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ORIGINAL PAPER

Sequential extraction of calcium in lake sediments for investigating the cycle of phosphorus in water environment

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Abstract The role of calcium (Ca) in the cycle of phosphorus in water environment depends on the speciation of Ca in sediments, and reliable Ca sequential extraction method is useful for obtaining information about Ca transport processes from sediment to water. Experiments have been carried out to develop a simple but robust Ca sequential extraction method for identification of Ca portioning in sediments. The sequential extraction protocol was modified for extractants, extracting time, concentration and pH of the reagents in the first three steps of Tessier sequential procedure. With optimum conditions, there were 1:25 sediment to solution ratio and 3 h of extracting time shaken with NH_4AC (1 mol L^{-1}, pH 7.0) (exchangeable Ca fraction); 1:25 sediment to solution ratio and extracted with NH_4AC (1 mol L^{-1}, pH 5.0) for 5 h (carbonate-bound Ca fraction); and 1:30 sediment to solution ratio and extracted with $NH_2OH{\cdot}HCl$ (0.5 mol L^{-1}, pH 1.5) for 6 h (Fe and Mn oxides bound Ca fraction). The recovery for Tessier procedure ranged form 35.6 to 71.1 %, while the recovery for the modified Tessier procedure ranged form 46.1 to 86.9 %. These results revealed that Tessier procedure underestimated the proportion of Ca in exchangeable fraction. In sediments, Ca was mainly exchangeable and carbonate bound, which was considered as the most liable fractions.

Keywords Fraction protocol · Modified Tessier procedure · Condition selection · Recovery

Introduction

Calcium (Ca) has been demonstrated that it could influence aquatic systems in a number of ways: (1) Ca together with Mg is the main determinant of water hardness and in drinking water it is considered a natural and mineral nutrient (Yang et al. 2006; Molinero et al. 2013); (2) in water column, Ca^{2+} would precipitate with inorganic carbon when the ion activity product ($[Ca^{2+}] \times [CO_3^{2-}]$) exceeds the solubility product (K_{sp}) of the corresponding carbonate mineral (Glunk et al. 2011; Reddy and Hoch 2012); (3) water column P, regarded as one of the key factors responsible for eutrophication in surface water bodies (Schelske 2009), could be partly removed in the process of adsorption to or co-precipitation with calcite (Hartley et al. 1997; Dittrich et al. 2011); (4) Ca is an essential nutritional element for many different types of aquatic biota. In natural water, Ca is liable to combine with inorganic carbon and phosphorus (P), triggering co-precipitate of $CaCO_3$ with phosphorus that results in the P transport of water column. Calcium bound P is insensitive to redox potential and once deposited in bottom sediments, it may get long-term retention (Kufel et al. 2013). Sediment is an important storage sink for metals (Mishra et al. 2008; Nemati et al. 2011). The mobility and bioavailability of metals strongly depend on their specific chemical forms and ways of binds to each of the different phase (Karadas and Kara 2012). The distribution of Ca among sediment components is important for assessing the potential of sediments to release Ca and to supply sufficient nutrient for plant growth.

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Indeed, changes in environmental conditions such as acidification, changes in the redox potential conditions or increase in organic ligand concentrations can cause element mobilization from solid to liquid phase and migrating to waters (Delgado et al. 2011). Sequential extraction methods are often intended to simulate the various possible natural and anthropogenic modifications of environmental conditions such as acidification or oxidation (Cappuyns et al. 2007). A wide variety of sequential extraction procedures for metals have been developed. The most widely used sequential extraction protocols are those recommended by Tessier et al. (1979) and the Community Bureau of Reference (BCR) (Quevauviller et al. 1993). However, due to non-selectivity of each reagent in successive steps and possibility of metal readsorption during the extraction (Gilmore et al. 2001), the accuracy and validity of sequential extraction methods for the purpose of metal speciation have been questioned. Furthermore, any change in the sequential extraction procedure such as the type of reagent (Wenzel et al. 2001), reagent concentration and pH (Nemati et al. 2009a), reaction time (Outola et al. 2009), temperature (Sahuquillo et al. 1999), soil to solution ratio (Taylor et al. 2012) or the order in which the extractions are used (Kim and McBride 2006) can influence the outcome.

