Molecular Speciation of Phosphorus Present in Readily Dispersible Colloids from Agricultural Soils

Speciation of colloidal P ($P_{\text{col}}$) is vital yet little known. For the first time ever, the P species in readily released colloids from agricultural soils were determined by P K-edge X-ray absorption near-edge structure (XANES) and solution $^{31}$P nuclear magnetic resonance (P-NMR) spectroscopy. Water-dispersible $P_{\text{col}}$ was the dominant fraction of readily released P ($<1 \mu m$) from the studied soils cultivated with rice (Oryza sativa L.) (RS; 80.9%) and vegetables (VS; 55.1%). The $P_{\text{col}}$ in these samples was predominantly in inorganic form, which XANES showed to be moderately labile Fe- and Al-associated P (total 70.4–83.3%) and nonlabile hydroxyapatite (16.8–19.7%). The P-NMR analysis showed that the dominant organic P compound class in colloids from RS was orthophosphate monoesters, of which inositol hexakisphosphate was the largest component. These results strongly suggested that colloids are richer in stable P forms and poorer in labile and mineralizable P than the bulk soils.

Abbreviations: Al-P, phosphorus associated with aluminum (hydro)oxides; DCP, dibasic calcium phosphate; EDTA, ethylenediaminetetraacetic acid; Fe-P, phosphorus associated with iron (hydro)oxides; HAP, hydroxyapatite; IHP, inositol hexakisphosphate; LCF, linear combination fitting; MCP, monobasic calcium phosphate; MRP, molybdate-reactive phosphorus; MUP, molybdate-unreactive phosphorus; P-NMR, phosphorus-31 nuclear magnetic resonance; Pi, inorganic phosphorus; Po, organic phosphorus; RS, soil cultivated with rice; TP, total phosphorus; VS, soil cultivated with vegetables; WDC, water-dispersible colloid; XANES, X-ray absorption near-edge structure.

Agricultural P loss is a global concern due to nutrient enrichment and eutrophication in water bodies (Correll, 1998). For years, descriptions and predictions of soil P transport for effective environmental risk management have been documented. However, most of these studies have focused on particulate and dissolved P operationally discriminated by membrane filtration (typically 0.45-μm pore size; Heckrath et al., 1995; Andersson et al., 2013). This fractionation neglects mobile colloids, particles ranging from 1 nm to 1 μm (Baalousha et al., 2005), by which P could be transported across long distances. Accumulated evidence indicates that colloid-facilitated P transport is an important mechanism for P transfer from agricultural land to aquatic ecosystems (Heathwaite et al., 2005; Ilg et al., 2005; Siemens et al., 2008; Regelink et al., 2013). Colloidal P ($P_{\text{col}}$) has been reported to contribute >50% of total P (TP) in soil water samples (Hens and Merckx, 2001). Due to their large specific surface area, soil colloids tend to have high P concentrations compared with bulk soils (Schoumans and Chardon, 2003). Colloidal P also represents a major sink that contributes to algae-available P in water bodies (Van Moorleghem et al., 2013). This role of $P_{\text{col}}$ highlights the importance of P species in colloids: the environmental behavior of $P_{\text{col}}$ is a function
of its speciation, which is directly linked to P solubility, reactivity, and bioavailability. For example, P associated with Fe (hydr)oxides (Fe-P) is sensitive to reducing conditions (Beauchemin et al., 2003). P sorbed on Al (hydr)oxides (Al-P) or calcium phosphate precipitates is likely to be more vulnerable to pH changes (Lindsay et al., 1989), and organic P (Porg) is more bioavailable (Li and Brett, 2013). To date, however, the speciation of Pcoll has been characterized very generally by the colorimetric method or inductively coupled plasma mass spectrometry coupled with different size-fractionated techniques (Hens and Merckx, 2001; Van Moorleghem et al., 2011; Henderson et al., 2012; Regelink et al., 2013). Molecular speciation of Pcoll should be addressed to understand the long-term fate and subsequent impact of soil-derived Pcoll in aquatic systems.

