

Article

Speciation of Phosphorus from Suspended Sediment Studied by Bulk and Micro-XANES

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Abstract: Mobilization, transformation, and bioavailability of fluvial suspended sediment-associated particulate phosphorus (PP) plays a key role in governing the surface water quality of agricultural catchment streams. Knowledge on the molecular P speciation of suspended sediment is valuable in understanding in-stream PP cycling processes. Such information enables the design of appropriate catchment management strategies in order to protect surface water quality and mitigate eutrophication. In this study, we investigated P speciation associated with fluvial suspended sediments from two geologically contrasting agricultural catchments. Sequential chemical P extractions revealed the operationally defined P fractions for the fluvial suspended sediments, with Tintern Abbey (TA) dominated by redox-sensitive P (P_{CBD}), Al, and Fe oxyhydroxides P (P_{NaOH}) and organic P (P_{Org}) while Ballyboughal (BB) primarily composed of acid soluble P (P_{Detr}), redox-sensitive P (P_{CBD}), and loosely sorbed P (P_{NH4Cl}). The dominant calcareous (Ca) elemental characteristic of BB suspended sediment with some concurrent iron (Fe) influences was confirmed by XRF which is consistent with the catchment soil types. Ca-P sedimentary compounds were not detected using bulk P K-edge XANES, and only P K-edge μ-XANES could confirm their presence in BB sediment. Bulk P K-edge XANES is only capable of probing the average speciation and unable to resolve Ca-P as BB spectra is dominated by organic P, which may suggest the underestimation of this P fraction by sequential chemical P extractions. Notably, µ-XANES of Ca K-edge showed consistent results with P K-edge and soil geochemical characteristics of both catchments where Ca-P bonds were detected, together with calcite in BB, while in TA, Ca-P bonds were detected but mostly as organic complexed Ca. For the TA site, Fe-P is detected using bulk P K-edge, which corresponds with its soil geochemical characteristics and sequential chemical P extraction data. Overall, P concentrations were generally lower in TA, which led to difficulties in Fe-P compound detection using µ-XANES of TA. Overall, our study showed that coupling sequential chemical P extractions with progressively more advanced spectroscopic techniques provided more detailed information on P speciation, which can play a role in mobilization, transformation, and bioavailability of fluvial sediment-associated P.

Keywords: phosphorus; sediment; chemical P extraction; microanalysis; X-ray absorption near-edge structure (XANES) spectroscopy

1. Introduction

There has been increasing awareness of the importance of fluvial suspended sediments in the transport of nutrients from agricultural catchments, which can degrade water quality and cause



eutrophication [1]. A significant proportion of total phosphorus (TP) loads in agricultural streams is transported as particulate phosphorus (PP) or within the fluvial suspended sediment PP [2,3]. Suspended sediment-associated P is deposited on the riverbed channel or on floodplains and its subsequent remobilization must therefore have an important impact on the transport, delivery pathway and fate of P species within agricultural catchments. Deposition on the river channel bed or floodplains can result in short- or long-term P storage. Similarly, remobilization of riverbed sediments coupled with bank erosion can reintroduce P to the river channel. Hence, information on P fluxes, storage, mobilization, and bioavailability within agricultural streams is required for appropriate catchment scale management policies. While research has addressed the increasing recognition of the importance of sediment PP within freshwater systems, relatively little attention has been given to P in suspended and streambed sediments within agricultural catchments, with the majority of research focusing on P in soils and lentic sediments (lakes and reservoirs, etc.). Relatively few studies have specifically characterized and quantified P species within streambed sediments [4,5], and fewer still in fluvial suspended sediments [6]. Many studies have shown that in catchments with diffuse sources, episodic flooding events and surface water runoff control stream bed and suspended solid composition and fluxes over time [7–9]. In addition to P and organic matter, the concentration and form of metal complexes and their link to microbial mineralization processes are likely impacted by fluvial and stream bed sediments. For example, it has been shown that organic matter remineralization predominates P cycling in Chesapeake Bay sediments [10,11] and the formation of phosphate–Fe(III)–humic complexes significantly impact P cycling and sedimentary Fe(III) stabilization in organic matter Fe-rich lake sediments, which is rarely recognized [12,13]. Hence, the molecular forms of P and their association to metal species of fluvial and stream bed sediments are important for understanding P transformation, mobility, and the potential impact on surface water eutrophication.