But nearly scarce effort has been made for the improvement of Ca extraction. Since most of sequential extractions are universally applied to trace metals (Herreweghe et al. 2003), difference between the amount of trace metals and Ca was significant, specially in sediments. The extraction condition for trace metal might not be applicable to major element. The five-step sequential extraction scheme developed by Tessier et al. (1979) has been used extensively to determine the amounts of metals associated with several different phases in soils and sediments (Chakraborty et al. 2012). In the scheme, metals are divided into five fractions (exchangeable, bound to carbonate, bound to Fe/Mn oxides, bound to organic matter and residual).

The objectives of the present study were to develop a sequential extraction procedure (the modified Tessier procedure) for fractionation of sediment Ca and to compare the modified and unmodified Tessier procedure. We selected the extraction conditions from September 20, 2012, to March 20, 2013, by comparing different reagents, extracting time, solid to extract ratio, concentrations and pH of reagents in the first three steps of the five steps, which are the most liable fractions. Both modified and unmodified Tessier procedures have been demonstrated by the fractionation of Ca in 12 different lake sediments.

Materials and methods

Sampling of sediments

Sediment samples were collected from Lake Tangxunhu, Lake Donghu, Lake Yuehu and Lake Nanhu in Wuhan City, China, and were grabbed at three different locations in each of the lake with a Petersen grasp sampler. And all samples were air-dried at room temperature and passed through a 0.14 mm sieve. There are 12 different sediments (T1, T2, T3 from Lake Tangxunhu; D1 D2, D3 from Lake Donghu; Y1, Y2, Y3 from Lake Yuehu; and N1, N2, N3 from Lake Nanhu). The sediments were divided into two categories: (1) T sediment, a mixture of T1, T2 and T3, and Y sediment, a mixture of Y1, Y2 and Y3, were used in condition selection tests in a sequential extraction procedure; (2) T1, T2, T3, D1, D2, D3, Y1, Y2, Y3, and N1, N2, N3 were used for the comparison of modified and unmodified Tessier procedure. There were large differences in the composition of the sediments such as sediments from Lake Yuehu (Y1, Y2 and Y3) had highest pH range (7.54–7.62) and high content of total calcium (27.45–34.69 g kg^{-1}) and organic matter (76.9–99.5 g kg^{-1}). On the contrary, the sediments from Lake Tangxunhu (T1, T2 and T3) had lowest ranges of pH (6.50–6.76), total calcium (4.90–7.39 g kg^{-1}) and organic matter (37.5–51.5 g kg^{-1}).

Condition selection for extracting procedures

The selective sequential extractions of the modified Tessier procedure were conduced that sediment sample (1 g) was placed in 50-mL centrifuge tubes. Tubes were then shaken at room temperature in a reciprocating shaker (SHA-C, Changzhou Guohua, Jiangsu, China) with speed of 200 rpm. After each extraction step, the tubes containing the suspension were centrifuged for 10 min at 4,000 rpm by centrifuge (SF-TDL-5A, Feiqiaer, Shanghai, China). Ca, Fe or/and Mn were measured in the centrifuged supernatants by AAS (AA240FS, Varian, Palo Alto, USA). Deionized water (25 mL) was added to the solid residues prior to addition of next extractant solution, and the tube contents were vortex mixed by vortex mixer (M37610-33CN, Thermo Fisher, Waltham, USA) for 1 min and shaken for 10 min in the reciprocating shaker, centrifuged. The supernatants were decanted. All extractions were performed in duplicate. All the chemicals used in our tests were produced in Siopharm Chemical Reagent Co., Ltd., Shanghai, China.

The parameters optimized were type of extractants, extracting time, the ratio of reagent to sediment, pH and concentration of extractants. The ideal conditions selected produced the maximum fractional release of Ca^{2+}, and phase specificity of the extractions was monitored by measuring the concentration of Ca^{2+} in the extractant solutions.

