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HOW CLOSELY DO DIFFERENT OLSEN P MEASURES CORRELATE?

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Abstract
Olsen P is a commonly used method for the estimation of available P in New Zealand soils for fertiliser recommendations and as an indicator in regional soil quality assessment. It is also under consideration as a measure of soil quality for national reporting by government agencies, and as part of the Environmental Monitoring and Reporting (EMAR) process, where method consistency is very important. However, Olsen P may be reported on a gravimetric or volumetric basis and there are differences in the analytical methods that appear to confound ready comparison of results reported from different laboratories. We aim to overcome this confounding issue and the potential of methodological differences by determining the best method for comparing the different Olsen P datasets. Results from regression analysis of Olsen P from a set of samples analysed by different laboratories and converted between volumetric and gravimetric results using different approaches (field bulk density, volume weight) are presented.

Introduction
Regional and national reporting
Regional authorities in New Zealand regularly monitor soil quality (soil health) in State of the Environment (SoE) monitoring. This reporting has a focus on environmental protection and sustaining the environment for future generations. The Land Monitoring Forum (LMF- a group of unitary and regional council soil and land scientists) has developed a set of standard methods (Hill and Sparling 2009). The LMF initiated a national review of the soil quality monitoring programmes with a view to improving the programme for regional and national reporting (Cavanagh et al. 2017). Regional councils are also contributing to the development of the land-based component of the Environmental Monitoring and Reporting (EMaR) project with the Ministry for Environment and other agencies. The EMaR project relates to the national *Environmental Reporting Bill*.

One indicator of soil nutrient status used in the monitoring is Olsen P. It is also a commonly used soil fertility indicator of plant-available soil phosphorus used by agricultural and horticultural industries to help assess on-farm nutrient management. It is also used by researchers to study interactions of soil and water quality. Olsen P is commonly measured on a gravimetric (weight) basis and therefore avoids the confounding influence of soil field bulk density (McDowell and Condron 2004). The gravimetric method is used internationally and by most research agencies in New Zealand. In New Zealand a modified method has been developed for soil fertility assessment, as discussed below. In addition, to report stocks of Olsen P, field bulk density measurements are used to convert gravimetric measure to a volumetric basis as is conventionally done for the assessment of C and nutrient stocks (e.g. Reganold and Palmer, 1995) This can be considered a specific application and differs from the "volumetric Olsen P" measurements described below.

Olsen P in New Zealand – a modified method

The agricultural industry has for many years in association with current and former government and research organisations used Olsen P to measure soil P fertility on farms for assessing nutrient and fertiliser requirements.

Sinclair et al. (1997) reported that the Olsen P soil test used by the extensive Ministry of Agriculture and Fisheries (MAF) and AgResearch trials was a modification of the original test, in that a volume rather than a weight of soil was used. This method is termed "volumetric Olsen P" for this paper. Considerable research in soil fertility and plant yield response has been undertaken in New Zealand using the modified method (e.g. Cornforth and Sinclair 1984; Sinclair et al. 1997; Edmeades et al. 2006). Much of this work has contributed to widely used industry recommended targets (e.g. Roberts and Morton 2009). Further details are presented in Drewry et al. (2013). In New Zealand, several large commercial laboratories also measure the weight of soil by volume of sieved and dried sample prior to the chemical extraction; this is referred to as volume weight.

Conversion between gravimetric and volumetric results should be straight-forward as it simply requires conversion between the units of reporting using a density measurement. However, previous comparisons using field bulk density conversions have revealed discrepancies (Drewry et al. 2013 and references therein). No comparisons have previously been undertaken using volume weight and with an increasing focus on national reporting for SOE there is an increasing imperative to be able to appropriately compare results and understand the reason for any discrepancy. Use of the "volume weight", which is effectively the bulk density of the prepared sieved and air-dried soil in the laboratory, is another way to compare the results. However, there appears little, if any validation of the two conversion methods in the published literature. In addition, it is unclear which method (or if both methods) is best suited for SoE reporting.