Sequential chemical extractions (SCEs) have been widely used to assess and quantify P species with different binding mechanisms and bioavailability. The basis of such fractionation analyses is in the differential reactivity of solid substrates to various chemical extractants [14]. Hence, such chemical extraction methods provide only operationally defined P pools and do not directly determine P speciation [15]. Notwithstanding their widespread application, there are various limitations associated with many sequential chemical P extraction schemes, including: (1) the specificity of extracting agents for sedimentary chemical P forms is relative; (2) transformation processes during the extractions between fractions (i.e., P sorption on calcite from calcareous sediments may be extracted in the Fe-oxide CBD extractant step). For example, during extraction of organic matter-rich sediments using the original Psenner method, Al and Fe associated with humic acid complexes are often misappropriated [16–18]. In the original method, Fe-bound P is extracted using bicarbonate-buffered dithionite followed by extraction of Al-oxide-bound P using NaOH. Concurrently, within this NaOH treatment, significant organic matter-bound P is extracted. Hence an additional step involving the acidification of the NaOH treated sediments (pH ~1) precipitated humic acid (HA) associated Fe and Al resulting in a clear supernatant with precipitate containing up to 30% of the total sediment P [17]. Similarly, another SCE [19] for sedimentary P was modified for organic-rich sediments with insertion of an additional extraction step (Na₂CO₃) prior to the Fe-bound P focused on bicarbonate-buffered dithionite step in order to extract Fe and Al humic complexes [12,20]. Despite such limitations, SCEs are still useful to get initial estimates of sedimentary chemical P pools. However, more recently, synchrotron-based P K-edge X-ray absorption near-edge structure (XANES) spectroscopy [21,22] and solution ³¹P nuclear magnetic resonance (NMR) [23,24] have been applied to directly probe and distinguish different P species in terms of the inorganic form (XANES) and organic P species (NMR). More importantly, the feasibility and advantages of the combined use of these techniques in soil and sediment speciation have been demonstrated [11,12,25–27]. While such advanced spectroscopic techniques are capable of providing bulk speciation information for soil and sediment P, microclusters of concentrated P may be overlooked. Such P speciation information on microclusters of concentrated P is important, particularly for heterogeneous samples where correlations between P and metal

species are necessary to understand the transfer and transformation of P in dynamic systems [28,29]. In this study, our objectives were to: (i) couple chemical P fractionation with the bulk and P K-edge micro(μ)-XANES to show the tiered approach in studying P compositional dynamics in suspended fluvial sediments from geologically contrasting agricultural and; (ii) apply bulk and P K-edge μ -XANES to give progressively more accurate and detailed compositional information compared to chemical P fractionations; (iii) show how bulk and P K-edge μ -XANES can identify P species in detail and the correlation between P, Ca, and Fe elements from suspended solids from two geologically contrasting agricultural catchments in Ireland.

2. Materials and Methods

Suspended sediment samples were collected from two agricultural catchments located in the east and southeast of Ireland, namely, Ballyboughal (BB) and Tintern Abbey (TA), as shown in Figure 1. Both catchment streams are medium- to high-level eutrophic according to the 2015–2017 water quality map released by the Irish Environment Protection Agency [30], which makes them suitable locations to study the influences of agricultural catchment sediments to fluvial waters. The BB site has an area of 23 km², with soils primarily composed of river alluvium, fine loamy drift with limestones, and siliceous stones. TA has an area of 10 km², with soils composed of primary river alluvium and fine loamy drift with siliceous stones.