Synchrotron-based P K-edge XANES spectroscopy provides an extraordinarily valuable method to investigate the solid-phase species of P in heterogeneous samples such as soils (Ajiboye et al., 2008; Beauchemin et al., 2003; Kizewski et al., 2011), sediments (Giguet-Covex et al., 2013), and wastes (Toor et al., 2006). This technique is a nondestructive molecular probe for P speciation and is especially efficient for inorganic P (Pi) forms with unique spectral fingerprints. More importantly, XANES requires only minor amounts (milligram level) of samples for analysis; thus, it is an ideal tool to probe the speciation of Pcoll, especially considering the low yield of colloidal samples isolated from soils. To our knowledge, however, there has only been indirect use of Fe X-ray absorption spectroscopy on colloid- and nanoparticle-associated P transport (Rick and Arai, 2011); there has been no direct application of P-XANES to speculate Pcoll. Additionally, P-XANES spectroscopy provides limited information about Porg species (e.g., Kruse and Leinweber, 2008). Alternatively, solution P-NMR spectroscopy offers low detection limits and is powerful for Porg characterization (Cade-Menun et al., 2002; Doolette et al., 2009); however, it requires extraction before analysis, which may lead to possible species alteration (Kizewski et al., 2011). Moreover, the higher concentrations of P needed for P-NMR require the extraction of grams, rather than milligrams, of material. This has limited the use of P-NMR for identifying P species in colloidal samples due to their low yields from surface waters or soil solutions. Accordingly, there are no published reports to date using P-NMR to speculate Pcoll, and only the molecular speciation of particulate P in surface water has been investigated using solution P-NMR spectroscopy (Cade-Menun et al., 2006; Shinohara et al., 2012). In light of the need for detailed information on Pcoll speciation, the objective of this study was to determine if P K-edge XANES and solution P-NMR spectroscopy could be used to complementarily characterize P species in Pcoll. This was tested with readily released colloids from two agricultural soils.

**MATERIALS AND METHODS**

**Isolation and General Characterization of Colloidal Phosphorus**

Soils cultivated with rice (RS) and vegetables (VS) were compositely sampled from well-characterized field plots located in Jingshan Village of Zhejiang Province, China. Both soils were classified as Ultisols (Soil Survey Staff, 1988). Detailed information on these soil samples can be found in our previous study (Liu et al., 2013). Water-dispersible colloids (WDCs), generally an indicator of readily mobile colloids (de Jonge et al., 2004), were isolated and measured following a modified procedure of Ilg et al. (2005). For the modification, a 1-μm microporous membrane instead of a 1.2-μm filter was used to isolate WDCs according to the definition of colloids with at least one-dimension size ranging from 1 μm to 1 μm by IUPAC (Baalousha et al., 2005). Triplicate 10-g (dry weight) soil samples were shaken with 80 mL of deionized water for 24 h. The soil suspensions were then centrifuged at 3000 × g for 10 min to remove coarse particles. The subsequent suspensions were filtered through a 1-μm microporous membrane to remove particles > 1 μm. An aliquot of the filtrate was ultracentrifuged at 300,000 × g for 2 h (Optima TL, Beckman) to collect the soil WDC fraction, and the supernatant was considered to be the truly dissolved phase. The soil WDCs described in this study were operationally defined to be particles ranging from 1 to 0.02 μm (for organo-mineral colloids, whose averaged density is 2.65 g cm⁻³) according to Stokes’ Law (Gimbert et al., 2005). Soil WDC samples were freeze-dried for subsequent speciation analysis.

Masses of colloids were determined gravimetrically by placing 40-mL aliquots of non-ultracentrifuged samples in tared Teflon beakers and drying at 100°C to constant weight (Seta and Karathanasis, 1996). Colloidal TP (TPcoll), molybdate-reactive P (MRPcoll), molybdate-unreactive P (MUPcoll), total organic C (TOCcoll), Fe(coll), Al(coll) and Ca(coll) were measured as the difference between their concentrations in the non-ultracentrifuged (< 1 μm) and ultracentrifuged (truly dissolved fraction) samples. We determined TP with peroxidisulfate digestion (Pagel et al., 2008), and concentrations of TP and MRP were determined colorimetrically (Murphy and Riley, 1962). Molybdate-reactive P in each phase was calculated as TP minus MRP. The concentration of TOC was measured by a TOC analyzer (Multi N/C 3100, Analytikjena AG). Iron, Al, and Ca concentrations were analyzed by inductively coupled plasma–optical emission spectrometry (Model IRAS-AP, TJA) after microwave digestion (USEPA, 1994). All of the above analyses were conducted in triplicate.

