)	Mean of 2 sites	√

Audit Commodity Classification	Agroecological region	System	NAAR mean	NAAR range	Reference	Comment	NLWRA
			kg $CaCO_3$/ha/yr				
Grazed pasture	1, NW wet/dry tropics	Stylosanthes spp - based pastures	60	25-90	Noble et al. (1997)	Mean of two sites	√
Grazed pasture	3, NE wet/dry tropics	Stylosanthes spp - based pastures	60	0-175	Noble et al. (1997)	Mean of 3 sites (range 0-3.5)	√
Grazed pasture	6, Subtropical slopes and plains	Stylosanthes spp - based pastures	55		Noble et al. (1997)	1 site	√
Grazed pasture	7, Wet subtropical coast	White clover / paspalum/ carpet grass	125	60-180	Helyar et al. (1990) citing Mears (unpubl)	Changes relative to nil super treatment. Mean of 3 super rates	√
Grazed pasture	9, Temperate highlands	Sub clover / annual grasses; sub clover /perennial grasses	120	40-220	2 soil groups of Bromfield et al. (1983); 2 pasture treatments of Reeves and Ellington (1985); mean of 11 paired sites of Ridley et al. (1990a); 2 fert'd treatments of Ridley et al. (1990b); 1 treatment of Ridley et al. (1990c); Helyar et al. (1990)		√
Grazed pasture	10, Temperate slopes and plains	Continuous pasture	45		Dolling et al. (1994)	1 treatment of Dolling et al. (1994). Annual pasture.	√

Audit Commodity Classification	Agroecological region	System	NAAR mean	NAAR range	Reference	Comment	NLWRA
			kg $CaCO_3$/ha/yr				
Grazed pasture	10, Temperate slopes and plains	Grazing	29	25-33	Merry et al. (unpub)	Upper SE of SA; central Vic; 2 sites	√
Grazed pasture	8. Wet temperate coasts	Med intensity grazing	17	11-22	Merry et al. (unpub)	SE SA, sub clover, per grass; subject to inundation most years, alkaline groundwaters; 2 sites	√
Grazed pasture	8. Wet temperate coasts	Low intensity grazing	34	13-59	Merry et al. (unpub)	Adelaide Hills; sub clover, perennial grass; 5 sites	√
Grazed pasture	8. Wet temperate coasts	Low intensity grazing	38	15-55	Merry et al. (unpub)	SE S Aust, annual grass and legume; low intensity grazing; 5 sites	√
Grazed pasture	8. Wet temperate coasts	Med-high intensity grazing	107	62-132	Merry et al. (unpub)	Adelaide Hills; sub clover, perennial grass; 3 sites	√
Grazed pasture	8. Wet temperate coasts	High intensity dairy	0.05	-11-12	Merry et al. (unpub)	Adelaide Hills; sub clover, perennial grass; high rate of import of alkalinity through stock feed; 2 sites	√
Grazed pasture	10, Temperate slopes and plains	Dryland lucerne, grazed	54	29-78	Merry et al. (unpub)	Upper SE of SA; N central Vic; 2 sites	√
Grazed pasture	Subtropical Highlands	Pasture (sheep)		10-32	McCaskill et al. (2003)	Barraba	
Grazed pasture	Subtropical Highlands	Pasture (sheep)		11-50	McCaskill et al. (2003)	Manilla	
Grazed pasture	Subtropical Highlands	Pasture (sheep)		40- 47	McCaskill et al. (2003)	Nundle	
Grazed pasture	Subtropical Highlands	Pasture (sheep)		46-223	McCaskill et al. (2003)	Carcoar	

Audit Commodity Classification	Agroecological region	System	NAAR mean	NAAR range	Reference	Comment	NLWRA
			kg $CaCO_3$/ha/yr				
Grazed pasture	10, Temperate slopes and plains	Pasture (sheep)		25- 48	McCaskill et al. (2003)	Wagga Wagga	
Grazed pasture	9, Temperate highlands	Pasture (sheep)		82-230	McCaskill et al. (2003)	Maindample	
Grazed pasture	10, Temperate slopes and plains	Pasture (sheep)		62-218	McCaskill et al. (2003)	Ruffy	
Grazed pasture	10, Temperate slopes and plains	Pasture (sheep)		78- 98	McCaskill et al. (2003)	Vasey	
Grazed pasture	10, Temperate slopes and plains	Pasture (sheep)		61-238	McCaskill et al. (2003)	Albany	
Grazed pasture	10, Temperate slopes and plains	pasture (sheep)		9-26	Cayley et al. (2002)	Hamilton: product removal and supplements	
grazed pasture		Leucaena pasture		50	Noble et al. (1998)	Samford	
grazed pasture/hay		N-fert grass/legume/grass		255	Noble et al. (1998)	Samford	