Figure 1. Location of the Ballyboughal (BB) and Tintern Abbey (TA) catchments in Ireland.

Fluvial sediment was gathered using time-integrated sediment traps, which were deployed to collect in-stream suspended solids over a 10-week period. One time period of samples was collected for this study, and taking into account the significant period of time (10 weeks) the traps were left in place, it is reasonable to consider the samples are representative of the catchment areas. Such sediment traps

are known as Philips samplers [31], and their ability to collect suspended soils is based on slowing down the water velocity, resulting in sediment accumulation within the sediment trap tube. These samplers were installed horizontally in the middle of the channel and installed securely at approximately 60% of the average water depth using steel uprights and plastic cable ties to steel rebar embedded deep into the river channel [28]. The sediment traps were carefully removed from streams and emptied into clean 10 L containers which are kept as near as possible to the stream temperature while being transported back to the laboratory. The sediments were stored in a refrigerator for a few hours and processed by wet sieving the fluvial sediment through 63 μ m steel stainless sieves, then centrifuged, and the supernatant decanted. The sediments were then freeze-dried for further analyses.

The sediment samples were sequentially extracted using a modified chemical extraction procedure [16,32], as shown in the flow diagram (Figure 2). Briefly, 1 M NH₄Cl was used to extract P adsorbed loosely to surfaces (P_{NH4Cl}); bicarbonate-dithionate (BD) extraction represents redox-sensitive P that is mainly bound to oxidized Fe and Mn compounds (P_{CBD}); 0.1 M NaOH was used to extract inorganic P compounds, such as Al and Fe oxyhydroxides (P_{NaOH}) and poly-P, P in detritus or complexes (P_{NRP}); humic P complexes (P_{hum}), acid-soluble P mainly bound to Ca (especially apatite), and Mg were differentiated using 0.5 M HCl (P_{Detr}); and, lastly, the residual P (P_{Res}) represents refractory organic P and non-extractable mineral P extracted using 1 M HCl at 120 °C. Phosphorus assumed to be associated with humic matter was precipitated by adding 2 M H₂SO₄ to a subsample of the NaOH extract [17]. Organic P (Figure 2) is calculated as the difference in TP between the first NaOH step and the second digested NaOH step [18].



Figure 2. Modified Psenner sequential chemical P extraction procedure flow diagram [16,32].

The bulk and μ -XANES at P, Ca, and Fe K-edges were recorded using the Soft X-ray Microcharacterization Beamline (SXRMB) beamline at the Canadian Light Source. At SXRMB, a DCM monochromator using Si (111) crystals is used to cover an energy range of 2–10 keV. At the bulk station, the powder samples were mounted on the double-sided carbon tape and loaded into the vacuum chamber. The bulk spectra were recorded using a 7-element Si drift detector for sediment samples with low P concentration, and in TEY mode for reference samples. A pair of KB mirrors was used to focus the beam to a spot size of 10 μ m × 10 μ m with 10⁹ photons/100mA/s flux [33]. A high-resolution and large area CCD camera is equipped to obtain the optical image of sample. A 4-element Si drift detector is used for μ -XANES analysis. A thin layer of sediment was spread on the carbon tape, and a large area of sample (3 × 3 mm²) was first mapped with coarse resolution. Fine-resolution μ -XRF maps were acquired by selecting areas based on the elemental distribution and correlation. P, Ca, and Fe μ -XANES

were acquired for selected hotspots. A photon energy of 7200 eV was used to record the XRF maps so that the distribution of P and other relevant elements can be tracked.