**Phosphorus K-edge XANES Spectroscopy**

The XANES spectra of freeze-dried WDCs and P reference standards were collected at the Soft X-ray Micro-characterization Beamline (SXRM1) equipped with a Si(111) double-crystal monochromator at the Canadian Light Source, Saskatoon, Canada. Phosphorus standards, purchased from Sigma-Aldrich, included berlinitie (AlPO₄), dibasic calcium phosphate dehydrate (CaHPO₄·2H₂O), dibasic calcium phosphate (CaHPO₄·DCP), monobasic calcium phosphate [Ca(H₂PO₄)₂, MCP], hydroxyapatite [Ca₁₀(PO₄)₆·OH, HAP], tricalcium phosphate [(Ca₃(PO₄)₂), FePO₄, and phytic acid (myo-inositol hexakisphosphate, myo-HP)]. After grinding through a 100-mesh (0.15-mm) sieve, P standards and freeze-dried WDC samples (~mg) were...
thinly spread over a P-free and double-sided carbon tape for the XANES data collection. The WDC spectra were collected in partial fluorescence yield mode using a four-element fluorescence detector with a dwell time of 4.0 s, while spectra of P reference standards were measured in total electron yield mode absent of self-absorption effects. Multiple spectra (two for each P standard and three for soil WDC samples) were collected and averaged. Radiation damage during the XANES experiment was excluded by a good reproducibility of repeated measurements on the same spot and repeated scans over different spots for each sample. The energy range of the scans was set from 2110 to 2200 eV with the following multiple scans: Region 1 (2110–2145 eV), step 1 eV; Region 2 (2145.25–2180 eV), step 0.25 eV; and Region 3 (2180.5–2200 eV), step 0.5 eV. All XANES spectra were analyzed by ATHENA (Ravel and Newville, 2005). The absolute energy scale was calibrated to 2149 eV ($E_0$) as the maximum energy of the first peak in the first derivative spectrum of AlPO$_4$ (Beauchemin et al., 2003). Spectra were background corrected by a linear regression fit through the pre-edge region and normalized total K-edge intensity to one unit edge jump by defining the continuum regions (>50 eV above absorption edge) as the post-edge region. Linear combination fitting (LCF) of WDC spectra was performed across the spectral energy region from 2139 to 2164 eV using all possible binary and ternary combinations of all collected reference spectra with fixed $E_0$ (Beauchemin et al., 2003). Weights of all P standards used were forced to sum to 1. The goodness-of-fit was judged by the chi-squared values and $R$ values, and P standards yielding the best fit were considered as the most probable P species in the investigated soil WDC samples.

Solution Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy

Large masses of WDCs need to be isolated to obtain enough samples for P-NMR. Both the yield of WDCs from isolation (5.8 g kg$^{-1}$ soil) and the ratio of MUP to TP in the WDCs (40.3%) were much higher in the RS than the VS (WDCs, 3.8 g kg$^{-1}$ soil; MUP coll/TP coll, 26.7%; Supplemental Table S1). As such, we chose only the RS to repeatedly isolate WDCs for P-NMR, assuming that colloidal P$_0$ affected TP$_{coll}$ speciation more for the RS than the VS, based on MUP$_{coll}$ results (Supplemental Table S1). The WDCs from the RS (0.65 g) were extracted with NaOH–ethylenediaminetetraacetic acid (EDTA) for P-NMR (Cade-Menun et al., 2010). Solution P-NMR spectra were obtained at the Saskatchewan Structural Sciences Centre (University of Saskatchewan, Saskatoon, Canada) using a Bruker Avance 500-MHz spectrometer equipped with a 10-mm broadband probe. The NMR parameters were: 90° pulse, 0.68-s acquisition time, 4.32-s pulse delay, 12-Hz spinning, 20°C, 2200 scans (3 h), and no proton decoupling. To facilitate peak identification, a spiking experiment was conducted using myo-IHP (purchased from Sigma-Aldrich; Doolette et al., 2009). The chemical shift of the orthophosphate peak was standardized to 6 ppm. Signals were assigned to individual P compounds or functional groups based on the spiking experiment and other publications (Doolette et al., 2009; He et al., 2011). Signal areas were calculated by integration using NUTS software (Acorn NMR). Spectra were plotted with a line broadening of 7 Hz for the overall spectrum and 1 Hz to preserve fine resolution in the orthophosphate monoester region.