Audit Commodity Classification	Agroecological region	System	NAAR mean	NAAR range	Reference	Comment	NLWRA
			kg $CaCO_3$/ha/yr				
Pasture cut for hay	4, Wet tropical coast	Grass - legume pasture	160+		Moody and Aitken (1997)	1 site.	√
Pasture cut for hay	4, Wet tropical coast	Grass + N0	175	50-300	Gilbert et al. (1995), Moody and Aitken (1997)	Grass cut and removed. Mean of 2 sites.	√
Pasture cut for hay	4. Wet tropical coast	Grass + N250 as urea	55	50-55	Gilbert et al. (1995), Moody and Aitken (1997)	Grass cut and removed. Mean of 2 sites.	√
Pasture cut for hay	10, Temperate slopes and plains	Annual pasture	40	30-50	Dolling (1996)	Mean of 2 rotation expts.	√
Pasture cut for hay	8. Wet temperate coasts	Regular hay cutting; med to high intensity grazing		143	Merry et al. (unpub)	W Vic; SE SA;sub clover; perennial grass; 5 sites	√
Pasture cut for hay	3, NE wet/dry tropics	simulated pasture - Jarra grass		500	Armour et al. (unpub)	Mareeba - cut and carry	
Pasture cut for hay	3, NE wet/dry tropics	simulated pasture - Pinto peanut		435	Armour et al. (unpub)	Mareeba - cut and carry	
Pasture cut for hay	3, NE wet/dry tropics	simulated pasture - Scabra stylo		315	Armour et al. (unpub)	Mareeba - cut and carry	
Seed production	3, NE wet/dry tropics	Stylosanthes seed production	530		Noble et al. (1997)	1 site, irrigated	√
Fodder		woody fodder	50		Bloesch et al. (2006)		
Summer crop /pasture rotation	3, NW wet/dry tropics	Crop - pasture rotation	75		Moody and Aitken (1997)	Single site, 6 yr crops, 16 yr pasture	√

Audit Commodity Classification	Agroecological region	System	NAAR mean	NAAR range	Reference	Comment	NLWRA
			kg $CaCO_3$/ha/yr				
Summer crop rotations	3, NW wet/dry tropics	Summer crop – winter fallow	75	40-150	Moody and Aitken (1997)	Mean of 5 sites	√
Summer crop rotations	6, Subtropical slopes and plains	Summer crop – winter fallow	125	70-175	Moody and Aitken (1997)	Mean of 2 sites	√
Wheat/fallow rotation	9, Temperate highlands	Wheat - fallow, - N	0	-25 – 20	Helyar et al. (1990) citing Reeves and Ellington (1985); Ridley (unpub)	Averaged over P rates and relative to N0, P0.	√
Wheat/fallow rotation	9, Temperate highlands	Wheat - fallow, + N	50		Helyar et al. (1990) citing Reeves and Ellington (1985) and Ridley (unpub)	N50 as ammonium sulfate	√
Wheat/pasture rotation	9, Temperate highlands	Wheat – fallow – pasture, +N+P	255		Helyar et al. (1990) citing Reeves and Ellington (1985); Ridley (unpub)	Relative to –N+P	√
Wheat/pasture rotation	9, Temperate highlands	Wheat – pasture, - N	115	63-195	Helyar et al. (1990) citing Reeves and Ellington (1985); Ridley (unpub); Coventry (1992); Helyar et al. (1997)	8 yr P, 3 yr W at Rutherglen. Mean of 4 lime rates at Lilliput. Mean of 6 treatments of Helyar et al. and overall mean of NSD treatments of Conyers et al.	√
Wheat/pasture rotation	10, Temperate slopes and plains	Pasture – wheat	20	10-40	Loss et al. (1993); Dolling (1995); Dolling et al. (1994)	3 sites of Loss et al. (1993), survey of Dolling (1995) and 2 treatments of Dolling et al. (1994)	√

Audit Commodity Classification	Agroecological region	System	NAAR mean	NAAR range	Reference	Comment	NLWRA
			kg $CaCO_3$/ha/yr				
Wheat/lupin rotation	9, Temperate highlands	Wheat - lupin	140	70-205	Coventry and Slattery (1991); Conyers et al. (1996)	Mean of two rotation expts. Coventry and Slattery 0-20 cm, 11 yr. Conyers et al. 0-20, 12 yr	√
Wheat/lupin rotation	10, Temperate slopes and plains	Wheat - lupin	60	15-170	Loss et al. (1993), Dolling (1995), Dolling (1996)	3 sites of Loss et al. (1993) and 2 surveys of Dolling (1995) and 2 sites of Dolling (1996)	√
Wheat/lupin rotation	10, Temperate slopes and plains	Pasture - wheat - lupin	10	8-12	Dolling and Porter (1994), Dolling et al. (1994)	Surveys of Dolling and Porter (1994) and Dolling et al. (1994)	√
Winter crop/ pasture rotation	10, Temperate slopes and plains	Crop - pasture rotation	67	41-93	Merry et al. (unpub)	N Adelaide Plains, Upper SE SA; 4 sites	√
Winter crop/ pasture rotation	10, Temperate slopes and plains	Crop - pasture rotation; intensive croppping, high N use	199	170-228	Merry et al. (unpub)	Upper SE of SA. High N use, closer to cont cropping in recent years; Eyre Peninsular; 2 sites	√
Winter crop/ pasture rotation	10, Temperate slopes and plains	Crop - pasture rotation	84.0	38-115	Merry et al. (unpub)	Eyre Peninsula; mid N SA; N central Vic; 9 sites	√
Winter crop/ pasture rotation	8. Wet temperate coasts	Crop - pasture rotation		111	Merry et al. (unpub)	Willunga Basin, S of Adelaide	√
Irrigated rice /wheat/pasture rotations	10, Temperate slopes and plains	Rice - wheat - pasture (irrigated)	470	395-520	Helyar et al. (1990) citing Dunstan (unpub)	Meaned over 3 soil groups. N as AS and urea.	√
Many	10, Temperate slopes and plains; 9, Temperate highlands	mixed farming to long term pasture		76	Scott et al. (2007)	Cootamundra/NSW-VicBorder Tumbarumba/Berrigan	

Appendix 5: Ash alkalinities for various crop and pasture plants.