Conditions for exchangeable Ca

1. Both neutral NH_4AC and NaAC were compared to extracted exchangeable Ca. The sediments were extracted with 25 mL of either 1 mol L^{-1} NH_4AC (pH adjusted to 7.0 with HAC) or 1 mol L^{-1} NaAC (pH adjusted to 7.0 with HAC) with continuous agitation in different time (0.5, 1.0, 1.5, 3.0, 5.0, 8.0 and 24 h), respectively. Reagent and shaking time were evaluated and adapted in the next test.
2. The sediments were extracted for the selected time with the variable volumes (10, 15, 20, 25 and 30 mL) of the selected reagent solution (1 mol L^{-1}, pH adjusted to 7.0 with HAC) with continuous agitation, respectively. The suitable extract volume was selected and adapted in the next test.
3. The sediment was extracted for the selected time with the selected volume of variable concentrations (0.1, 0.2, 0.5, 0.8, 1.0 and 1.5 mol L^{-1}) of the selected reagent solution (pH adjusted to 7.0 with HAC), respectively. The suitable concentration of reagent was selected and adapted in the next test.
4. The sediment was extracted for the selected time with the selected volume of the variable pH (5.5, 6.0, 6.5, 7.0 and 7.5) of the selected reagent solution (adjusted with HAC, 1 mol L^{-1}), respectively. Effect of pH on solubility of $CaCO_3$ (powder) was also performed, meanwhile. The optimized pH of the extract was selected and adapted.

Conditions for carbonate-bound Ca

A sediment sample was taken to study the conditions for carbonate-bound Ca fraction. Before beginning, the sample was first treated with the selected conditions in “Conditions for exchangeable Ca” section and then the residue was used in the procedure below after washed with deionized water.

1. NH_4AC and NaAC of pH 5.0 were compared to extracted carbonate-bound Ca. The residue was mixed with 25 mL of 1 mol L^{-1} NaAC (pH 5.0 adjusted with HAC) or 1 mol L^{-1} NH_4AC (pH 5.0 adjusted with HAC) with continuous agitation in different time (0.5, 1.0, 1.5, 3.0, 5.0, 8.0 and 24 h), respectively. And extractant and shaking time were evaluated and adapted in the next test.
2. The residue was mixed with different volumes (10, 15, 20, 25 and 30 mL) of the selected extractant (NH_4AC, pH 5.0) and shaken for the selected time, respectively. The suitable volume of extractant was selected and adapted in the next test.
3. The residue was mixed with variables concentration (0.1, 0.2, 0.5, 0.8, 1.0 and 1.5 mol L^{-1}) of the selected extractant (NH_4AC, pH 5.0) and shaken for the selected time, respectively. The suitable concentration of extractant was selected and adapted in the next test.
4. The residue was mixed with variables pH solutions (4.5, 5.0, 5.5, 6.0 and 6.5) of the selected extractant (NH_4AC) and shaken for the selected time, respectively. The optimized pH of the selected extractant was selected and adapted.

Conditions for Fe/Mn oxides bound Ca

A sediment samples was taken to study the conditions for Fe/Mn oxides bound Ca fraction. Before beginning, the sample was first treated with the selected conditions in “Conditions for exchangeable Ca” section and “Conditions for carbonate bound Ca” section in sequence and then the residue was used in the procedure below after washed with deionized water.

1. The residue was extracted with citrate–bicarbonate–dithionite (CBD) as prescribed by Tessier et al. (1979) or 25 mL of $NH_2OH{\cdot}HCl$ (0.04 mol L^{-1}, 50 °C) with continuous agitation in different time (1/12, 1/6, 1/2, 1, 2, 4, 6, 8 and 11 h for CBD; 1/6, 1/2, 1, 2, 4, 7 and 11 h for $NH_2OH{\cdot}HCl$), respectively. Extractant and shaking time were evaluated and adapted in the next test.
2. The residue was extracted with different volumes (15, 20, 25, 30 and 35 mL) of the selected $NH_2OH{\cdot}HCl$ (0.04 mol L^{-1}, 50 °C) and shaken for the selected time, respectively. The suitable volume of extractant was selected and adapted in the next test.
3. The residue was mixed with different concentration and pH of the selected $NH_2OH{\cdot}HCl$ (50 °C) set as that (0.1 mol L^{-1}, pH 2.0; 0.5 mol L^{-1}, pH 1.5; 0.5 mol L^{-1}, pH 1.0; 0.8 mol L^{-1}, pH 1.5; and 0.8 mol L^{-1}, pH 2.0) and shaken for the selected time, respectively. The residual organic matter after extraction was determined. The optimized concentration and pH of $NH_2OH{\cdot}HCl$ (50 °C) were adapted.