To evaluate possible improvements in regional and national soil quality reporting, in this paper we present a preliminary study comparing the two methods of reporting and the use of bulk density and volume weight as conversion factors.

Methods

Overview of monitoring programme

The soil quality monitoring programme was developed across many regional areas of New Zealand (Hill et al. 2003). Many regional councils continued the programme and a standardised set of procedures was developed by the LMF (LMF 2009). Unlike production targets, limits for environmental protection are presented as mg/kg (MacKay et al. 2013). In the present study, the samples were taken from sites in the Auckland, Waikato and Wellington regions. Further details of the monitoring programmes in these regions are available in Taylor et al. (2017) and Drewry et al. (2017). For this study samples were taken from 74 sites in the Auckland region for 2014 - 2016 from 30 sites in the Waikato region for 2016, and from 45 sites in the Wellington region for 2016 - 2017. Sites were from a range of seven land uses;

native, forestry, cropping (with annual tillage), market gardening (vegetables), horticulture (orchards), dairy pasture and other pasture (pasture not in dairy); and nine soil orders; Allophanic, Brown, Gley, Granular, Organic, Pallic, Pumice, Recent and Ultic.

Measurements and indicators

Details of field methods are reported in Hill and Sparling (2009). Briefly, at each site a 50 m transect was used to take 10 cm depth soil cores, taken approximately every 2 m. Individual cores were bulked and mixed to obtain a representative sample. In addition, three undisturbed (intact) soil samples were obtained from each site for field bulk density (Hill and Sparling 2009). The intact cores were collected along the transect by pressing steel liners (10 cm in diameter and 7.5 cm in depth) into the soil. From these intact cores, a 3 cm subsample ring was used in the Landcare Research laboratory in Hamilton to determine field bulk density. Field bulk density can be used to convert gravimetric data to a volumetric basis.

Analysis (A) gravimetric results (mg/kg)

Olsen P is measured on a gravimetric (weight) basis and therefore avoids the confounding influence of soil field bulk density. Soil Olsen P measurements were analysed on air-dried <2 mm subsample of the composite field sample by Landcare Research Environmental Chemistry Laboratory on a gravimetric (weight) basis, i.e. results are expressed as mg/kg (Blakemore et al. 1987).

Analysis (B) direct 'scoop' volumetric results (mg/L)

A second air-dried <2 mm sub-sample of the composite field sample was analysed for Olsen P by Hill Laboratories (volumetric 'scoop' basis). The 'scoop' is 3 mL in size. The weight of the sieved and air-dried sample filling the scoop volume is the volume weight in g/mL. (Note that this is a laboratory estimate; *not* the same as undisturbed intact field bulk density). The volumetric scoop basis is obtained on a sieved and air-dried sample prior to the chemical extraction. Laboratory volume weight can be used to convert volumetric data to a gravimetric basis.

Calculations

Conversions were carried out between the methods using Equations 1-2.

Equation 1. Volumetric Olsen P/volume weight = mg/kg

Equation 2. Gravimetric * bulk density = mg/L

Statistical analysis

Regression analysis of Olsen P by the volumetric and gravimetric methods, and results from conversions using field bulk density and volume weight was carried out using Excel. Boxplots were created using the statistical package 'R' version 3.4.1 (R Core Team 2017).

To compare results we present: Analysis (A) *reported as gravimetric results*, for the Landcare Research gravimetric data (mg/kg). Analysis (B) *reported as calculated volumetric results;* gravimetric laboratory data converted to volumetric equivalent units by multiplying by undisturbed field bulk density. The influence of soil order and landuse were also investigated.

Results

Correlations and relationships between gravimetric and volumetric methods, and conversions using bulk density and volume weight are presented in Figures 1-3. Overall correlations were high ($R^2 \geq 0.94$) but slopes deviated from the 1:1 line and this was associated with bulk density (Figures1, 2A and B). The same slope deviation was also seen with volume weight but the slopes were not as close to the 1:1 line (data not shown). However slopes were much closer to the 1:1 line for Olsen P values <100 (Figures 3A and B). The best relationship below Olsen P 100 was between gravimetric and volumetric/ volume weight methods.