In the tables below, column “Ref1” refers to the original reference; column “Ref2” refers to the source of that reference; IFA is the International Fertiliser Industry Association; and IPNI is the International Plant Nutrition Institute. If the source is IFA then the original reference has not been checked and is not listed in the reference list in this document. Column “Method” indicates how the results were generated; Ash means the sample was ashed in a muffle furnace and the resultant alkalinity titrated; all others have been calculated from the anion/cation balance with the elements used in the calculation listed.

Num-Crop	Part	Comment	Yield (t/ha)	Ash Alk				Ref1	Ref2
				(kmol+/t)	(kg lime/t)	(kmol+/ha)	(kg lime/ha)		
001-Abaca		Manila hemp (Musa)	100	0.14	7.2	14.5	723		IFA
002-Annual grasses	tops			0.20	10.0	0.0	0	Merry (unpub)	Merry
003-Apple		Red delicious	44.8	0.04	1.8	1.6	82	Greenham 1980	IFA
004-Apple		Cox's/M2	23.3	0.04	2.0	0.9	46	Greenham 1980	IFA
005-Apple		Cox's/M7	28.8	0.04	2.1	1.2	61	Greenham 1980	IFA
006-Asparagus			6	0.30	14.8	1.8	89	various	IFA
007-Asparagus			4.5	0.96	48.2	4.3	217	various	IFA
008-Asparagus			6.4	1.40	70.0	9.0	448	various	IFA
009-Asparagus			5	0.50	24.9	2.5	125	various	IFA
010-Asparagus			5.7	0.48	24.2	2.8	138	various	IFA
011-Asparagus			4	0.38	19.0	1.5	76	various	IFA

Num-Crop	Part	Comment	Yield (t/ha)	Ash Alk				Ref1	Ref2
				(kmol+/t)	(kg lime/t)	(kmol+/ha)	(kg lime/ha)		
012-Asparagus			2.2	0.64	32.0	1.4	70	various	IFA
013-Avacado	fruit			0.13	6.4	0.0	0		IPNI
014-Avocado			10	0.04	2.1	0.4	21	Lahav 1980	IFA
015-Avocado			10	0.13	6.3	1.3	63	Marchal 1980	IFA
016-Banana	Whole Fruit		40	0.14	7.0	5.6	279		IFA
017-Banana	fruit			0.16	8.1	0.0	0		IPNI
018-Banana	fruit			0.49	24.3	0.0	0	Aitken (unpub)	Merry
019-Barley				0.05	2.7	0.0	0	Hyland 1995	
020-Barley	tops	in head		0.24	12.0	0.0	0	Merry (unpub)	Merry
021-Barley	grain			0.16	8.0	0.0	0	Slattery et al. (1991)	Merry
022-Barley-spring	Grain		4.8	0.10	5.1	0.5	24	Heyland 1961	IFA
023-Barley-spring	Whole tops		9	0.28	13.8	2.5	125	Heyland 1961	IFA
024-Barley-winter	Grain		6.8	0.10	4.8	0.7	33	Heyland 1961	IFA
025-Barley-winter	Whole tops		11	0.35	17.7	3.9	195	Heyland 1961	IFA
026-Bean, soy	seed			0.50	24.9	0.0	0		IPNI
027-Beans		tropical conditions	13	0.29	14.6	3.8	189		IFA
028-Beans, long	bean			0.07	3.5	0.0	0		IPNI
029-Beans, mung	seed			0.63	31.6	0.0	0		IPNI
030-cabbage		tropical conditions	29	0.10	4.8	2.8	140		IFA
031-Canola	seed		1.96	-0.48	-23.9	-0.9	-47		IFA
032-Canola				-0.10	-5.2	0.0	0	Hyland 1995	
033-Capsicum		tropical conditions	21	0.24	12.0	5.0	251		IFA
034-Carrot	root			0.11	5.3	0.0	0		IPNI
035-Carrot	tops	mature		1.82	91.0	0.0	0	Pierre & Banwart (1973)	Merry

Num-Crop	Part	Comment	Yield (t/ha)	Ash Alk				Ref1	Ref2
				(kmol+/t)	(kg lime/t)	(kmol+/ha)	(kg lime/ha)		
036-Carrot	roots			0.84	42.0	0.0	0	Pierre & Banwart (1973)	Merry
037-Carrot – temperate			30	0.14	7.1	4.3	213	various	IFA
038-Carrot – tropical		tropical conditions	43	0.27	13.6	11.7	586		IFA
039-Cashew	fruit		15.5	0.03	1.4	0.4	21	Mohaptra 1973	IFA
040-Cashew	nut		2.4	0.02	1.2	0.1	3	Mohaptra 1973	IFA
041-Cassava			45	0.14	6.8	6.1	304	Amarasiri 1975	IFA
042-Cassava			37	0.08	4.2	3.1	155	Howeler 1985	IFA
043-Cassava			18	0.07	3.5	1.2	62		IFA
044-Cassava			9	0.04	2.0	0.4	18		IFA
045-Cassava	tuber			0.07	3.6	0.0	0		IPNI
046-Cauliflower			37	0.35	17.6	13.0	652	Anstett 1961	IFA
047-Cauliflower			37	0.16	8.0	6.0	298	Average	IFA
048-Celery			81	0.19	9.5	15.4	771	Anstett	IFA
049-Cereal	hay			0.44	22.0	0.0	0	Pierre & Banwart (1973)	Merry
050-Cereal	grain			0.06	3.0	0.0	0	Pierre & Banwart (1973)	Merry
051-Chick Pea	grain		1.373	0.99	49.7	1.4	68	Saxena 1984	IFA
052-Chick Pea	grain		3.726	1.03	51.3	3.8	191	Saxena 1984	IFA
053-Chick Pea	grain		1.5	1.87	93.7	2.8	140	Aulakh 1985	IFA
054-Chick Pea	grain		1.15	0.47	23.4	0.5	27	Horton 1990	IFA
055-Chickpeas		Desi		0.20	10.0	0.0	0	Hyland 1995	
056-Chickpeas		Kabuli		0.15	7.3	0.0	0	Hyland 1995	
057-Chillies	pod			0.76	37.8	0.0	0		IPNI
058-Cloves	clove			0.59	29.7	0.0	0		IPNI
059-Cocksfoot	tops			0.51	25.5	0.0	0	Slattery et al. (1991)	Merry