Comparison of two methods

The comparison of Tessier procedure (Tessier et al. 1979; Outola et al. 2009; Chakraborty et al. 2012) with the modified Tessier procedure (M-Tessier) was undertaken for Ca fractionation in 12 different samples. And the modified Tessier procedure was selected optimally in “Condition selection for extracting procedures.”

The pH of the extracts was also determined (after each extraction in the first three fractions) with an electrode pH (PHs-3c, Leici, China).

Data analysis

All treatments in this study were repeated three times, and values presented in this paper were the mean ± standard error of three replicated experiments. MS Excel 2003 and Origin 8.0 statistical software were used in the statistical analysis.

Results and discussion

Selection of extracting conditions for exchangeable Ca extraction

The exchangeable fractionation of Ca in sediment, also described as non-specifically adsorbed fraction, can be released by the action of cations such as K^+, Na^+, Ba^{2+}, Mg^{2+} or NH_4^+ displacing metals weakly bound electrostatistically on organic or inorganic sites (Rao et al. 2008). Many reagents, including ammonium acetate (NH_4AC) (Yu et al. 2001; Relic et al. 2005; Arcega-Cabrera et al. 2009), sodium acetate (NaAC) (Yousfi et al. 1999) and magnesium chloride ($MgCl_2$) (Wang et al. 2005; Abollino et al. 2006; Alvarez et al. 2006), have been employed to liberate exchangeable metals.

$MgCl_2$ was a popular reagent in this operation, which was used in the original Tessier procedure (Tessier et al. 1979) and did not attack organic matter, silicates or metal sulfides. However, high concentration of Mg^{2+} (1 mol L^{-1}) might disturb calcium determination, which could cause an inaccuracy of Ca in the exchangeable fraction. Extraction with acetate salts has also been used frequently in soil and sediment studies. In our modified scheme to extract Ca, NH_4AC or NaAC was chosen to replace $MgCl_2$. Moreover, because of the buffering capacity of the solutions, variations in pH could be reduced.

To evaluate the optimum time for extracting the exchangeable fraction, Ca^{2+} was measured in centrifuged supernatants from T sediment and Y sediment after different time intervals. Figure 1 showed that for both sediments, a lesser amount of Ca^{2+} was found when NH_4AC rather than NaAC was used in the extraction. For this reason, NH_4AC was finally selected as the initial reagent in the sequential extraction procedure. For T sediment, dissolution of calcium with NH_4AC was complete within 0.5 h. However, for Y sediments with high Ca content, longer extracting time, 3 h, was necessary. Thus, a leaching time of 3 h was adopted.

