Response to Comment on "The Chemical Nature of Phosphorus in Subtropical Lake Sediments", by Kenney et al.

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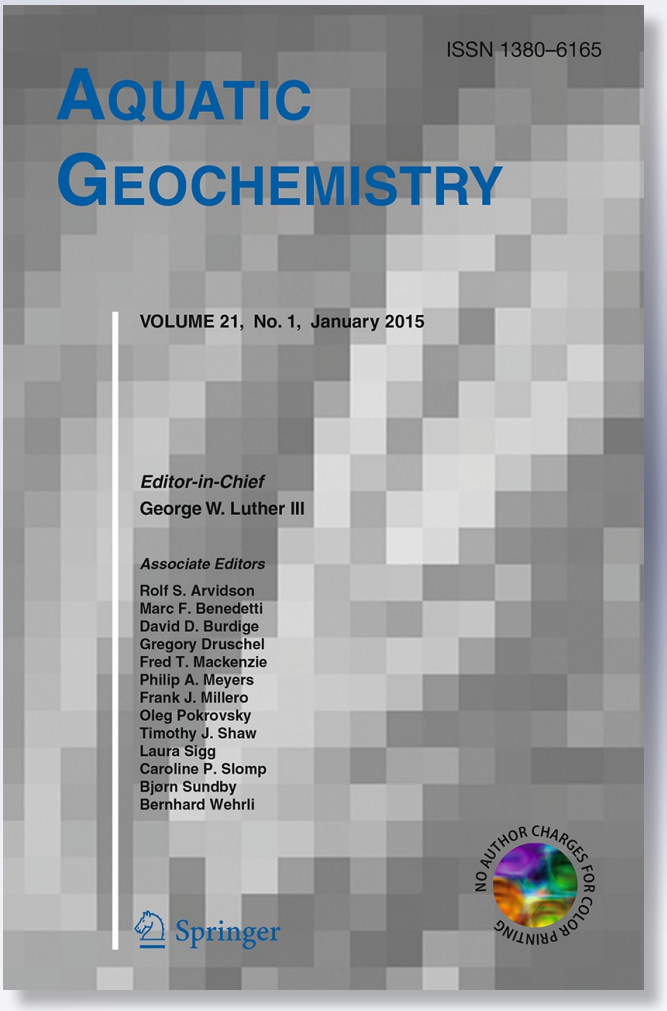

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ORIGINAL PAPER

Response to Comment on "The Chemical Nature of Phosphorus in Subtropical Lake Sediments", by Kenney et al.

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Abstract Polyphosphate is a quantitatively important and dynamic component of the sedimentary phosphorus in many lakes. Kenney et al. correctly note that we misrepresented their data on polyphosphate in Lake Apopka in our article on the phosphorus composition of subtropical lake sediments, and we regret this error. However, we reiterate that their operationally defined heat extraction procedure overestimates polyphosphate in lake sediments because it includes phosphorus from a number of non-polyphosphate sources. In contrast, our measurements by solution ^{31}P NMR spectroscopy provide direct quantification of polyphosphate in Lake Apopka sediments and are therefore closer to the true values. Future studies addressing the origins and dynamics of polyphosphate in the environment should employ analytical procedures that unequivocally identify and quantify polyphosphate.

Keywords Polyphosphate · Lake Apopka · Solution phosphorus-31 NMR spectroscopy · Sediment

1 Main Text

Polyphosphate is a quantitatively important and dynamic component of the sedimentary phosphorus in many lakes and wetlands (e.g., Hupfer et al. 2004; Cheesman et al. 2012). Kenney et al. (2014) correctly note that we misrepresented their previous data on polyphosphate concentrations in Lake Apopka (Kenney et al. 2001) in the discussion section of

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our recent manuscript, and we thank them for rectifying this mistake. We appreciate their detailed analysis and further interpretation of our results in the context of previous studies of the three Florida lakes, which raise further hypotheses warranting assessment.

In their comment, Kenney et al. (2014) note a relatively close agreement between their estimates of polyphosphate in Lake Apopka sediment determined by heat extraction and molybdate colorimetry (18 % of the total sediment phosphorus; Kenney et al. 2001) and our values determined by alkaline extraction and solution ^{31}P NMR spectroscopy (8–11 % of the total sediment phosphorus; Torres et al. 2014). The authors then suggest that the difference between the two sets of measurements probably reflects the degradation of polyphosphate during freezing and lyophilization of our sediment samples prior to extraction and analysis. However, there is little evidence that freezing and lyophilization reduces polyphosphate concentrations in either sediments (Cade-Menun et al. 2005) or alkaline extracts (Hupfer et al. 2008). Instead, we interpret the difference between the two sets of measurements to be a consequence of the non-specific nature of the analytical procedure used by Kenney et al. (2001).

First, and as acknowledged by Kenney et al. (2014), the operationally defined heat extraction procedure is not specific for polyphosphate, but potentially includes all forms of intracellular phosphorus (Pettersson 1980). Second, autoclaving induces physical and chemical changes in soils and sediments that almost certainly influence the stability and solubility of inorganic and organic phosphorus compounds (Wolf et al. 1989; Xie and MacKenzie 1990). As a result, phosphorus concentrations determined by heat extraction and molybdate colorimetry do not provide a reliable measure of polyphosphate in lake sediments.

In contrast, solution ^{31}P NMR spectroscopy allows the direct identification and quantification of polyphosphate in environmental samples, and was described in a comprehensive review of analytical methodology as the most powerful procedure for determining polyphosphate in lake sediments (Hupfer et al. 2008). The procedure can lead to a reduction in polyphosphate chain length in alkaline extracts by metal-induced hydrolysis, although this is obviated by inclusion of EDTA in the alkaline extractant or by pre-extraction in dilute EDTA (Hupfer et al. 1995), both of which were used in our study of subtropical lake sediments. Solution ^{31}P NMR spectroscopy has proven suitable for the determination of polyphosphate in a variety of contrasting freshwater and marine environments. These studies have revealed the widespread occurrence of polyphosphate in surface sediments worldwide, as well as the abrupt down-core disappearance of polyphosphate within the first few centimeters of the sediment profile (Hupfer et al. 2004; Ahlgren et al. 2005; Reitzel et al. 2007; Özkundakci et al. 2013; Torres et al. 2014). Based on the latter observation, there is little support for the suggestion by Kenney et al. (2014) that polyphosphate is sufficiently stable during long-term diagenesis to be used as a geochemical marker.

As concluded by Kenney et al. (2014), there are a number of important questions concerning the origins and fate of polyphosphate in aquatic environments. Future studies should address these questions using spectroscopic, cytochemical, or microscopic procedures that allow the direct identification and quantification of polyphosphate in sediments (Hupfer et al. 2008).

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