Num-Crop	Part	Comment	Yield (t/ha)	Ash Alk				Ref1	Ref2
				(kmol+/t)	(kg lime/t)	(kmol+/ha)	(kg lime/ha)		
060-Cocoa	dry bean	7% moisture	1	0.44	22.1	0.4	22	Boyer 1973	IFA
061-Cocoa	husk		1.4	1.57	78.3	2.2	110	Lotode 1981	IFA
062-Cocoa	dry bean	7% moisture	1	0.23	11.6	0.2	12	Omotoso 1975	IFA
063-Cocoa	husk		1.4	1.19	59.3	1.7	83	Thang 1978	IFA
064-Cocoa	dry bean	7% moisture	1	0.09	4.3	0.1	4		IFA
065-Cocoa	husk		1.4	1.36	68.0	1.9	95		IFA
066-Cocoa	dry bean	7% moisture	1	0.43	21.6	0.4	22		IFA
067-Cocoa	husk		1.4	1.04	52.2	1.5	73		IFA
068-Cocoa	bean			0.35	17.3	0.0	0		IPNI
069-Coconut	nut			0.32	16.2	0.0	0		IPNI
070-Coffee	green bean	Arabica		0.55	27.5	0.0	0	Malavolta 1990	IFA
071-Coffee	green bean	Arabica		0.61	30.5	0.0	0	hart 1969	IFA
072-Coffee	green bean	Robusta		0.77	38.7	0.0	0	hart 1970	IFA
073-Coffee	green bean	Excelsa		0.87	43.4	0.0	0	Ledreux 1928	IFA
074-Coffee	green bean	Liberica		0.57	28.6	0.0	0	Ledreux 1929	IFA
075-Coffee	bean			0.82	41.0	0.0	0		IPNI
076-Cotton	seed		2.5	2.68	134.1	6.7	335	Malavolta 1987	IFA
077-Cotton	seed	Mature		0.35	17.5	0.0	0	Pierre & Banwart (1973)	
078-Cotton	lint	Mature		0.20	10.0	0.0	0	Pierre & Banwart (1973)	
079-Cowpea	grain			0.54	26.8	0.0	0		IPNI
080-Cucumber		glasshouse	300	0.11	5.5	33.2	1660		IFA
081-Cucumber		outdoor	30	0.04	1.9	1.1	57		IFA
082-Cucumber		outdoor	15	0.08	4.0	1.2	60		IFA
083-cucumber		tropical conditions	20	0.14	7.1	2.9	143		IFA
084-Cucumber	fruit			0.06	3.1	0.0	0		IPNI

Num-Crop	Part	Comment	Yield (t/ha)	Ash Alk				Ref1	Ref2
				(kmol+/t)	(kg lime/t)	(kmol+/ha)	(kg lime/ha)		
085-Durian			6.72	0.15	7.4	1.0	49	Ng & Thamboo 1967	IFA
086-Durian	fruit			0.13	6.6	0.0	0		IPNI
087-eggplant		tropical conditions		0.06	2.9	0.0	0		IFA
088-Eggplant	fruit			0.06	3.2	0.0	0		IPNI
089-Faba beans				0.20	9.9	0.0	0	Hyland 1995	
090-Field Bean	bean		6.5	0.20	10.1	1.3	65	El-Fouley 1989	IFA
091-Field Bean	Total		21	0.19	9.6	4.1	203	El-Fouley 1989	IFA
092-Field Bean	bean		6	0.11	5.7	0.7	34	Taureau 1984	IFA
093-Field Bean	bean		5	0.36	18.2	1.8	91	Poulain 1989	IFA
094-Field Bean	haulms		3.7	0.82	40.8	3.0	151	Poulain 1989	IFA
095-Field Bean	beans + haulms		8.7	0.56	27.8	4.8	242	Poulain 1989	IFA
096-Field Bean	total		10	0.83	41.7	8.3	417	Finck 1982	IFA
097-Field Bean	total		9.5	0.65	32.6	6.2	309	NRC-GTZ 1991	IFA
098-Field Pea	grain		6	0.41	20.5	2.5	123	Poulain 1989	IFA
099-Field Pea	haulms		3	1.77	88.5	5.3	266	Poulain 1989	IFA
100-Field Pea	grain		6	0.18	8.9	1.1	53	ITCF 1984	IFA
101-Field Pea	haulms		3	0.65	32.4	1.9	97	ITCF 1984	IFA
102-Field Pea	grain		6	0.33	16.6	2.0	100	Poulain 1989	IFA
103-Field Pea	grain		6	1.13	56.3	6.8	338	Taureau 1984	IFA
104-Flax	whole tops		6.5	0.33	16.3	2.1	106	Eyssautier (ITL) 1990	IFA
105-Flax	whole tops		9.3	0.53	26.6	4.9	247	Eyssautier (ITL) 1988	IFA
106-Flax	whole tops		16.5	0.39	19.4	6.4	320	Eyssautier (ITL) 1987	IFA
107-Fodder Legumes			10	1.12	55.8	11.2	558		IFA
108-Fodderbeet	roots stems leaves		15	0.91	45.6	13.7	684		IFA