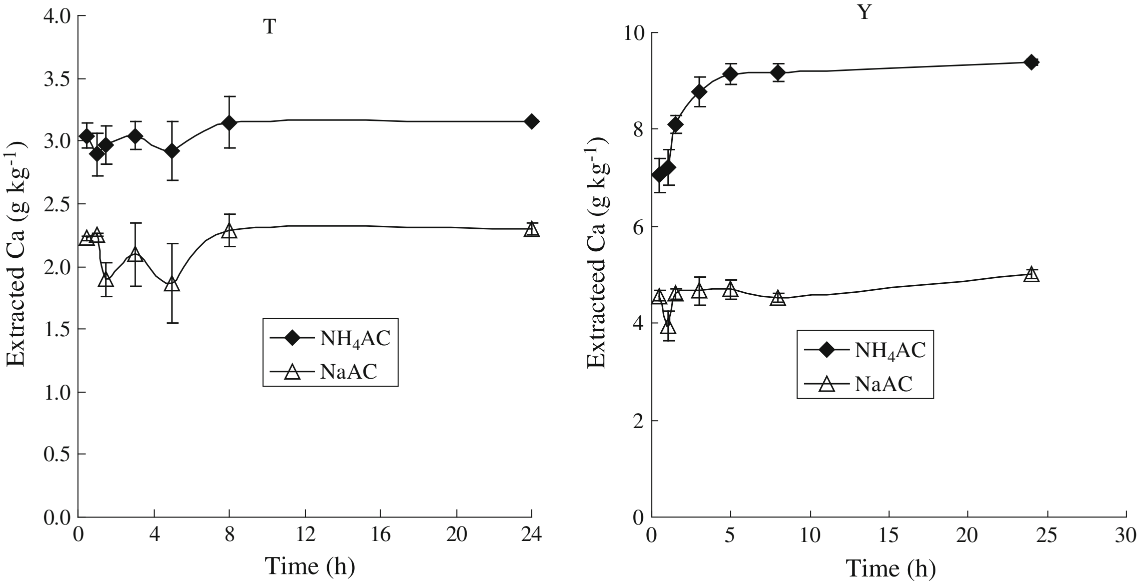

Fig. 1 Effect of extracting time on calcium amounts in 1 mol L^{-1} NaAC (pH 7.0) or 1 mol L^{-1} NH_4AC (pH 7.0) extracting solution for sediments T and Y

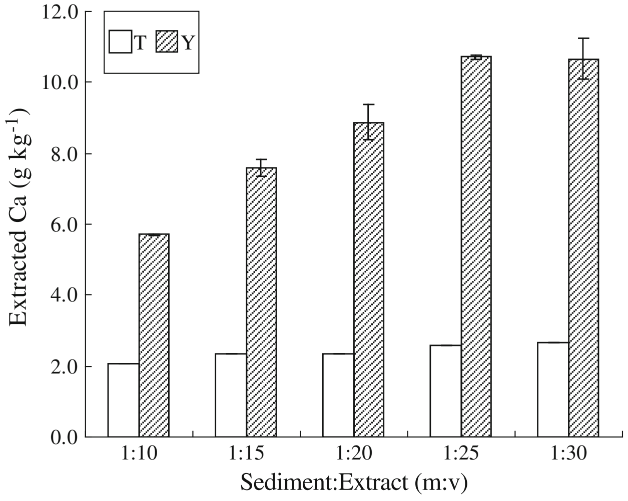

Fig. 2 Effect of extractant volume of NH_4AC (1 mol L^{-1}, pH 7.0) on calcium amounts for sediments *T* and *Y*

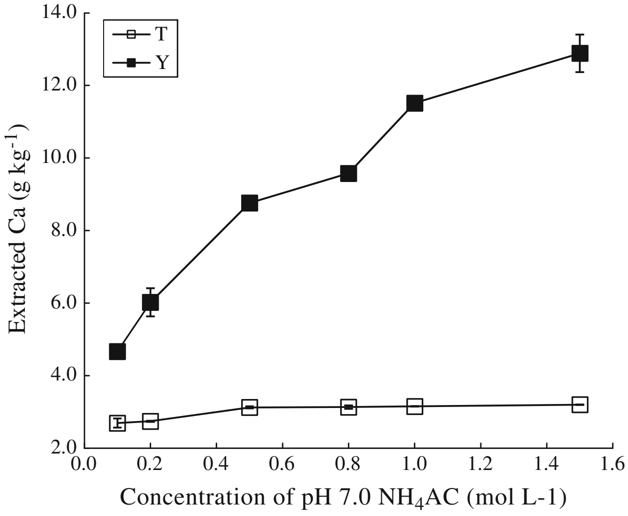

Fig. 3 Effect of concentration of NH_4AC (pH 7.0) on calcium amounts for sediments *T* and *Y*

To evaluate the optimum volume of extractant for extracting the exchangeable fraction, Ca extracted with different volume of NH_4AC for T or Y sediment was compared. Figure 2 showed the changes in amount of extracted Ca^{2+} as a function of extract volume. The amount of extracted Ca^{2+} increased with solution volume and slightly with 25 mL of reagent. Based on the study, the sediment to solution ratio in exchangeable Ca fraction of Tessier procedure extracted with NH_4AC (pH 7.0) was adjusted from 1:8 to 1:25.