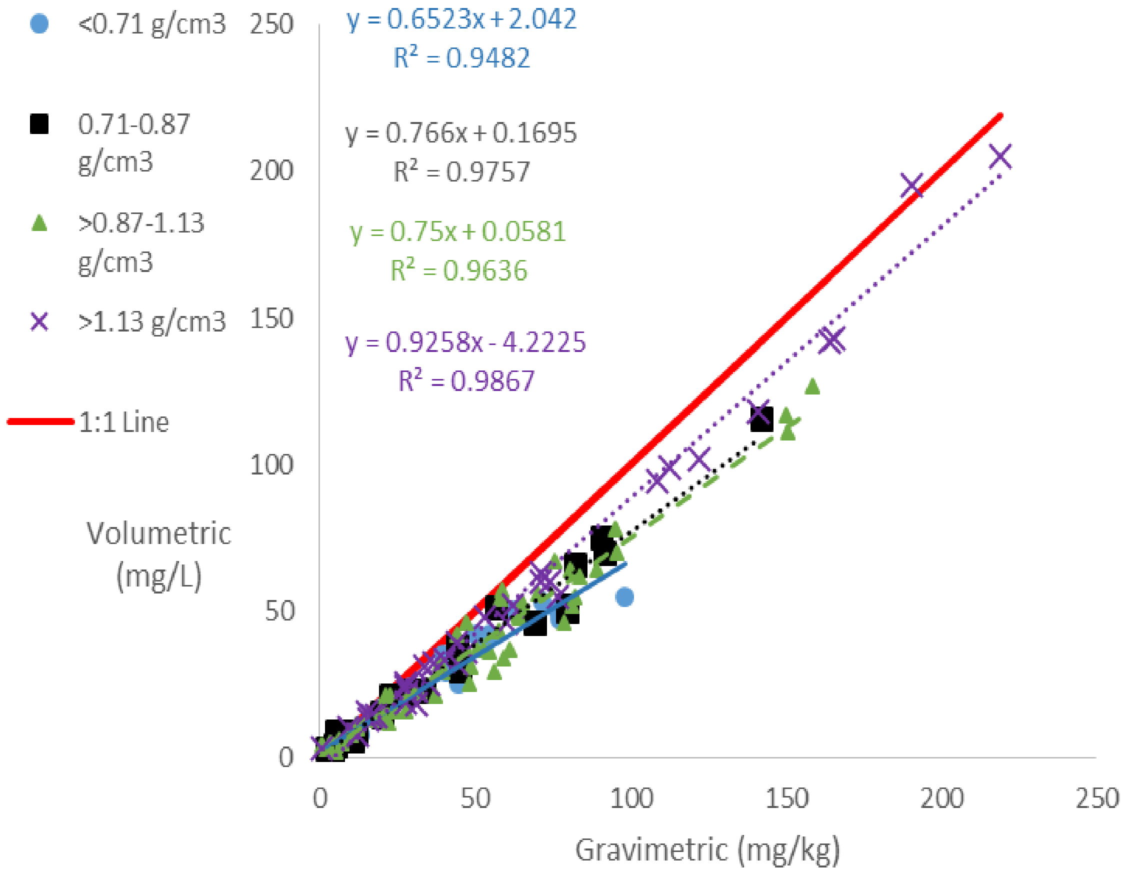

Figure 1. Scatterplot showing relationship between volumetric and gravimetric methods of Olsen P grouped by bulk density.