Num-Crop	Part	Comment	Yield (t/ha)	Ash Alk				Ref1	Ref2
				(kmol+/t)	(kg lime/t)	(kmol+/ha)	(kg lime/ha)		
109-Forage grasses				0.69	34.5	0.0	0	Pierre & Banwart (1973)	Merry
110-Grape	bunch			0.20	9.8	0.0	0	Aitken (unpub)	Merry
111-Grapefruit				0.07	3.6	0.0	0	Koo 1958; Chapma 1968; Malavolta 1989	IFA
112-Grapes			7	0.30	15.0	2.1	105	Fregoni 1984	IFA
113-Grapes			25	0.45	22.4	11.2	560	Fregoni 1984	IFA
114-Groundnut	pods		3	0.14	6.9	0.4	21	p 203 IFA	IFA
115-Groundnut	kernels		1.023	0.25	12.6	0.3	13	p 203 IFA	IFA
116-Groundnut	grain			0.16	7.9	0.0	0		IPNI
117-Hazelnut			1.2	0.77	38.7	0.9	46	Carpentieri	IFA
118-Hemp	whole tops		6	1.18	59.1	7.1	354	Bredemann 1945	IFA
119-Hemp	whole tops		7.1	0.35	17.7	2.5	125	Jakobey 1970	IFA
120-Hemp	whole tops		11.3	0.14	7.1	1.6	80	Ritz 1972	IFA
121-Hops (dried)	cones,leaves,pet,vine		1.86	3.93	196.4	7.3	365	Zattler 1954/56	IFA
122-Hops (dried)	cones,leaves,pet,vine		2.84	4.68	233.8	13.3	664	Marocke 1957	IFA
123-Hops (dried)	cones,leaves,pet,vine		2.42	1.83	91.4	4.4	221	Roberts 1961	IFA
124-Hops (dried)	cones,leaves,pet,vine		2	5.78	288.9	11.6	578	Rossbauer 1978	IFA
125-Jute	Fibre		3	3.43	171.3	10.3	514	Mandal 1979	IFA
126-Jute	Fibre		2	4.32	215.8	8.6	432	Mandal 1979	IFA
127-Kiwifruit	3 yr old vine	3 yr old vine	10	0.51	25.4	5.1	254	smith 1989	IFA
128-Kiwifruit	4 yr old vine	4 yr old vine	20	0.42	21.1	8.5	423	smith 1989	IFA
129-Kiwifruit	>5 yr old vine	>5 yr old vine	20	0.33	16.6	6.6	332	smith 1989	IFA
130-Kiwifruit	>5 yr old vine	>5 yr old vine	30	0.30	15.2	9.1	455	smith 1989	IFA

Num-Crop	Part	Comment	Yield (t/ha)	Ash Alk				Ref1	Ref2
				(kmol+/t)	(kg lime/t)	(kmol+/ha)	(kg lime/ha)		
131-Kiwifruit	>5 yr old vine	>5 yr old vine	40	0.29	14.5	11.6	582	smith 1989	IFA
132-Lemon				0.07	3.4	0.0	0	Koo 1958; Chapma 1968; Malavolta 1989	IFA
133-Lentil	grain		2	0.63	31.6	1.3	63	Saxena 1981	IFA
134-Lentil	grain		1.8	0.50	25.1	0.9	45	Prasad 1990	IFA
135-Lentil	grain		1	-0.15	-7.7	-0.2	-8	Horton 1990	IFA
136-Lentils				0.08	3.8	0.0	0	Hyland 1995	
137-Lettuce				0.17	8.5	0.0	0		IFA
138-Lettuce		tropical conditions	18	0.20	10.0	3.6	179		IFA
139-Lime				0.07	3.4	0.0	0	Koo 1958; Chapma 1968; Malavolta 1989	IFA
140-Lucerne	hay			1.19	59.3	0.0	0	Hyland 1995	
141-Lucerne	seed			0.41	20.3	0.0	0	Hyland 1995	
142-Lucerne	leaves			1.69	84.5	0.0	0	Pierre & Banwart (1973)	Merry
143-Lucerne	stems			0.91	45.5	0.0	0	Pierre & Banwart (1973)	Merry
144-Lucerne	tops			1.20	60.0	0.0	0	Slattery et al. (1991)	Merry
145-Lupin	tops	immature pod		0.62	31.0	0.0	0	Merry (unpub)	Merry
146-Lupin	grain			0.40	20.0	0.0	0	Slattery et al. (1991)	Merry
147-Lupins		sweet		0.21	10.4	0.0	0	Hyland 1995	
148-Lupins		white		0.21	10.3	0.0	0	Hyland 1995	
149-Maize	Grain		9.5	0.01	0.5	0.1	5	Barber & Olsen	IFA
150-Maize	Grain		6.3	0.01	0.7	0.1	4	Aldrich	IFA
151-Maize	grain			0.02	0.9	0.0	0		IPNI
152-Maize	grain			0.02	1.2	0.0	0		IPNI

