Comparison of Extraction Procedures Used in Determination of Phosphorus Species by $^{31}$P-NMR in Chilean Volcanic Soils

Margarita Briceño $^a$, Mauricio Escudey $^b$, Gerardo Galindo $^b$, Dan Borchardt $^c$ & Andrew C. Chang $^d$

$^a$ Department of Chemistry, Arturo Prat University, Iquique, Chile
$^b$ Department of Chemistry of Materials, Faculty of Chemistry and Biology, University of Santiago of Chile, Santiago, Chile
$^c$ Department of Chemistry, University of California, Riverside, California, USA
$^d$ Department of Environmental Sciences, University of California, Riverside, California, USA

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Comparison of Extraction Procedures Used in Determination of Phosphorus Species by $^{31}$P-NMR in Chilean Volcanic Soils

Margarita Briceño
Department of Chemistry, Arturo Prat University, Iquique, Chile

Mauricio Escudey and Gerardo Galindo
Department of Chemistry of Materials, Faculty of Chemistry and Biology, University of Santiago of Chile, Santiago, Chile

Dan Borchardt
Department of Chemistry, University of California, Riverside, California, USA

Andrew C. Chang
Department of Environmental Sciences, University of California, Riverside, California, USA

Abstract: Four procedures were employed to extract phosphorus (P) from volcanic soils for $^{31}$P-NMR experiments. The procedures involve 0.5 M NaOH extraction, 0.5 M NaOH and Chelex 100 cation exchange resin extraction, NaOH-EDTA extraction, and HCl-NaOH two step sequential extraction with Chelex 100 clean up. Results showed that inorganic-P, monoester-P, diester-P and pyrophosphate were present. Their detection was dependent on the extraction procedure used.

The NaOH procedure gives only a broad and vaguely defined signal with poor signal to noise ratio. The incorporation of Chelex 100 in the extraction enhanced the signal to noise ratio and allowed the distinction of inorganic-P, monoester-P, diester-P and pyrophosphate. The two step sequential extraction involving HCl, NaOH, and
Chelex 100 significantly improve the signal to noise ratio. The NaOH-EDTA extraction procedure is efficient only in samples with low OC contents.

When soils have low OC content, any of the four extraction procedures can be successfully used. If the OC and the Fe concentration in the extracted solutions are high, the Chelex 100 became essential in clean up the metallic ions. Both the NaOH and Chelex 100 and the HCl-NaOH-Chelex produced satisfactory results and the later procedure by far the best resolved spectra.

**Keywords:** P forms, P extraction procedures, variable charge soils

**INTRODUCTION**

High-resolution $^{31}$P nuclear magnetic resonance ($^{31}$P-NMR) spectroscopy has been used to investigate the distribution and transformation of P species in soils. The $^{31}$P-NMR technique is capable of distinguishing simultaneously various forms of inorganic and organic P in a system (Newman and Tate 1980; Tate and Newman 1982; Hawkes et al. 1984; Condon, Goh, and Newman 1985; Adams and Byrne 1989; Preston 1996; Dai et al. 1996; Guggenberger et al. 1996; Turrión 2000; Makarov, Haumaier, and Zech 2002).

Prior to the $^{31}$P-NMR experiment, however, the P must be extracted from the soils by chemical reagents. To produce high-quality $^{31}$P-NMR spectra, the P must be present in the testing solutions in relatively high concentrations, generally between 50 to 100 mg P L$^{-1}$. To be representative of the chemical compositions, it is imperative that the procedures are effective in extracting soil P and preserving the integrity of P forms originally present in the soil (Cade-Menum and Preston 1996; Leinweber, Haumaier, and Zech 1997).

The most commonly used extraction procedure employed an alkaline reagent such as 0.5 M NaOH that was effective for identifying the organic P forms (Newman and Tate 1980; Robinson, Johnston, and Reddy 1998). Modifications have been suggested to improve the effectiveness of extraction by adjusting the strength of the extracting reagent to minimize the organic P hydrolysis (Cade-Menum and Preston 1996; Leinweber, Haumaier, and Zech 1997) and expediting the chemical reactions by sonically dispersing the suspension (Cade-Menum and Preston 1996). Usually no more than 50% of the total P was recovered. Condon, Goh, and Newman (1985) reported that 80% of the total organic P was recovered when the soils were extracted sequentially with 0.5 M HCl and then 0.5 M NaOH.