RESULTS AND DISCUSSION

For the water-extracted P (water-dispersed <1-µm fraction), 80.9 and 55.2% were bound to colloids in the RS and VS samples, respectively (Table 1), which indicated that P$_{coll}$ was potentially significant for P loss from the soil–water interface in the investigated soils, particularly the RS. This confirmed previous studies showing the dominance of P$_{coll}$ in water-extracted P in different agricultural lands (Ilg et al., 2005; Zang et al., 2013). For both studied soils, MRP$_{coll}$ comprised a substantial component of TP$_{coll}$ (RS, 59.7%; VS, 72.9%). Additionally, most readily released MRP ( <1 µm) was colloidal (RS, 91.2%; VS, 55.2%). This large distribution of MRP in the colloid fraction further indicates the potential risk of colloid-facilitated MRP losses from soils to water bodies because MRP is regarded as the readily algae-available form in aquatic systems (Van Moorleghem et al., 2013). However, risk assessment of P$_{coll}$ based on MRP$_{coll}$ alone may be misleading because various MRP forms (e.g., mineral phosphate and weakly absorbed phosphate) in colloids act differently in response to environmental changes (Turner et al., 2004).

Molecular speciation of P$_{coll}$ is essential to reliably interpret and predict the long-term behavior of P$_{coll}$. The dominance of MRP in P$_{coll}$ (Table 1) in this study facilitated characterizing P speciation by P K-edge XANES spectroscopy, allowing the direct identification of P$_{s}$ species associated with soil minerals at the molecular level (Beauchemin et al., 2003). Figure 1 shows the P$_{coll}$ species obtained by LCF of P K-edge XANES spectra. Iron-associated P was the predominant P$_{s}$ species in both samples, accounting for 61.1 and 70.4% of TP$_{coll}$ for the RS and VS, respectively. These results imply that Fe minerals are the major carriers of P$_{coll}$ in these soils. Previous studies also indirectly implied the binding of P to Fe minerals in colloids according to the enrichment of Fe and P in soil-derived colloidal fractions (Turner et al.,

<table>
<thead>
<tr>
<th>Soil</th>
<th>Colloidal phase</th>
<th>Truly dissolved phase</th>
<th>TP$_{coll}$/TP</th>
<th>MRP$_{coll}$/MRP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TP kg$^{-1}$</td>
<td>MRP kg$^{-1}$</td>
<td>MRP/TP</td>
<td>TP kg$^{-1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>(µg L$^{-1}$)</td>
</tr>
<tr>
<td>RS</td>
<td>6.87 (0.04)*</td>
<td>4.10 (0.04)</td>
<td>59.7</td>
<td>1.62 (0.09)</td>
</tr>
<tr>
<td>VS</td>
<td>20.3 (1.74)</td>
<td>14.8 (1.51)</td>
<td>72.9</td>
<td>16.5 (2.09)</td>
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</table>

*Means with standard errors in parentheses.

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Direct evidence of P associated with Fe minerals has not been previously reported for colloidal samples. Moreover, LCF analysis showed that soil colloids contained hydroxyapatite (HAP), comprising 16.8 and 19.7% of TPcoll in the RS and VS, respectively. Turner et al. (2004) observed enrichment of both MRP and Ca in colloidal fractions (0.3–3 nm) isolated from calcareous soils; however, the WDCs containing HAP in our study originated from acidic soils. Beauchemin et al. (2003) also detected HAP in a range of acidic to slightly alkaline soils using XANES and reported that HAP occurred in all studied soils, regardless of pH. Additionally, Al-P was determined to be 22.2% of TPcoll from the RS, while MCP was 9.9% of TPcoll from the VS (Fig. 1). These results were consistent with the relatively higher Al but lower Ca contents in WDCs from the RS compared with the VS (Supplemental Table S1). Aluminum (hydr)oxides are important sorbents of P in soils (Van der Zee and Van Riemsdijk, 1986; Zhu et al., 2007) and have been detected by P-XANES in agricultural soils (Beauchemin et al., 2003) and Cd-contaminated soils amended with bone char (Siebers et al., 2013). Beauchemin et al. (2003) reported that Al-P was present only in the soil with the highest ammonium oxalate extractable Al content (673 mmol kg⁻¹). The lack of detected Al-P by XANES in soils may result from its relatively low abundance due to inhibition of the formation of Al-P by Fe (hydr)oxides (Lookman et al., 1994).