Num-Crop	Part	Comment	Yield (t/ha)	Ash Alk				Ref1	Ref2
				(kmol+/t)	(kg lime/t)	(kmol+/ha)	(kg lime/ha)		
153-Maize	grain	harvest		0.05	2.5	0.0	0	Pierre & Banwart (1973)	Merry
154-Maize	leaves	harvest		0.93	46.5	0.0	0	Pierre & Banwart (1973)	Merry
155-Mandarin				0.07	3.7	0.0	0	Koo 1958; Chapma 1968; Malavolta 1989	IFA
156-Mango	fruit			0.13	6.4	0.0	0		IPNI
157-Medic	hay			0.87	43.5	0.0	0	Hyland 1995	
158-Medic	seed			-0.18	-8.8	0.0	0	Hyland 1995	
159-Medicago	tops	0.8		0.75	37.5	0.0	0	Merry (unpub)	Merry
160-Mixed grass				0.60	30.0	0.0	0	Slattery et al. (1991)	Merry
161-Mulberry	leaves for silk		24.8	0.54	27.0	13.4	670		IFA
162-Mung beans				0.31	15.3	0.0	0	Hyland 1995	
163-Mungbean			0.7	2.28	114.2	1.6	80	Kothari 1984	IFA
164-Oats	Grain		5	0.09	4.6	0.5	23		IFA
165-Oats	Whole tops		9.8	0.44	21.9	4.3	215		IFA
166-Oats				0.05	2.4	0.0	0	Hyland 1995	
167-Oats	grain			0.06	3.0	0.0	0	Pierre & Banwart (1973)	
168-Oil Palm	bunch			0.13	6.6	0.0	0		IPNI
169-Okra	pods		20	0.16	8.1	3.2	161		IFA
170-Okra	fruit			0.17	8.7	0.0	0		IPNI
171-Onion			30	0.27	13.5	8.1	406		IFA
172-Onion			40	0.22	11.1	8.9	445		IFA
173-onion		tropical conditions	41	0.09	4.5	3.7	185		IFA
174-Onion	bulb			0.04	2.0	0.0	0		IPNI

Num-Crop	Part	Comment	Yield (t/ha)	Ash Alk				Ref1	Ref2
				(kmol+/t)	(kg lime/t)	(kmol+/ha)	(kg lime/ha)		
175-Orange				0.11	5.3	0.0	0	Koo 1958; Chapma 1968; Malavolta 1989	IFA
176-Orange	fruit			0.10	4.9	0.0	0		IPNI
177-Papaya	fruit			0.05	2.5	0.0	0		IPNI
178-Peach			28	0.09	4.7	2.6	131	Janik 1986	IFA
179-Pear			25	0.05	2.7	1.3	66	Boulay 1984	IFA
180-Peas		field		0.16	8.1	0.0	0	Hyland 1995	
181-Peas			7	0.42	20.8	2.9	146	Anstett	IFA
182-Peas			10	0.43	21.6	4.3	216	Peningsfeld	IFA
183-Pecan	nut		1.2	0.23	11.5	0.3	14	Sparks 1975	IFA
184-Pepper	seed			0.58	28.9	0.0	0		IPNI
185-Perennial ryegrass		av 2 N levels		0.87	43.5	0.0	0	Jarvis & Robson (1983)	Merry
186-Phalaris	tops			0.59	29.5	0.0	0	Slattery et al. (1991)	Merry
187-Pidgeonpea			2	0.52	25.9	1.0	52	Ahlawat 1980	IFA
188-Pidgeonpea			1.2	2.64	132.1	3.2	159	Aulakh 1985	IFA
189-Pidgeonpea			3.1	1.06	53.2	3.3	165	Dalal 1977	IFA
190-Pineapple			81	0.06	3.0	4.8	240	Stewart in Py 1956	IFA
191-Pineapple			55	0.07	3.3	3.7	183	Martin-Prevel 1961	IFA
192-Pineapple	fruit			0.06	2.9	0.0	0		IPNI
193-Pistachio			1	0.26	12.9	0.3	13	Woodroof 1967	IFA
194-Potato	tuber	Min	100	0.06	3.0	6.0	300	Burton 1989	IFA
195-Potato	tuber	Max	100	0.08	3.8	7.7	384	Burton 1989	IFA
196-Potato	tuber		57.9	0.11	5.7	6.6	332	Anderson 1978	IFA
197-Potato	tuber		77.7	0.07	3.7	5.8	289	Evans 1977	IFA
198-Potato	tuber		90	0.11	5.7	10.3	514	ADAS 1976	IFA