3. Results and Discussion

3.1. Total P and P Fractionation in Suspended Sediments

In this study, the overall median TP concentrations in the fluvial suspended sediments from the sum of all sedimentary P fractions at the Ballyboughal (BB) outflow was $3.4 \text{ mg} \cdot \text{g}^{-1}$, and for the Tintern Abbey (TA) outflow, it was $0.9 \text{ mg} \cdot \text{g}^{-1}$ (Figure 3a). Such TP concentrations are comparable with previous studies on fluvial suspended and streambed sediments [5]. There is a relatively high TP concentration observed for the BB fluvial suspended sediment, likely due to additional sedimentary P contributions from domestic septic tanks and village wastewater treatment plant (WWTP) outflows [34] as the catchment is a relatively highly populated agricultural catchment in north county Dublin, Ireland.



Figure 3. (a) Sequential chemical P fraction pools including total P (mg g^{-1} DW) for (a) Ballyboughal outflow (BB) and (b) Tintern Abbey outflow (TA); (b) sequential chemical P fractionations in relative percent (%) for (i) Ballyboughal (BB) outflow and (ii) Tintern Abbey (TA) outflow.

Within the BB suspended sediments, the most dominant P fractions included P_{CBD}, P_{Ore}, and P_{NH4Cl} with concentrations of 1.18, 0.3, and 0.75 mg·g⁻¹, respectively. By contrast, the most prevalent P fractions in the TA sediments were the P_{CBD}, P_{NaOH}, and P_{Org} with concentrations of 0.29, 0.18, and 0.16 mg·g⁻¹ (Figure 3a). Figure 3b presents the relative proportional percentage chemical P fractionation results of representative fluvial suspended sediments from (i) BB and (ii) TA sites. The sequential chemical P fractionations separated the fluvial sediment TP into pools with diverse bioavailability. The distribution of P fractions differs in the suspended solids of the two geologically contrasting agricultural catchments. Loosely sorbed (P_{NH4Cl}) was elevated at 22% in BB while there was a lower percentage at 7.5% in TA. The BB agricultural catchment is typical of many Irish agricultural catchments in that additional P contributions, including P_{NH4Cl}, may come from domestic septic systems or from village WWTP outflows [34]. The relative P_{CBD} fraction which constitutes P bound to reducible species of Fe and Mn was almost the same in the suspended solids of both catchments being slightly elevated at the TA outflow at ~32% in comparison to ~35% at the BB outflow. Within the BB suspended solids, there is a relatively elevated percentage composition of POrg, PDetr (P bound to Ca and Mg), and P_{Res} at ~9% for all three. The relative percentage composition of organic P for TA is ~17%. A previous study on fluvial suspended solids from the mixed land-use Bras d'Henri River watershed in Quebec City, Canada, reported POrg comprising up to 20% of TP using sequential chemical P fractionations, which was an order of magnitude greater than streambed sediments [5]. Previous studies have shown that mineralization of organic P (P_{Org}) to inorganic P ($_iP$) through enzymatic hydrolysis has a direct effect on P bioavailability in freshwater systems [35,36]. In addition, the TA outflow suspended sediment contains relatively elevated P_{Hum} and P_{NaOH} at ~7% and ~20.5%, which may be associated with the higher Fe and Al concentrations reflected in the catchment soils [34]. The P_{Hum} fraction may include Fe(III)-bearing colloids or organic matter–Fe(III)–P ternary complexes which can play an important role in P transport [8,12,17]. BB sediment samples clearly showed a higher relative fraction of P extracted by HCl (P_{Detr}) ~15%, indicating the presence of relatively elevated Ca-bound P, in agreement with the calcareous soils of the catchment [37]. The BB catchment does contain some areas rich in sandstone with elevated Fe, which may influence the relatively elevated percent composition redox-sensitive P (P_{CBD}) fraction. The relative percentage of redox-sensitive P (P_{CBD}) and NaOH-extracted P (P_{NaOH}) are both elevated in the TA sediment, consistent with the Fe-rich composition of the local mineralogy in the TA catchment [34]. The origin of such redox-sensitive P (P_{CBD}) and Al and Fe oxyhydroxide P (P_{NaOH}) fractions is associated with redox fluctuations impacting Fe(III)-oxides in hyporheic and riparian environments [38]. Organic matter degradation creates reducing anoxic conditions in such environments, particularly in summer, which can lead to reductive dissolution of Fe(III)-oxides to release Fe(II) and sorbed P [38,39].