In examining the soil systems, the NMR methods are especially susceptible to the interferences of paramagnetic elements such as iron and manganese. Most of the $^{31}$P-NMR studies involved mineral soils with low iron and organic matter contents (Adams and Byrne 1989; Gil-Sotres, Zech, and Alt 1990; Sumann et al. 1998; Zhang, Mackenzie, and Sauriol 1999; Rubæk et al. 1999). Only a limited number of studies included soils that were high in organic matter contents (Condon et al. 1996). Ingall, Schroeder,
and Berner (1990) experimented with the citrate–dithionite–bicarbonate extraction as a pretreatment to remove the paramagnetic elements. Volcanic soils present challenging problems in the $^{31}$P-NMR studies. Because of the strong reactions with both iron and organic matter made, the P in volcanic soils was difficult to extract (Bishop, Chang, and Lee 1994; Escudey et al. 1997; Briceño et al. 2004). When the P in these soils is examined, the inherent paramagnetic elements such as Fe and Mn will be readily dissolved and present in the extracts. They subsequently cause signal broadening and distortion of the $^{31}$P-NMR spectra (Cade-Menum and Preston 1996). Soils in central and southern Chile are predominantly derived from volcanic parent material and are characterized by pH-dependent variable surface charge, relatively high organic matter and iron contents, and high phosphate fixation on the predominant minerals, namely allophane and ferrihydrite (Besoaín 1985). Consequentially, heavy and frequent applications of phosphate fertilizers are required to maintain adequate available P levels for crop production. The fertility management strategy may be greatly enhanced if the P distributions in these soils are clearly delineated.

Adams and Byrne (1989) added sodium-saturated Chelex 100 cation exchange resin to the aqueous suspension of soils for the extraction. The resin has strong affinities for Fe and other polyvalent cations in the order Fe $> \text{Al} > \text{Mn} > \text{Ca} > \text{Na}$, and the Na$^+$ released from the exchange reactions provides the alkalinity that facilitates the solubilization of organic-P in the soil. The amounts of P extracted in this manner were comparable to those dissolved by the customarily used 0.5 M NaOH, and the quality of the spectra was much improved (Adams and Byrne 1989). It nevertheless was not a practical method for routine analysis because the resins were mixed with soils and could not be recovered and reused. Bowman and Moir (1993) used a mixture of NaOH and EDTA to extract the organic-P in soils for $^{31}$P-NMR. The inclusion of EDTA appeared to enhance the amounts of P extracted, in comparison to using the 0.5 M NaOH alone. However, it failed to improve the quality of the spectra (Cade-Menum and Preston 1996).

The objective of this study was to compare the recovery efficiencies and the $^{31}$P-NMR spectra quality of volcanic soils extracted by four soil P extraction procedures.

**MATERIALS AND METHODS**

**Soils Collection**

Samples were obtained from both the virgin and the cultivated fields of two volcanic soils at the 0-to-15-cm and 15-to-30-cm depths. These two soils, an Ultisol (Collipulli, 36° 58′ S 72° 09′ W) and an Andisol (Diguillin, 36° 53′ S 72° 10′ W), are representative of soils that cover the major agricultural regions in south central Chile. The soils were screened in the field to pass a
sieve with 2-mm openings and stored in a cold room at the field moisture content.

Characterization

The pH was measured in soil suspension with the soil-to-water ratio of 1 to 2.5 w/v. The organic carbon content (OC) was determined by the combustion method (Allison 1965). The active iron oxides (Fe$_{\text{a}}$) were extracted using a 0.2 M ammonium oxalate solution at pH 3 (McKeague and Day 1996). In addition, the free iron oxides (Fe$_{\text{DCB}}$) were extracted using the dithionite–citrate–bicarbonate solution (Mehra and Jackson 1960), and the Fe complexed with organic matter (Fe$_{\text{PYRO}}$) was extracted using a 0.1 M sodium pyrophosphate solution at pH 10 (Wada and Higashi 1976). The Fe contents in extract were determined by atomic absorption spectroscopy. Total soil phosphorus (P$_{\text{total}}$) was determined by oxidizing the soil with sodium hypobromite and then determining the concentration of phosphorus in solution colorimetrically using the molybdate blue method (Murphy and Riley 1962; Dick and Tabatabai 1977).

