Copyright is owned by the Author of the thesis. Permission is given for a copy to be downloaded by an individual for the purpose of research and private study only. The thesis may not be reproduced elsewhere without the permission of the Author. AN EVALUATION OF WATER EXTRACTION AS A SOIL-TESTING PROCEDURE FOR PHOSPHATE

A thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in Soil Science at Massey University

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#### ABSTRACT

In New Zealand, the fertilizer P requirements of developed pasture, maintained at a steady level of production, are currently calculated using a model which is based on the concept that the size of the P cycling pool remains constant. Consequently, fertilizer P is required only to replace P lost from the cycle through animals and in the soil. A soil test is required to assess whether the amount of available soil P is appropriate for the desired level of production and to monitor the effectiveness of the maintenance fertilizer P programme indicated by the model. A water-extraction procedure offers potential as a soiltesting procedure for this purpose. The water-extraction procedure involves an extraction period of 1 h and a soil: solution ratio of 1:120.

In an initial evaluation in the glasshouse with 20 soils, water-extractable P was highly correlated with plant uptake of P ( $r = 0.90^{**}$ ). Unlike the prediction by the Olsen test, the prediction of plant-available P using water extraction was not improved by inclusion of an estimate of P buffering capacity (P retention value or the slope of the desorption isotherm). Consequently, the waterextraction procedure may have advantages over other soil P tests because the interpretation of the results obtained appears to be independent of buffering capacity and soil type.

The effect of seasonal variations, sampling depth, and fertilizer P additions on water-extractable P values was investigated in field experiments, involving two soils of contrasting P sorption capacity (Ramiha and Tokomaru) under permanent pasture over 12 months. It was found that the levels of water-extractable P in soil were always lower than those of Olsen-extractable P. Over the 12-month period, the average value of water-extractable P in the unfertilized Ramiha soil (0-7.5 cm depth) was 1.8  $\mu$ g g<sup>-1</sup> soil compared to the Olsen-extractable P value of 12.6. The variability associated with water-extractable P at each sampling time was comparable with that for Olsen-extractable P. However, the relative seasonal variation over 12 months was larger for water-extractable P (coefficient of variation = 23% for the Ramiha soil) than for Olsen-extractable P (coefficient of variation = 16% for the Ramiha soil). Both extractants showed a seasonal fluctuation that was closely related to the pattern of pasture P uptake. Low levels of extractable P were generally associated with autumn and spring flushes of pasture growth, while high values were obtained during periods of slow growth in winter. The levels of water- and Olsen-extractable P were higher in samples taken from the 0-4.0 than the 0-7.5 cm sampling depth. For example, waterextractable P values of the unfertilized Ramiha soil averaged over the 12-month period were 3.7 and 1.8  $\mu$ g g<sup>-1</sup> soil for the 0-4.0 and 0-7.5 cm sampling depths, respectively. The relative variability of P level at each sampling depth varied between soils.

Fertilizer P addition resulted in larger increases in water-extractable P in the 0-4.0 cm sampling depth than those in the 0-7.5 cm depth. Furthermore, the effect of fertilizer P on water-extractable P in the 0-7.5 cm depth became undetectable within a few months of addition, inspite of the continuing response of pasture to fertilizer P. Consequently, water-extractable P in soil sampled from the 0-4.0 cm depth may better reflect the effect of fertilizer P addition than water-extractable P in the 0-7.5 cm depth. The relative increase in water-extractable P as a result of fertilizer P addition was larger than that of Olsenextractable P. At two weeks after 40 kgP ha<sup>-1</sup> was added to both the Ramina and Tokomaru soils, water-extractable P (0-4.0 cm depth) was increased by 150% whereas the increase in Olsen-extractable P was only 100%.

Although seasonal variations were observed in both water-extractable P and soil microbial biomass P in unfertilized and fertilized soils, they were not related. Neither were the seasonal changes in soil microbial biomass P related to P uptake by pasture. It appears that microbial

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biomass P may be a less sensitive index of soil P availability than previously thought.

The addition of lime in an incubation and a glasshouse study caused significant decreases in Olsen-extractable P but very little change in water-extractable P in two soils of contrasting P sorption capacities. Decreases in Olsenextractable P of approximately 20% were obtained for both soils of medium P status as a result of the addition of Ca(OH)<sub>2</sub> at rates equivalent to 2,000 and 6,000 kg CaCO<sub>3</sub> ha<sup>-1</sup>, respectively. No such decreases were found in plant data or other soil P tests. Evidence from a laboratory study indicated that the decline was a result of an artifact in the Olsen procedure by which calcium phosphates may be precipitated under the conditions of high calcium concentration and high pH. Results from a field experiment on a Tokomaru soil under permanent pasture over 21 months also confirmed that liming caused a decrease in Olsen-extractable P. In fact, a significant reduction of 30% in the Olsen-extractable P was still obtained at 21 months after the application of 5,000 kg  $CaCO_3$  ha<sup>-1</sup>. Because water-extractable P values are much less influenced by soil pH, water extraction may have an advantage over the Olsen test as a soil-testing procedure for limed soils.