The effect of extractant strength was tested on two different sediments using NH_4AC (pH 7.0). As the strength of NH_4AC solution increased from 0.1 to 0.5 mol L^{-1}, extracted Ca^{2+} from T sediment increased substantially (from 2.7 to 3.3 g kg^{-1}), while increasing from 0.5 to 1.5 mol L^{-1} had no apparent effect on the amount of Ca^{2+} extracted [Fig. 3(T)]. Therefore, 0.5 mol L^{-1} of extractant was sufficient in dissolving exchangeable Ca from T sediment. However, in the case of high Ca sediment (Y) [Fig. 3(Y)], extracted Ca^{2+} increased sharply when the concentration of NH_4AC increased from 0.1 to 1.0 mol L^{-1} (from 4.8 to 11.8 g kg^{-1}). Only slight increase was observed when the concentration increased from 1.0 to 1.5 mol L^{-1} (from 11.8 to 13 g kg^{-1}). Based on the findings, in these two sediments (T and Y), we selected reagent strength of 1.0 mol L^{-1} for NH_4AC to extract the exchangeable fraction.

In order to select the optimum pH of NH_4AC for exchangeable fraction extraction, two different sediments (T and Y) were studied. The second fraction of our scheme is carbonate fraction and also called acid fraction, which is sensitive to pH changes. An ideal reagent for exchangeable fraction was expected not to attack carbonate, but totally dissolve exchangeable Ca. In our study, solubility of $CaCO_3$ in NH_4AC solution with varied pH was determined. As shown in Fig. 4 ($CaCO_3$), in acid condition ($pH < 7.0$), progressively greater amounts of Ca^{2+} was released with lower pH. When at pH 5.0, $CaCO_3$ could be completely dissolved by NH_4AC. For T sediment [Fig. 4(T)], in both acid condition ($pH < 7.0$) and base condition ($pH > 7.0$), greater amounts of Ca^{2+} was released with lower pH and reached a maximum of approximately 3.7 g kg^{-1} at pH 6.5–8.0. It was interesting to find that much Ca^{2+} was extracted with NH_4AC at pH 7.0 than at pH 6.5. In the case of Y sediment [Fig. 4(Y)], Ca^{2+} extraction increased with a decrease in pH of NH_4AC (1 mol L^{-1}). This increase at $pH < 7.0$ could be ascribed to the dissolution of Ca at acid condition. As a result, we decided to choose medium setting as a compromise. Therefore, NH_4AC (1 mol L^{-1}) at pH 7.0 was selected for the extraction of exchangeable fraction.

Selection of extracting conditions for carbonate-bound Ca extraction

Carbonate-bound Ca fraction is sensitive to pH changes, and metal release is achieved through dissolution of a fraction of the solid material at pH close to 5 (Gleyzes et al. 2002). A buffered acetic acid/sodium acetate solution (HAC-NaAC) is generally used (Tessier et al. 1979; Rao

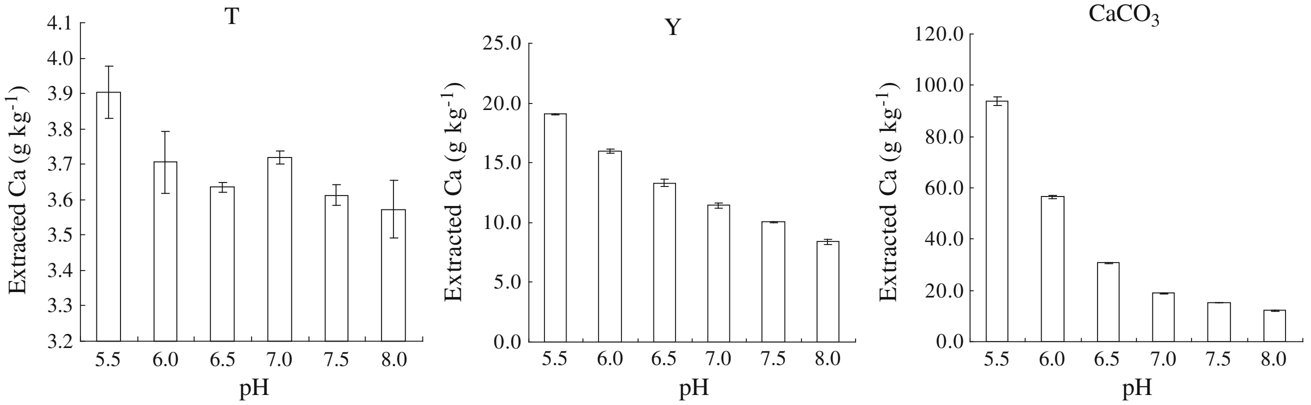

Fig. 4 Effect of pH of the NH_4AC extraction solution on the calcium amounts for two sediments (*T* and *Y*) and the solubility percent of Ca for $CaCO_3$ powder