Num-Crop	Part	Comment	Yield (t/ha)	Ash Alk				Ref1	Ref2
				(kmol+/t)	(kg lime/t)	(kmol+/ha)	(kg lime/ha)		
199-Potato	tuber		50	0.11	5.4	5.4	271	Cooke 1972	IFA
200-Potato	tuber		46.1	0.12	6.0	5.5	275	Widowson 1975	IFA
201-Potato	tuber		50	0.08	3.8	3.8	188	Cooke 1974	IFA
202-Potato	whole plant		30	0.23	11.7	7.0	352	Wirsing 1990	IFA
203-Potato	tuber			0.30	14.8	0.0	0	Smith 1990	IFA
204-Potato	tuber			0.08	3.9	0.0	0	Harris 1978	IFA
205-Potato	tuber			0.11	5.3	0.0	0	Bedin 1989	IFA
206-Potato	tuber			0.08	4.2	0.0	0		IPNI
207-Radish		tropical conditions	19	0.85	42.3	16.1	804		IFA
208-Rambutan			7.34	0.10	5.1	0.7	37	Ng 1967	IFA
209-Rambutan	fruit			0.09	4.4	0.0	0		IPNI
210-Rice	Grain		9.8	0.04	2.0	0.4	20	De Datta 1989	IFA
211-Rice	Straw		8.3	0.92	45.9	7.6	381	De Datta 1989	IFA
212-Rice	grain			0.09	4.4	0.0	0		IPNI
213-Rubber	latex			0.97	48.6	0.0	0		IPNI
214-Rye	Grain		5.9	0.05	2.3	0.3	14		IFA
215-Rye	Whole tops		11.9	0.27	13.4	3.2	159		IFA
216-Safflower	seed?		1.8	0.62	31.2	1.1	56	Thorup 1984	IFA
217-Safflower	seed?		2.2	0.35	17.7	0.8	39	Singh 1980	IFA
218-Safflower				-0.06	-2.9	0.0	0	Hyland 1995	
219-Safflower	tops	pre-flowering		0.78	39.0	0.0	0	Merry (unpub)	Merry
220-Sisal				0.21	10.3	0.0	0		IFA
221-Sorghum	grain	mature		0.07	3.5	0.0	0	Pierre & Banwart (1973)	
222-Sorrel				0.77	38.5	0.0	0	Slattery et al. (1991)	Merry

Num-Crop	Part	Comment	Yield (t/ha)	Ash Alk				Ref1	Ref2
				(kmol+/t)	(kg lime/t)	(kmol+/ha)	(kg lime/ha)		
223-Soy beans				0.28	14.1	0.0	0	Hyland 1995	
224-Soybean	grain			0.56	28.0	0.0	0	The fertiiser handbook	IFA
225-Soybean	grain			1.16	58.2	0.0	0	Bataglia 1977	IFA
226-Soybean	grain			0.49	24.4	0.0	0	Bataglia 1978	IFA
227-Soybean	total			2.07	103.7	0.0	0	Bataglia 1978	IFA
228-Soybean	grain			0.49	24.4	0.0	0	Cordeio 1979	IFA
229-Soybean	total			1.13	56.3	0.0	0	Cordeio 1979	IFA
230-Soybean	grain			1.50	75.0	0.0	0	Guo 1991	IFA
231-Soybean	leaves	harvest		2.54	127.0	0.0	0	Pierre & Banwart (1973)	Merry
232-Soybean	stem			0.96	48.0	0.0	0	Pierre & Banwart (1973)	Merry
233-Soybean	pods	pods (yellowing)		0.83	41.5	0.0	0	Pierre & Banwart (1973)	Merry
234-Spinach		tropical conditions	21	0.38	18.8	7.9	395		IFA
235-Strawberry				0.17	8.4	0.0	0		IFA
236-Sub clover		pre-flowering, no N fert		1.47	73.5	0.0	0	Jarvis & Robson (1983)	Merry
237-Sub clover	whole tops			0.82	41.0	0.0	0	Slattery et al. (1991)	Merry
238-Sub Clover	tops	0.8		0.95	47.5	0.0	0	Merry (unpub)	Merry
239-Sub Clover, annual grass	tops	20% sub clover		0.30	15.0	0.0	0	Merry (unpub)	Merry
240-Sub Clover, annual grass	tops	40% sub clover		0.60	30.0	0.0	0	Merry (unpub)	Merry
241-Sub Clover, annual grass	tops	60% sub clover		0.75	37.5	0.0	0	Merry (unpub)	Merry
242-Sub Clover, annual grass	tops	60% sub clover		0.95	47.5	0.0	0	Merry (unpub)	Merry
243-Sub Clover, perennial ryegrass	tops	30% sub clover		0.50	25.0	0.0	0	Merry (unpub)	Merry
244-Sugar Cane				0.02	1.2	0.0	0	Zende 1983	IFA
245-Sugar Cane				0.05	2.4	0.0	0	Malavolta 1982	IFA
246-Sugar Cane				0.18	9.0	0.0	0	Thompson 1988	IFA

Num-Crop	Part	Comment	Yield (t/ha)	Ash Alk				Ref1	Ref2
				(kmol+/t)	(kg lime/t)	(kmol+/ha)	(kg lime/ha)		
247-Sugarbeet	beet + foliage		10	0.22	11.1	2.2	111	Buchner 1985	IFA
248-Sugarbeet	beet + foliage		10	0.19	9.5	1.9	95	Finck 1979	IFA
249-Sugarbeet	beet		10	0.02	1.0	0.2	10	Michigan S U	IFA
250-Sugarbeet	beet + foliage		10	0.17	8.6	1.7	86	Faustzablen 1983	IFA
251-Sugarbeet	beet		10	0.08	3.8	0.8	38	Faustzablen 1984	IFA
252-Sugarbeet	beet + foliage		10	0.12	5.9	1.2	59	Hills 1982	IFA
253-Sugarbeet	beet + foliage		10	0.18	9.2	1.8	92	Beiss 1975	IFA
254-Sugarcane	cane			0.04	2.2	0.0	0		IPNI
255-Sugarcane	stem			0.44	22.0	0.0	0	Pierre & Banwart (1973)	Merry
256-Sugarcane	stalk			0.08	3.8	0.0	0	Aitken (unpub)	Merry
257-Sugarcane	leaves			0.28	14.1	0.0	0	Aitken (unpub)	Merry
258-Sunflower	removal		3.5	0.58	29.2	2.0	102		IFA
259-Sweet Corn		tropical conditions	20	0.29	14.7	5.9	294		IFA
260-Sweet Corn	cob			0.14	7.1	0.0	0		IPNI
261-Sweet pepper	fruit			0.06	3.0	0.0	0		IPNI
262-Sweet Potato	tuber		10	0.11	5.6	1.1	56	Wenkam 1983	IFA
263-Sweet Potato	Leaf		4	0.18	8.8	0.7	35	Wenkam 1983	IFA
264-Sweet Potato	tuber		10	0.08	3.9	0.8	39	Bradburg 1990	IFA
265-Sweet potato	tuber			0.16	8.1	0.0	0		IPNI
266-Taro	tuber			0.08	4.2	0.0	0		IPNI