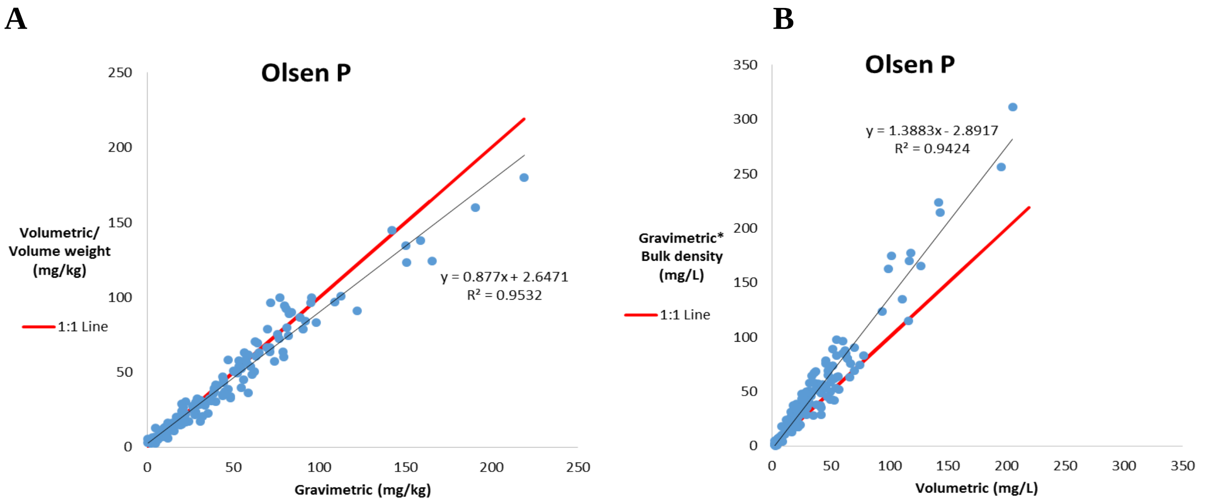

Figure 2. Scatterplot showing relationships between (A) the gravimetric method of Olsen P and conversion from the volumetric method using volume weight; (B) the volumetric method of Olsen P and conversion from the gravimetric method using field bulk density.

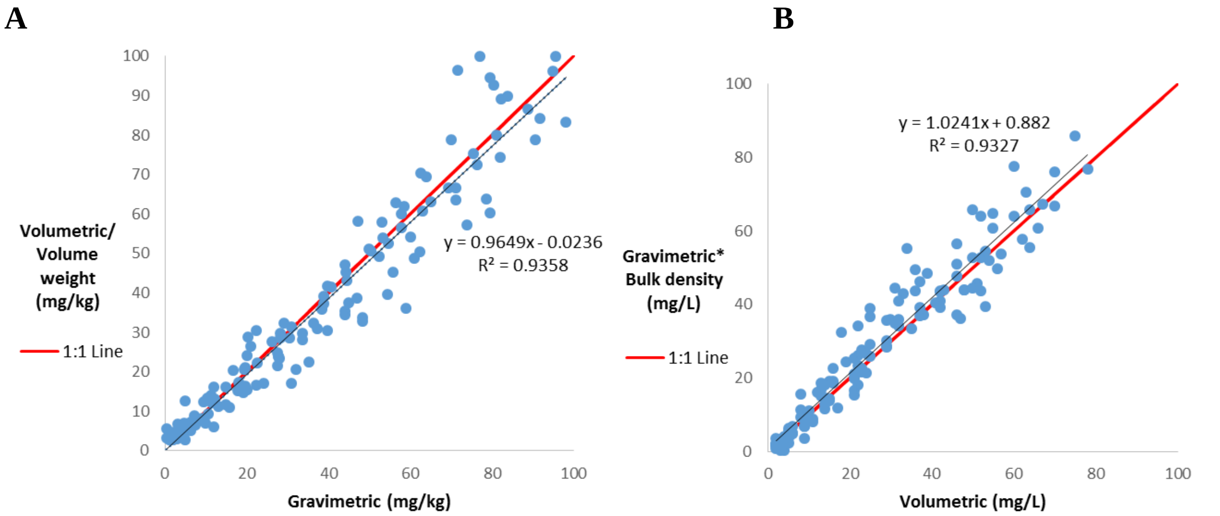

Figure 3. Scatterplot showing relationships between (A) the gravimetric method of Olsen P <100 mg/kg and conversion from the volumetric method using volume weight; (B) the volumetric method of Olsen P <100 mg/L and conversion from the gravimetric method using field bulk density

Land use and Olsen P

Land use impacted Olsen P levels (Figure 4). The highest values of Olsen P were found for soil under market gardening and horticulture, while the lowest values were found in soil under native forest.