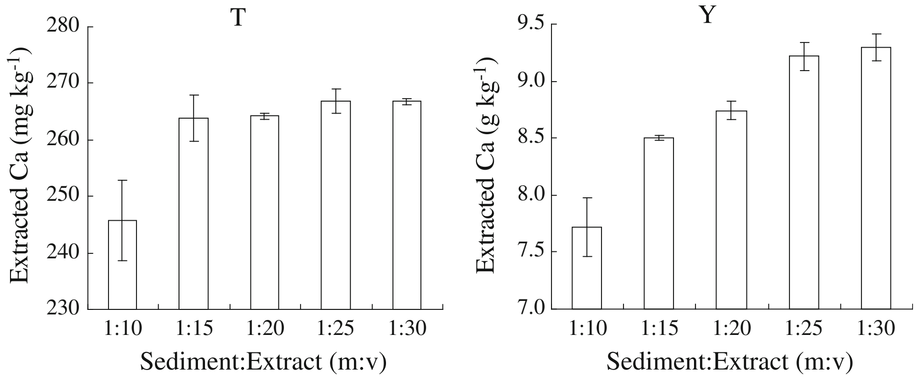

Fig. 5 Effect of extract volume on the calcium amounts in the NH_4AC (1 mol L^{-1}, pH 5.0) extracting solution for sediments (*T* and *Y*) previously extracted for exchangeable Ca with 1 mol L^{-1} NH_4AC (pH 7.0)

et al. 2008), and acetic acid/ammonia acetate solution (HAC-NH_4AC) (Outola et al. 2009) was used to compare with it in our study. These extractants were expected not to attack oxides and silicates, but totally dissolve calcium carbonate as well as carbonates of most metals.

To evaluate the optimum time for extracting the carbonate fraction, the sediment samples were first extracted during 3 h for exchangeable Ca with 1 mol L^{-1} NH_4AC (pH 7.0) and then further extracted with 1 mol L^{-1} NH_4AC (pH 5.0, adjusted with HAC) or NaAC (pH 5.0, adjusted with HAC). The results showed that a more amount of Ca^{2+} was found in step 2 when NH_4AC rather than NaAC was used in the extraction. NH_4AC was finally selected to extract carbonate-bound Ca. The results indicated that for T sediment, extraction of carbonate-bounded Ca with NH_4AC (1 mol L^{-1}, pH 5.0) was essentially complete after 3 h. Extraction with 3 h was enough for complete dissolution of carbonate fraction for sediment with low Ca content, however, maybe not enough in the case of sediment with high carbonate content. Incomplete carbonate dissolution might lead to an over estimation of the third fraction since its dissolution could be continued during the following step of the scheme. For Y sediment (with high Ca content), extraction was complete after 5 h. To ensure a complete dissolution, a leaching time of 5 h with NH_4AC was adopted for the extraction of carbonate-bound fraction in subsequent experiments,

The effect of extract volume for carbonate-bound fraction was tested (Fig. 5). Increasing the volume of NH_4AC from 10 to 15 mL had increase of Ca^{2+} extractability from T sediment, while no apparent effect on the amount of Ca^{2+} extracted when increasing the volume from 15 to 30 mL. Fifteen milliliters of NH_4AC was suitable to extract carbonate-bound fraction for T sediment. Reagent volume was found to have a positive effect on release of Ca^{2+} in the case of Y sediment. The release of Ca^{2+} increased with increasing reagent volume, not significant difference was observed with volume of 25 and 30 mL. Twenty-five milliliters of reagent was selected for Y sediment.