3.2. Compositional Validation of Suspended Sediment Using X-Ray Fluorescence (XRF) and X-ray Absorption Near-Edge Structure (XANES)

The elemental compositions of these sediments as detected by X-ray fluorescence (XRF) (Figure 4) also show that the BB sediment has a much higher Ca concentration, while the TA sediment has a relatively higher Fe content. This is in general agreement with results from sequential chemical P fractionations which indicated more Ca-associated P within BB sediments and more Fe and/or redox associated P with TA sediments (Section 3.1; Figure 3). Previous studies have used synchrotron XRF coupled with operationally defined chemical P fractionation results to establish the dominant elements governing sediment composition [40–44].



Figure 4. X-ray fluorescence spectra of bulk TA and BB sediments. The intensity was calibrated relative to the scattered X-ray (to an intensity of 10000 at 7000 eV), so that the comparison of elemental intensities is possible. The incident photon energy is 7200 eV.

Figure 5 shows the P K-edge spectra of (a) bulk TA and BB sediments and in comparison to (b) the spectra of selected P reference compounds. The Fe phosphate-related compounds have a unique pre-edge peak, as indicated by the arrow in the spectrum of FePO₄.2H₂O shown in Figure 5b, while the Ca phosphate compounds, such as apatite, have several distinct shoulders in their P K-edge XANES [21,25]. P K-edge spectra of bulk sediment samples were dominated by featureless post-edge peak, similar to that of phytic acid [45]. This indicates the relatively significant presence of organic P (P_{Org}) in these samples, which may suggest the P_{Org} fraction of the chemical P fractionation results underestimate the significance of this P pool (Figure 3). The pre-edge peak, as indicated by the arrow, is clearly resolved in the spectrum of the TA sediment (Figure 5a), suggesting the presence of Fe-P in the bulk of TA sediment. This is in agreement with the chemical extraction and bulk XRF results (Figures 3 and 4). However, for Ca-rich BB sediment, no Ca-P related resonances are observed in the spectrum of BB sediment.



Figure 5. P K-edge XANES spectra of (a) bulk TA and BB sediments and (b) reference compounds.

This lack of Ca-P in the bulk spectrum of BB sediment implies the dominance of organic P and the inhomogeneous distribution of Ca-P in the BB sediment, which could be revealed by the microanalysis of these sediments. Chemical P fractionation results indicated a significant Ca-P pool normally associated with a recalcitrant mineral such as apatite. The tricolor µ-XAF maps of two sediments are shown in Figure 6. In this work, we chose to focus on the correlations between P, Fe, and Ca, as Fe oxides have been shown to complex with organic matter in sediments, thus impacting P mobility and surface water eutrophication [10–12]. The important role of Ca-P species in sediment weathering, P transformation in alkaline soil, and biogeochemical P cycling has been demonstrated by microscale XRF mapping, together with ³¹P NMR and chemical extraction [27,42,43]. In Figure 6, elemental correlation maps or hotspot maps down to the micron scale are shown for P (blue), Ca (green), and Fe (red). These are elemental correlation maps with comparison of relative elemental concentration within a specified hotspot/area and not absolute concentrations. Where necessary, the hotspot can be identified down to 10 microns for μ -XANES. It is obvious that there are more Ca-rich hotspot correlations with P in the BB catchment. The BB sample also has very few and weak Fe spots, but there are identifiable Ca- and P-correlated spots (such as A). The TA sediment is generally Fe-rich, with only one Ca-rich hotspot. This is consistent with the XRF analysis and the mineralogy of these sites. A few hotspots (A, B, C as P-rich, Fe-rich, and Ca-rich for BB sediment and D, E as Fe-rich and Ca-rich for TA sediment, respectively) are selected for P, Ca, and Fe µ-XANES.