Soil Order and Olsen P

There was no clear impacts on Olsen P by soil order and most soil orders had a wide range of values (Figure 5).

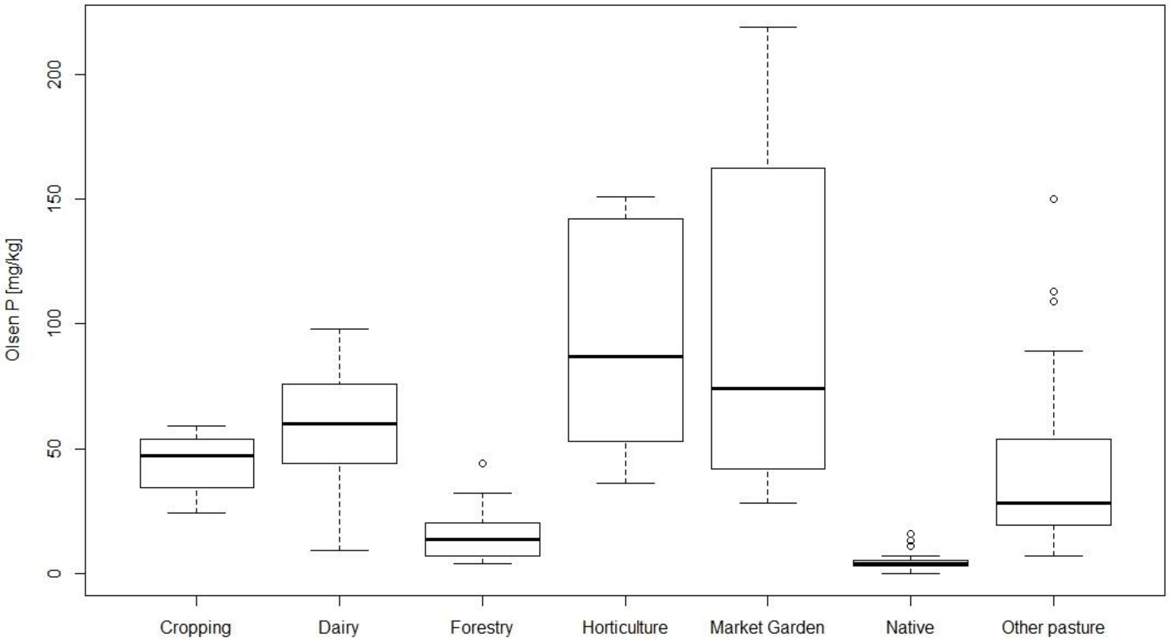

Figure 4. The relationship between the gravimetric method of Olsen P and land use.