Khare et al. (2004) reported that P preferentially adsorbed on ferrihydrite, with the adsorbed PO₄ concentration <100 mmol kg⁻¹ (~3100 mg P kg⁻¹) in a model system mixed ferrihydrite–boehmite (1:1 mass ratio) suspensions. Given the TP concentration in agricultural lands (100–3000 mg kg⁻¹; Condron et al., 2005), it is unlikely that the adsorbed P in soils would be >3100 mg kg⁻¹, which probably resulted in the dominance of Fe-P over Al-P in soils (Beauchemin et al., 2003).

The P composition in the WDC samples revealed the presence of MUP in the WDCs from both soils (Supplemental Table S1), which is thought to include Pₐ compounds and condensed phosphates (Haygarth and Sharpley, 2000). However, XANES LCF analysis did not reveal any Pₐ species in either investigated colloidal sample (Fig. 1), probably because they were below the detection limit of XANES spectroscopy or due to a lack of distinctive spectral features of Pₐ compounds (Beauchemin et al., 2003; Ajiboye et al., 2008; Kruse and Leinweber, 2008). As such, analysis with solution P-NMR was required to provide molecular speciation information about the P pool colorimetrically classified as MUP. In this study, the TP recovery by NaOH–EDTA extraction for the WDCs released from the RS (56%; Table 2) was consistent with other reported P-NMR studies on soils (e.g., Cade-Menun et al., 2002). Solution P-NMR does not identify the speciation of Pₐ minerals, which are shown as orthophosphate (75.2%; Table 3; Fig. 2) because the NaOH–EDTA extraction solubilizes P minerals. Other detected Pₐ compounds included polyphosphate and pyrophosphate, each of which accounted for 1.0% of extracted P (Table 3; Fig. 2; Supplemental Table S2). The Pₐ form present at the highest proportion of extracted P was IHP, including myo-IHP (5.2%) and scyllo-IHP (1.7%). Given the low proportion of IHP and other Pₐ forms (Table 3; Fig. 2; Supplemental Fig. S2), it is not surprising that Pₐ species were not identified by XANES, for which the detection limit was expected to be 10 to 15% of TP (Beauchemin et al., 2003).

**Table 2. Phosphorus form classes, in relative percentage or ratios of form classes, determined by ³¹P nuclear magnetic resonance (P-NMR) spectroscopy for water-dispersible colloids (WDCs) released from soils cultivated with rice (RS) and vegetables (VS) (HAP, hydroxyapatite).**

<table>
<thead>
<tr>
<th>Soil</th>
<th>NaOH–EDTA extract</th>
<th>P-NMR spectra</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>TP Recovery</td>
<td>Pₐ</td>
</tr>
<tr>
<td>WDCs</td>
<td>mg kg⁻¹</td>
<td></td>
</tr>
<tr>
<td></td>
<td>666</td>
<td>56</td>
</tr>
</tbody>
</table>

*Fig. 1. Linear combination fitting (LCF) results of X-ray absorption near-edge structure (XANES) data from water-dispersible colloid samples from soils cultivated with rice (RS) and vegetables (VS) (HAP, hydroxyapatite).*
The second largest $P_0$ category was monoester2 (5.2%), which is a general category of $P$ forms not specifically identified and which may contain sugar phosphates, other inositol phosphates, and degradation products of orthophosphate diester if present (Cade-Menun et al., 2010; He et al., 2011). Based on the spectra alone, 17.8 and 3.0% of the NaOH–EDTA extracted $P$ were orthophosphate monoesters and diesters, respectively (Table 2); however, some of the peaks in the detected orthophosphate monoester region may result from degradation of orthophosphate diesters during P-NMR analysis (Doolette et al., 2009; He et al., 2011; Liu et al., 2013). In light of this, corrected percentages of these two orthophosphate monoesters and diesters were calculated by including $\alpha$- and $\beta$-glycerophosphate (from degradation of phospholipids) and mononucleotides (from degradation of RNA) with the orthophosphate diesters rather than the monoesters, giving corrected values of 14.5% for orthophosphate monoesters and 6.3% for diesters (Table 2). Correspondingly, the uncorrected and corrected ratios of orthophosphate diesters to monoesters, an indicator of $P_0$ degradation (Shinohara et al., 2012), were 0.17 and 0.43, respectively. The true percentages of orthophosphate monoesters and diesters as well as the ratio of orthophosphate diesters to monoesters probably lie between the corrected and uncorrected values (Table 2).