Extraction Procedures for $^{31}$P-NMR Spectroscopy and Measurement Conditions

Four P-extraction procedures were employed to prepare the soil solutions for the high-resolution $^{31}$P NMR experiments.

NaOH Extraction

Aliquots of 1 g dry-weight-equivalent of soils at the field moisture contents were mixed with 20 mL of 0.5 M NaOH, ultrasonically dispersed for 3 min, centrifuged, decanted, and filtered through 0.45-μm-pore-size micro filters. The filtrate was freeze dried, redissolved in 3 mL of D$_2$O, shaken for 2 h, and centrifuged, and the clear solutions transferred to NMR tubes (Adams and Byrne 1989).

NaOH and Chelex 100 Extraction

Aliquots of 5 g dry-weight-equivalent of soils at field moisture content were mixed with 30 g of sodium-saturated Chelex 100 (Bio-Rad 142-2832) and 100 mL of 0.5 M NaOH. The mixtures were shaken overnight on a reciprocal shaker, centrifuged, and decanted, and the centrate filtered through 0.45-μm-pore-size micro filters. The filtrate was freeze dried, redissolved in 3.0 mL of D$_2$O, shaken for 2 h, centrifuged, and transferred to NMR tubes (Adams and Byrne 1989).
NaOH-EDTA Extraction

Aliquots of 5 g dry-weight-equivalent of soil were mixed with 100 mL of solution containing 0.1 M EDTA and 0.5 M NaOH. The mixtures were shaken at room temperature for 17 h on a reciprocal shaker, and the suspensions were filtered through 0.45-μm-pore-size micro filters. The filtrates were freeze dried, redissolved in 3.0 mL of D$_2$O, shaken for 2 h, centrifuged, and transferred to NMR tubes (Bowman and Moir 1993).

HCl and NaOH Sequential Extraction

Aliquots of 10 g dry-weight-equivalent of soil were extracted with 75 mL of 1 M HCl by shaking the mixture for 1 h at room temperature. The suspension was separated by centrifugation. The solid residue was sequentially treated with 125, 75, and 75 mL of 0.5 M NaOH and sonicated for 3, 1, and 1 min, respectively (Hinedi, Chang, and Lee 1988). The suspensions were separated by centrifugation and combined. Separately, the acid and alkaline extracts were equilibrated with 30 g of sodium-saturated Chelex 100, shaken for 17 h on a reciprocal shaker, and filtered through 0.45-μm-pore-size micro filters. The filtrates were freeze dried, redissolved in 3.0 mL of D$_2$O, shaken for 2 h, centrifuged, and transferred to NMR tubes.

NMR Experiment

The $^{31}$P-NMR spectra for soil extracts were obtained at 202.459 MHz on a Varian Inova 500-MHz spectrometer using a 45° pulse with 1.5-s delay and 0.506-s acquisition time. The chemical shifts were measured relative to orthophosphoric acid. The proton decoupler was gated on during the acquisition time to avoid nuclear Overhauser enhancement, using the standard waltz decoupling scheme. From 4,000 to 15,000 scans, depending on the samples, were required to obtain satisfactory spectra. The 0.002 M 2-aminoethylphosphonic was used as the standard to determine the abundances of P species found by the $^{31}$P-NMR.

RESULTS AND DISCUSSION

Soil Properties

The two soils we used have different mineralogy, general chemical properties, and P contents. The Diguillin soil is an Andisol consisted predominantly of allophone, and the Collipulli soil is an Ultisol whose clay fraction is predominantly kaolinite (Escudey et al. 2001). Although both soils have pH
in the acidic range, the indigenous pH of the Collipulli soil, pH 5.2, was considerably lower than that of the Diguillin soil, pH 6.2 (Table 1). Long-term cultivations reduced the pH of the Collipulli soil from 5.2 to 5.1 and the Diguillin soil from 6.2 to 5.3. The organic C contents of the Diguillin soils varied from 5.1 to 5.8% in the 0-to-15-cm layer to 4.3% in the 15-to-30-cm layer whereas that of the Collipulli soil were 1.5 to 1.8% in the 0-to-15-cm layer and 2.0% in the 15-to-30-cm layer. The cultivation reduced the free iron contents of the soils from 6.2 to 7.3% to 4.8 to 5.1% and 3.4 to 4.0% to 2.4 to 2.8% as Fe$_2$O$_3$ for the Collipulli soil and Diguillin soil, respectively. In general, higher percentages of the iron oxide in the Diguillin soil than the Collipulli soil were in the reactive Fe$_{OX}$ form. Although the organic C contents of the Collipulli soil were lower the Diguillin soil, higher amounts of iron oxides in Collipulli soil than the Diguillin soil formed complexes with organic matter, 0.7 to 1.1% vs. 0.4 to 0.9% as Fe$_2$O$_3$.