A model of P sorption, based on the Langmuir adsorption equation was used to predict changes in water-extractable P in soils following P addition. The predictive ability of the model was strongly influenced by estimates of sorption energy constants (K) for a high P-sorbing soil. Whereas for a low P-sorbing soil, estimates of sorption maxima (b) were more important. The predictions were satisfactory for a soil with high P sorption capacity but overestimated results were obtained for a low P-sorbing soil. A revised model was developed to use phosphate retention (PR) test data as an estimate of b. When tested on a group of 16 soils with a wide range of P sorption capacities, very good predictions (r =  $0.84^{**}$ ) of changes in waterextractable P following P addition were obtained. It was found that, in some soils, the amounts of P extracted by

water were still changing rapidly at 1 h but the rate of change became significantly smaller at 24 h. Improved predictions by the model ( $r = 0.91^{**}$ ) were obtained with an extraction period of 24 h compared to the original 1-h period. With such a modelling approach, it may be possible to use the water-extraction procedure to determine whether fertilizer application rates are in excess of the calculated maintenance requirements and also to quantify this estimate.

In a study using a double-labelling technique designed to characterise soil P, the soil was incubated with <sup>33</sup>P for a relatively long period of time (51 days) and 32p for a relatively short period of time (5 days). The  $32_{P}$ :  $33_{P}$ ratios in the Olsen and water extracts of the high P-sorbing Egmont soil showed a contrasting pattern to that of the low P-sorbing Tokomaru soil. An initial assumption of the technique is that as the exchangeability of soil P decreases, so should the ratio of  $32_{P}:33_{P}$ . The unexpected lower <sup>32</sup>P:<sup>33</sup>P ratios in the water extract as compared to the ratio in the Olsen extract of the Eqmont soil appears to be consistent with the larger difference between the amounts of water-extractable P and those of Olsen-extractable P which, in turn, seem to reflect the ratio of loosely-held P to more tightly-held P. A lower  ${}^{32}P:{}^{33}P$  ratio in the water extracts can occur when the exchange of  $3^{2}P$  between the soil solution and the surface has slowed down and the  $^{32}P$  is redistributed among various surface groups.

The <sup>32</sup>P:<sup>33</sup>P ratios of ryegrass grown on the labelled soils were always lower than the ratios of white clover, indicating that ryegrass can remove P from more tightly-held soil P than can white clover. This may be due to the ability of ryegrass to exploit P from different soil P pools as well as the larger depletion of soil P by ryegrass. I would like to express my sincere appreciation to the following people:

Professor Keith Syers for invaluable guidance, unending enthusiasm and encouragement during my study.

Mr. Russell Tillman for helpful supervision, ready advice, patience, and continual support throughout this study.

Dr. Ian Cornforth, of Ruakura Soil and Plant Research Station, Hamilton for his professional interest and helpful discussion.

Drs. Paul Gregg and Mike Hedley for helpful discussion with various aspects of the study.

Lance Currie and John Sykes for assistance with the glasshouse and field work.

Martin Lewis who helped with the development of computer programmes and analysis of results.

The staff of Massey University farms for their co-operation and assistance with the field experiments.

Margaret Wallace for friendship and help with proofreading.

Carolyn Hedley for the excellent illustration of figures.

Erin Temperton for patience and skill in typing this thesis.

Many past and present members of the Department of Soil Science, particularly Sally Roughan, Annette Richardson, and Ravindra Naidu, for their personal and professional interest, assistance and for providing the friendly and relaxed atmosphere to carry out this work. Margaret and Graham Bailey for being my kiwi parents.

My Thai and New Zealand friends for friendship and valuable support, particularly during the final stage of the study.

The Bilateral Aid Division of the New Zealand Ministry of Foreign Affairs for providing a scholarship and the Research Division of the New Zealand Ministry of Agriculture and Fisheries for funds for the project.

Massey University for the Faculty Graduate Study Award, Farmers' Union and MacMillan Brown Agriculture Research Scholarships.

Ban for his encouragement, understanding, and support.

And lastly, but most importantly, my family, especially my parents.

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