There were significant differences in $P$ speciation between readily released soil colloids and the bulk soils. Our previous study (Liu et al., 2013) indicated that $P$ in the investigated bulk soils corresponding to the WDCs of this study was distributed as Fe-P (65.3%), DCP (14.8%), and MCP (19.9%) for the RS and Fe-P (64.6%), DCP (30.7%), and HAP (4.7%) for the VS. As such, the colloids appear to be enriched in nonlabile HAP (RS and VS) and moderately labile Al-P (RS) compared with their bulk soils. Meanwhile, the colloids contained less of the labile MCP and DCP than the bulk soils. For the RS, the WDCs showed an increase in stabilized forms such as myo-IHP (5.2 vs. 3.8%), scyllo-IHP (1.7 vs. 0.7%) and polyphosphate (1.0 vs. undetected) and a decrease in the orthophosphate diester/monoester ratio (uncorrected 0.17 and corrected 0.43) compared with the bulk soil (uncorrected 0.23 and corrected 0.72). Thus, our

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Table 3. Relative percentage of $P$ forms, determined by $^{31}$P nuclear magnetic resonance (P-NMR) spectroscopy for water-dispersible colloids (WDCs) released from the soil cultivated with rice: orthophosphate (Orth), pyrophosphate (Pyro), polyphosphate (Poly), phosphonates (Phos), myo-inositol hexakisphosphate (MyoP), scyllo-inositol hexakisphosphate (ScyP), $\alpha$ and $\beta$ glycerophosphate ($\alpha$-Gl and $\beta$-Gl, respectively), mononucleotides (Nuc), glucose 6-phosphate (G6P), orthophosphate monoesters, regions 1, 2, and 3 (Mo1, Mo2, and Mo3, respectively), deoxyribonucleic acid (DNA), and orthophosphate diesters other than DNA (ODi).

<table>
<thead>
<tr>
<th>Inorganic P</th>
<th>Orth</th>
<th>Pyro</th>
<th>Poly</th>
<th>Phos</th>
<th>MyoP</th>
<th>ScyP</th>
<th>$\alpha$-Gl</th>
<th>$\beta$-Gl</th>
<th>Nuc</th>
<th>G6P</th>
<th>Mo1</th>
<th>Mo2</th>
<th>Mo3</th>
<th>ODi</th>
<th>DNA</th>
</tr>
</thead>
<tbody>
<tr>
<td>WDCs</td>
<td>75.2</td>
<td>1.0</td>
<td>1.0</td>
<td>2.0</td>
<td>5.2</td>
<td>1.7</td>
<td>0.8</td>
<td>0.8</td>
<td>1.7</td>
<td>0.8</td>
<td>0.8</td>
<td>5.2</td>
<td>0.8</td>
<td>1.0</td>
<td>2.0</td>
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</table>

Fig. 2. Phosphorus-31 nuclear magnetic resonance spectra of water-dispersible colloids and ratios of colloidal TP (TP_{col}) and MRP (MRP_{col}) to the corresponding TP and MRP in the <1-$\mu$m fraction released from the soil cultivated with rice (OthDi, orthophosphate diester other than DNA). The orthophosphate peak is truncated to more clearly show the smaller peaks.
results suggest that more stable P species and less labile and mineralizable P species are present in colloids than those in the bulk soil for RS. Similarly, Shinohara et al. (2012) recently reported that P in suspended particulates comprised more stable P species than the sediment in a shallow eutrophic lake system using solution P-NMR spectroscopy.

CONCLUSIONS

To the best of our knowledge, this study is the first to directly characterize the molecular speciation of P in readily dispersible soil colloids by P K-edge XANES and solution P-NMR spectroscopy. Although the comprehensive understanding of P_{colloid} speciation is preliminary to the inherent limitations of current methods of colloidal isolation and characterization, this study did demonstrate the usefulness of P K-edge XANES and solution P-NMR spectroscopy for molecular interpretations of P speciation in colloidal samples. Our results also strongly suggest that P in soil WDCs was more stable and less labile and mineralizable than that in the bulk soils, which should improve predictions of the long-term fate and assessments of the environmental risk of P_{colloid} from agricultural lands to the receiving aquatic systems. Future use of these combined techniques is warranted to better understand the transport of P in colloidal materials.

ACKNOWLEDGMENTS

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