In both soils, the total phosphorus contents of the 0-to-15-cm layer were higher than the 15-to-30-cm layer (Table 2). In the Collipulli soil, the cultivation slightly reduced the phosphorus content of soil from 1108 and 733 mg kg$^{-1}$ to 1094 and 620 mg kg$^{-1}$ for the 0-to-15 and 15-to-30-cm soil layers, respectively. In the Diguillin soil, the phosphorus accumulated in the soil profile through cultivation primarily in the 0-to-15-cm soil depth from 2216 to 2949 mg kg$^{-1}$ (Table 2).

**Phosphorus Extraction Efficiency**

The efficiency of the P extraction measured in amount of the total soil P extracted was in descending orders HCl-NaOH-Chelex > NaOH-EDTA > NaOH. Under the best conditions, up to 84% of the total P in Diguillin soils was recovered in the extract (Table 3). The soil depth and the cultivation made little difference in the amounts of P extracted. On the other end of the spectrum, approximately 40% of the total soil P was recovered in the NaOH single extraction. The OC contents of Diguillin soil were high (4.3 to 5.8%), and the ratio of inorganic and organic P components of the total soil P was approximately one to one. The Collipulli soils were so high in reactive iron, Fe$_{OX}$, that their inorganic to organic P ratios were approximately 2:1 (Table 1). In general, an average of 73 and 84% of the P in Collipulli and Diguillin soils, respectively, were extracted with the NaOH-EDTA is the inorganic P. For the HCl-NaOH-Chelex extraction procedure, comparable percentages of the inorganic P were extracted, but the inorganic P extracted accounted for 60% in the Diguillin soils because greater percentages of the organic-P was recovered (Table 3). Again, the soil depth and the cultivation practice did not significantly affect the outcomes.
<table>
<thead>
<tr>
<th>Constituent</th>
<th>Collipulli (virgin field)</th>
<th>Collipulli (cultivated field)</th>
<th>Diguillin (virgin field)</th>
<th>Diguillin (cultivated field)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 to 15 cm</td>
<td>15 to 30 cm</td>
<td>0 to 15 cm</td>
<td>15 to 30 cm</td>
</tr>
<tr>
<td>pH</td>
<td>5.2</td>
<td>5.2</td>
<td>5.1</td>
<td>4.9</td>
</tr>
<tr>
<td>Organic C (%)</td>
<td>1.8</td>
<td>2.1</td>
<td>2.3</td>
<td>2.3</td>
</tr>
<tr>
<td>Total P (mg kg$^{-1}$)</td>
<td>1108</td>
<td>733</td>
<td>1094</td>
<td>620</td>
</tr>
<tr>
<td>Fe$_{DCB}$ (%)</td>
<td>6.2</td>
<td>7.3</td>
<td>5.1</td>
<td>4.8</td>
</tr>
<tr>
<td>Fe$_{Ox}$ (%)</td>
<td>0.9</td>
<td>1.4</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>Fe$_{Pyro}$ (%)</td>
<td>0.7</td>
<td>1.1</td>
<td>0.6</td>
<td>0.7</td>
</tr>
</tbody>
</table>
Table 2. Soil phosphorus extracted by 0.5 M NaOH, 0.5 M NaOH, and 0.1 M EDTA mixture, and 1 M HCl and 0.5 M NaOH sequentially

<table>
<thead>
<tr>
<th>Extractable phosphorus</th>
<th>Collipulli (virgin field)</th>
<th>Collipulli (cultivated field)</th>
<th>Diguillin (virgin field)</th>
<th>Diguillin (cultivated field)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0 to 15 cm</td>
<td>15 to 30 cm</td>
<td>0 to 15 cm</td>
<td>15 to 30 cm</td>
</tr>
<tr>
<td>NaOH (mg kg⁻¹)</td>
<td>564</td>
<td>391</td>
<td>658</td>
<td>365</td>
</tr>
<tr>
<td>NaOH and EDTA (mg kg⁻¹)</td>
<td>653</td>
<td>352</td>
<td>620</td>
<td>232</td>
</tr>
<tr>
<td>HCl and NaOH (mg kg⁻¹)</td>
<td>696</td>
<td>497</td>
<td>867</td>
<td>291</td>
</tr>
<tr>
<td>Total P (mg kg⁻¹)</td>
<td>1108</td>
<td>733</td>
<td>1094</td>
<td>620</td>
</tr>
</tbody>
</table>
Table 3. Distribution of inorganic and organic soil P extracted by 0.5 M NaOH and 0.1 M EDTA mixture and HCl and NaOH sequential extractions