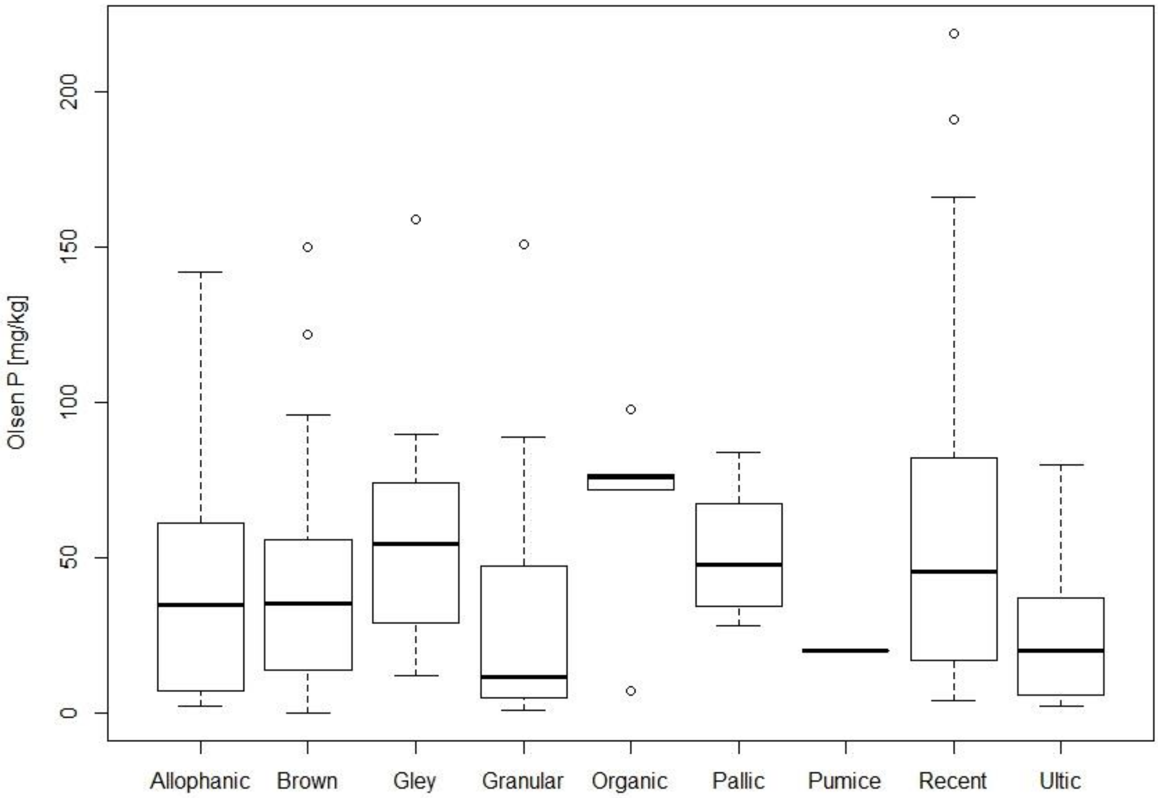

Figure 5. The relationship between the gravimetric method of Olsen P and soil Order.

Discussion

No matter which method is use, it is essential that the units of measure be included when reporting results. Both gravimetric and volumetric Olsen P methods use sieved dried soil, therefore volume weight is the only measure that is relevant to use for conversion between the different reported results for laboratory samples. However, if presenting information on stocks or if it is desired to express results on an area basis, then using the gravimetric method multiplied by the field bulk density is the appropriate measure.

This work and Drewry et al. (2013) show the observed differences between the volumetric and gravimetric measurements decrease as bulk density or volume weight increase, i.e. the slope of the trendline becomes closer to 1. Our results are consistent with Rajendram et al. (2003)'s conclusion that the ratio of soil to solution is critical to the amount of P extracted. In using a volume of soil, the soil: solution ratio varies depending on the soil volume weight in the laboratory. Soils with low volume weight such as peat and pumice would have less weight of soil in the extracting vessel (Rajendram et al. 2003). However, soils with higher bulk density will have a narrower extraction ratio and therefore less P extracted into solution, but at the same time, there is more weight of sample being extracted, i.e. two confounding errors. This is why the observed differences between the volumetric and gravimetric measurements do not increase as bulk density or volume weight increase above 1 g/cm^3.

Conversion using volume weight provided results closer to a 1:1 line than conversion using field bulk density. This result is because volume weight is a laboratory measurement using homogenised dried and ground soil, while field bulk density is the bulk density of the undisturbed soil. Deviation from a 1:1 line is increased with lower bulk density or volume weight as these create an analytical difference due to changes in the extraction ratio (Figure 1). Therefore conversion between units may be employed but careful consideration must be given to the purpose of the data and the conversion factor used.