Figure 6. Elemental mapping for P (blue), Ca (green) and Fe (red) of BB and TA sediments with selected spots.

Figure 7a,b present the P K-edge μ -XANES of hotspots or region of interests (ROI) for BB and TA sediments. The P spectra for TA sediments (D and E) were quite noisy and without distinct features associated with inorganic P (Figure 7b), confirming its weak and significant organic P (Figure 3). The μ -XRF map of the TA sample revealed that ROI *D* had high Fe and P correlation (Figure 6); unfortunately, Fe-P could not be resolved in its µ-XANES (Figure 7b), likely due to its low P concentration and interference from the high Si content (Figure 4). For the Ca- and P-rich hotspots of BB sediment, the post-edge resonances were clearly resolved (Figure 7a, spots A and C), indicating the high Ca-P in the BB site. This is in agreement with the chemical extraction result, demonstrating the advantage of the μ -XANES, as no Ca-P was detected in the bulk P K-edge (Figure 5a). On the contrary, no Ca-P is detected in the µ-XANES of spot B, as it shows high Fe and P correlation (Figure 6). There might be a hint of the pre-edge peak in the P K-edge of spot B, implying the presence of Fe-P. Results of Ca K-edge μ -XANES (Figure 7c) are also in agreement with the P K-edge μ -XANES, as Ca in spot A matches well with that of apatite, spots B and C being mostly calcite, and spots D and E being mostly organic Ca [25]. The Fe K-edge µ-XANES of all spots (Figure 7d) are similar to each other and to those of bulk samples, as they are dominated by Fe hydroxyl oxide species [11,45]. No Fe-P can be resolved in the Fe K-edge µ-XANES due to its relatively low concentration.



Figure 7. μ-XANES of selected spots identified in Figure 5: (**a**,**b**) P K-edge; (**c**) Ca K-edge and (**d**) Fe K-edge.

4. Conclusions

The chemical speciation of fluvial suspended sediment-associated PP from two geologically contrasting agricultural sites was studied by chemical extraction and bulk and μ -XANES. It was demonstrated that the microanalysis of P K-edge, combined with the µ-XANES of Ca and Fe K-edge, is critical to achieving a detailed characterization of the PP species. The limestone nature of BB was confirmed by XRF, which is consistent with the soil type at the BB site. The chemical confirmation of Ca-P-containing compounds in BB sediments was revealed only by P K-edge µ-XANES and not by its bulk spectrum, as the bulk XANES was only capable of probing the average speciation. Using bulk P K-edge XANES, it was difficult to resolve Ca-P peaks as the BB spectra is dominated by organic P. For the TA location, Fe-P containing compounds were detected by P K-edge XANES, which correlates with its soil geochemical characteristics and the sequential chemical P extraction data. Notably, the P concentration is generally lower in TA, which makes it difficult to detect Fe-P in the μ -XANES of TA. μ-XANES of Ca K-edge was consistent with the P K-edge and the geochemical characteristics of the study sites (i.e., both Ca-P associated with apatite and calcite detected in BB; TA has mostly organic Ca). A significant amount of organic P was detected in these sediments using P K-edge XANES which suggested the sequential chemical P extractions may have underestimated its importance. Overall, our study provided additional, detailed information on the P speciation associated with fluvial sediments by coupling sequential chemical P extractions with progressively more advanced spectroscopy, including XRF, bulk-XANES, and µ-XANES of multiple elements. This additional knowledge contributes to our understanding of the geochemical processes governing P mobilization, bioavailability, and transformation to potentially inform improved agricultural catchment management policies to protect the water quality of associated rivers and streams.

Author Contributions: D.O.; L.G. and Y.H. designed the study. Q.Z.; M.W.; D.O. collected the samples and performed most data measurement and analyses. Q.X. and Y.H. collected the XRF and XANES data. Y.H. and D.O. did most of the writing with inputs from all. All authors have read and agreed to the published version of the manuscript.

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