<table>
<thead>
<tr>
<th>Soil</th>
<th>Depth (cm)</th>
<th>Total P (mg kg(^{-1}))</th>
<th>NaOH/EDTA extracted (mg kg(^{-1}))</th>
<th>HCl/NaOH sequentially extracted (mg kg(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Inorganic</td>
<td>Organic</td>
<td>Inorganic</td>
</tr>
<tr>
<td>Collipulli</td>
<td>0 to 15</td>
<td>757</td>
<td>351</td>
<td>422</td>
</tr>
<tr>
<td></td>
<td>15 to 30</td>
<td>476</td>
<td>257</td>
<td>277</td>
</tr>
<tr>
<td>Diguillin</td>
<td>0 to 15</td>
<td>1198</td>
<td>1018</td>
<td>855</td>
</tr>
<tr>
<td></td>
<td>15 to 30</td>
<td>1017</td>
<td>1146</td>
<td>1094</td>
</tr>
</tbody>
</table>
NMR Characterization of Extracted Phosphorus

The NaOH reagent was capable of dissolving soil P that were associated with the mineral fraction and organic matter (Tate and Newman 1982; Hawkes et al. 1984; Escudey et al. 1997) and has been usually employed to determine the organic-P content (Newman and Tate 1980; Robinson, Johnston, and Reddy 1998). The $^{31}$P-NMR spectra of 0.5 M NaOH extracted Collipulli and Diguillin soils were compared (Figure 1). The assignment of peaks was based on measurements of chemical shifts relative to the orthophosphoric acid (Newman and Tate 1980; Hawkes et al. 1984; Turrión et al. 2000; Escudey et al. 1997; Pant, Warman, and Nowak 1999; Moller et al. 2000; Makarov, Haumaier, and Zeck 2002). All samples regardless of the soil origin, depth, and cultivation exhibited a single broad bandwidth signal at the vicinity of $+5.0$ ppm, which corresponded to unresolved peaks of inorganic P and monoester P. The signal of Diguillin samples is broader with a poorer resolution and signal-to-noise ratio compared with that of the Collipulli samples. A combination of low soil P-extraction efficiency and high concentration of active Fe adversely affect the resolution of the signals. Evidently, the P-extraction procedure employing NaOH alone was not suitable for the soils of the volcanic origins that were rich in iron oxides and recalcitrant organic matter.

Incorporating the metal-specific Chelex 100 ion exchange resins into the NaOH-extraction process for soil P presented the advantages of removing the interfering elements from the soil solution (Adams and Byrne 1989). The ion exchange resins immobilized the paramagnetic ions, thus lessening the line broadening and distortion of $^{31}$P-NMR spectra (Hawkes et al. 1984). By lengthening the equilibration time to 17 h (overnight), there would be assurance that the necessary reactions were complete for these volcanic soils. The NaOH and Chelex resin treatment significantly improved the $^{31}$P-NMR spectra of the same soils (Figure 2). They reveal the presence of inorganic P ($+7.0$ ppm), monoester P ($+6.5$ to $+5.0$ ppm), diester P ($+2.0$ to $0.0$ ppm), and pyrophosphate ($-3.5$ ppm) in the recovered extracts. No signal appeared at the chemical shift locations where polyphosphate (9 ppm) and phosphonate (23 ppm) were expected. The broad bandwidth of the signal appeared at $+6.5$ to $+5.0$ ppm, indicating possibly more than one species of monoester P were present. No diester P was found in the Collipulli soils, and no pyrophosphate signal was found in the 15-to-30-cm depth Diguillin soils, most likely because of their low concentrations in the soils. When the soil extracts had a very high organic P content in relation to the inorganic P, the resulting $^{31}$P-NMR spectra often exhibited overlaps between signals of inorganic P and monoester P species, as had been noted also by other investigators (Robinson, Johnston, and Reddy 1998; Gil-Sotres, Zeck, and Alt 1990). The results clearly demonstrated the advantages of the combined NaOH-Chelex procedure for extracting the soil P in volcanic soils for the NMR experiments. In general, the signal-to-noise ratios of spectra for Collipulli soils were better than those in the Diguillin soils. The dissolved organic matter of the extracts...
of the Diguillin soils might have complexed more Fe, thus more Fe was present to cause the interferences.