Both gravimetric and volumetric Olsen P methods give similar results below 100 mg/kg or mg/L (Figure 3). That results for the two methods diverge above 100 appears to be of little practical importance to production or environmental protection as Olsen P at these extreme values are well above production recommendations (Drewry et al. 2013 and references therein) and levels associated with P loss risk (Taylor et al. 2016, McDowell et al. 2015). However, whether or not Olsen P exceeds SOE monitoring targets is important to regional councils and values above recommended levels would be considered to be outside soil quality targets. So, there has to be some certainty for values around the target value.

There remains a question about which method (or if both methods) is best suited for SoE reporting and it is important to not confuse targets for production and environment protection. The current targets used by the LMF were from revision of the original target of Sparling et al. (2003), are in mg/kg, and largely based on the work of Rich McDowell and others using the gravimetric method (MacKay et al. 2013 and the references therein). Drewry et al. (2013), in raising awareness of the different Olsen P methods, reviewed the development of Olsen P as a method in New Zealand for production purposes. The extensive Ministry of Agriculture and Fisheries (MAF) and AgResearch trials (e.g. Cornforth and Sinclair 1984; Sinclair et al. 1997; Edmeades et al 2006; Roberts and Morton 2009) on which field-calibrated pastoral nutrient response curves and soil fertility recommendations were and are currently based were developed from the volumetric method. Saunders et al. (1987) concluded the Olsen P soil test, modified by using a volume of soil rather than weight, gave a very satisfactory prediction of probable minimum yield and this method was adopted by the Ministry of Agriculture and Fisheries in the mid 1970s as the standard on which to base fertiliser advice for New Zealand farms (Sinclair et al. 1997). Sinclair et al. (1997) also confirmed that the soil test was actually a modification of the original test, in that a volume rather than a weight of soil was used. Also, Mountier et al. (1966) reports the use of routine volumetric sampling in New Zealand laboratories for a variety of tests, while Grigg (1977) reported that Olsen P was measured on a volumetric basis as it yielded a better coefficient of determination to the relative yield of pasture and arable crops than if measured on a gravimetric basis. Grigg (1977) also reported several other reasons for adoption of the modified test.

It may be better to consider stocks rather than concentrations. The conventional assessment for stocks is using gravimetric measures converted to volumetric using bulk density and a set sample depth, e.g. carbon stocks. Thus, we may consider stocks of available P for sample depth 0-10 cm as a measureable factor of P loss risk (Taylor et al. 2016, McDowell et al. 2015). However, further research on the usefulness of Olsen P, whether gravimetric or volumetric, and the use of volume weight in this context is needed.

Despite the divergence from the 1:1 line above Olsen P of 100, both volumetric and gravimetric methods, converted or not by bulk density or volume weight, identify excessively high, adequate and very low values. There are few crops that require Olsen P to be above 50 mg/L.

Conclusions

- For Olsen P < 100, conversion between the gravimetric and volumetric/ volume weight methods and the volumetric and gravimetric/ volume weight methods were close to 1:1.

- At higher Olsen P concentrations, analytical differences between methods becomes more obvious. Further research including additional comparative analyses of samples at high Olsen P values are needed.

- Despite the divergence from the 1:1 line above Olsen P values of 100, both volumetric and gravimetric methods, converted or not by bulk density or volume weight, identify excessively high, adequate and very low values.

- Standardisation of Olsen P methodology is strongly recommended for national reporting. We recommend where direct comparison between gravimetric and volumetric results is required volume weight is used. If the data is to be used on an area basis or for stocks, then field bulk density should be used is used. Preliminary equations for converting between the different Olsen P methods are:
    - gravimetric = 0.965 x (volumetric/volume weight) - 0.024,

    - volumetric = 1.024 x (gravimetric x volume weight) - 0.882.

- However, further verification of this research, including a wider range and number of samples is needed Further research is needed to extend the range of soil types and to give national coverage.

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