Num-Crop	Part	Comment	Yield (t/ha)	Ash Alk				Ref1	Ref2
				(kmol+/t)	(kg lime/t)	(kmol+/ha)	(kg lime/ha)		
267-Tea	plucks		4	0.21	10.5	0.8	42	many	IFA
268-Tea	prunings (for fuel)		12.8	0.05	2.6	0.7	34		IFA
269-Tea	leaf			0.72	35.9	0.0	0		IPNI
270-Temperate Grassland		perma, sown, leys	2.5	0.84	41.8	2.1	104		IFA
271-Temperate Grassland		perma, sown, leys	5	0.85	42.3	4.2	211		IFA
272-Temperate Grassland		perma, sown, leys	10	0.85	42.3	8.5	423		IFA
273-Temperate Grassland		perma, sown, leys	12.5	0.84	42.2	10.5	527		IFA
274-Temperate Grassland		grass/legume sward	8	1.37	68.6	11.0	549		IFA
275-Tobacco	leaf			2.35	117.4	0.0	0		IPNI
276-Tobacco		flue cured	2	2.56	127.8	5.1	256	Hawks 1983	IFA
277-Tobacco		flue cured	2.15	4.01	200.5	8.6	431	Ryding	IFA
278-Tobacco		flue cured	2.6	3.25	162.3	8.4	422	Ryding	IFA
279-Tobacco		flue cured	2.25	5.64	282.1	12.7	635	Mao	IFA
280-Tobacco		Burley	2.913	2.23	111.7	6.5	326	Campbell	IFA
281-Tomato		outdoor	45	0.12	6.2	5.6	281		IFA
282-Tomato		greenhouse	100	0.15	7.5	14.9	745		IFA
283-Tomato		tropical conditions	24	0.54	26.9	12.9	645		IFA
284-Tomato	fruit			0.13	6.6	0.0	0		IPNI
285-Tomato	leaves	fruiting		1.52	76.0	0.0	0	Pierre & Banwart (1973)	Merry
286-Tomato	stems			1.07	53.5	0.0	0	Pierre & Banwart (1973)	Merry

Num-Crop	Part	Comment	Yield (t/ha)	Ash Alk				Ref1	Ref2
				(kmol+/t)	(kg lime/t)	(kmol+/ha)	(kg lime/ha)		
287-Triticale	grain			0.14	7.0	0.0	0	Slattery et al. (1991)	Merry
288-Trop Grass/Legume		20% legume	8	0.82	40.9	6.5	327		IFA
289-Trop Grass/Legume		20% legume	5	0.81	40.7	4.1	203		IFA
290-Tropical grasslands		mixed spp	8	0.77	38.5	6.2	308		IFA
291-Tropical grasslands		mixed spp	4	0.77	38.5	3.1	154		IFA
292-Tropical grasslands		mixed spp	2.5	0.71	35.7	1.8	89		IFA
293-Walnut	hull		0.9	0.55	27.5	0.5	25	Painter 1965	IFA
294-Walnut	shell		0.9	0.25	12.5	0.2	11	Painter 1965	IFA
295-Walnut	kernel		0.9	0.18	9.2	0.2	8	Painter 1965	IFA
296-watermelon				0.07	3.7	0.0	0		IFA
297-watermelon		tropical conditions	15	0.44	22.2	6.7	333		IFA
298-Watermelon	fruit			0.09	4.3	0.0	0		IPNI
299-Wheat				0.03	1.6	0.0	0	Hyland 1995	
300-Wheat	tops	in head		0.22	11.0	0.0	0	Merry (unpub)	Merry
301-Wheat		pre-flowering/av 2 N levels		0.62	31.0	0.0	0	Jarvis & Robson (1983)	Merry
302-Wheat	grain			0.18	9.0	0.0	0	Slattery et al. (1991)	Merry
303-Wheat-spring	Grain		4.5	-0.04	-1.9	-0.2	-9	Aigner 1988	IFA
304-Wheat-spring	Whole tops		9	0.20	10.2	1.8	92	Aigner 1988	IFA
305-Wheat-winter	Grain		6.7	0.08	4.0	0.5	27	Aigner 1988	IFA
306-Wheat-winter	Whole tops		13.7	0.33	16.7	4.6	229	Aigner 1988	IFA
307-White clover		pre-flowering, no N fert		1.63	81.5	0.0	0	Jarvis & Robson (1983)	Merry
308-Yam	tuber			0.06	3.2	0.0	0		IPNI

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