A similar P pattern distribution was found in virgin and cultivated samples; however, signals of diester P and pyrophosphate are associated to samples with high OC content. According to these results, NMR analysis can be used to estimate the cultivation effect.

The EDTA-NaOH extraction procedure was developed to extract P in soils that were low in OC content and with a mineralogy dominated by crystalline minerals (Bowman and Moir 1993). Cade-Menun and Preston (1996)

Figure 1. $^{31}$P-NMR spectra of 0.5 M NaOH extracts of virgin and cultivated samples of Collipulli and Diguillin soils.
adapted it to prepare soil extracts for the $^{31}$P-NMR analysis. The extraction efficiency was enhanced, and the metallic ions were chelated by the EDTA.

For the Collipulli soils, there was a good separation between the inorganic-P and organic-P signals (Figure 3). The spectra for P in the Diguillin soils however were not well resolved (Figure 3). The signal broadening for P extracted from the Diguillin soils was due to the presence of Fe (and probably Mn) in the extracts and the association of P with high-molecular-weight organic molecules.
The EDTA-NaOH treatment did not significantly improve the quality of spectra of extracted soil P over the NaOH-Chelex 100 treatment. Nevertheless, it allowed the detection of the diester-P and pyrophosphate signals (Escudey et al. 1997, 2004; Briceño et al. 2000a, 2000b, 2004).

The HCl-NaOH-Chelex two-step sequential extraction is based on the procedure used by Borie and Zunino (1983) to extract P in the volcanic soils. In this work, the procedure was modified by increasing the amounts of soil and extracting reagents used and by including the Chelex 100 to remove the metallic ions before the $^{31}$P-NMR analysis.

All of the spectra exhibited good signal-to-noise ratios. Low amounts of P were present in the acid extraction as indicated by a weak signal on the $^{31}$P-NMR spectra (figures not shown). The signals of the alkaline extracts

**Figure 3.** $^{31}$P-NMR spectra of NaOH-Chelex one-step procedure of virgin and cultivated samples of Collipulli and Diguillin soils.
were well resolved, and peaks assigned to inorganic P and organic P were clearly separated (Figure 4). It was noted that the monoester P was the most prominent P in the Diguillin soils. The HCl-NaOH-Chelex 100 treatment significantly enhanced the quality of the spectra with respect to the NaOH-Chelex treatment, especially in soils with high OC content such as the Diguillin soil. It would be logical to conclude that the HCl-NaOH two-step sequential extraction followed by removal of metallic ions in the extracts by Chelex 100 treatment is the most efficient in terms of P extraction and suitable to examine the P species distribution in soils derived from volcanic materials by $^{31}$P-NMR.

*Figure 4.* $^{31}$P-NMR spectra of alkaline extracts of HCl-NaOH-Chelex two-step procedure of virgin and cultivated samples of Collipulli and Diguillin soils.
CONCLUSIONS

Inorganic P and monoester P are the dominant P forms found in Chilean volcanic soils; small amounts of pyrophosphate and diester P (the main available P form in volcanic soils) were also observed.

The four extraction procedures give different resolution and signal-to-noise ratios. Phosphorus signal quality is associated to soil organic matter content and to the presence of paramagnetic ions in solution.

The NaOH procedure is not suitable for volcanic soils; the NaOH-Chelex spectra often exhibited overlaps between inorganic P and monoester P. The EDTA-NaOH procedure gives good signal separation in volcanic soils with low organic matter content. The HCl-NaOH-Chelex two-step sequential extraction procedure is the most efficient in terms of P extraction and determining the P form distribution and the most suitable for general use in volcanic soils.

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REFERENCES


Society Western Regional Meeting, American Chemical Society: Walnut Creek, California.


Leinweber, P., Haumaier, L., and Zech, W. (1997) Sequential extractions and P-31-NMR spectroscopy of phosphorus forms in animal manures, whole soils and...