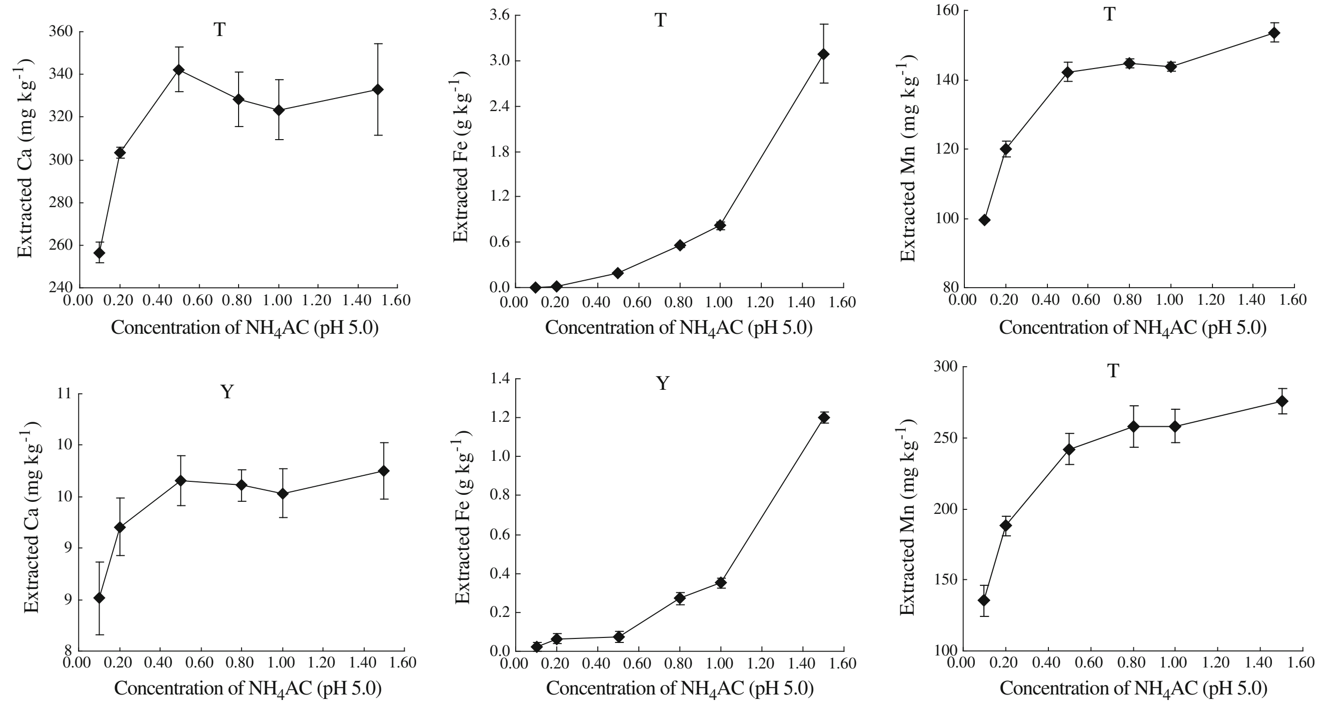

Fig. 6 Effect of concentration of the NH_4AC (pH 5.0) extracting solution on the Ca, Fe and Mn amount for sediments previously leached for exchangeable Ca with 1 mol L^{-1} NH_4AC (pH 7.0)

The failure of the acid extractable step in the Tessier procedure to dissolve all carbonates was also reported by Tack and Verloo (1996). They estimated that between 10 and 25 % of the metals extracted in the reducible fraction of calcareous sediment were related to dissolution of carbonates remaining after the step. Eight milliliters of NaAC (pH 5.0) might not sufficient for sediments with high carbonate content and was not able to extract maximum amount of metal without saturation. Thus, a higher sediment to solution ratio was demanded, 1:25 was selected to extract carbonate-bound Ca fraction.

We compared different concentrations of NH_4AC (pH 5.0) for their efficiency and specificity to extract Ca (Fig. 6). The results showed that 0.5 mol L^{-1} NH_4AC was effective in extracting Ca for T sediment (with low Ca content). The lower extraction of reagent concentration below 0.5 mol L^{-1} might be due to incomplete dissolve of $CaCO_3$. In the case of Y sediment, the removal of Ca increased with the concentration of extractant up to 1.0 mol L^{-1}, while little fluctuation above 1.0 mol L^{-1} of extractant.

It was notable that NH_4AC dissolved considerable Mn and Fe (Fig. 6). That Mn^{2+} showed a same change as Ca^{2+}. A simple linear regression analysis was performed to assess the relationships between Ca^{2+} and Fe^{3+}/Fe^{2+} or Mn^{2+} extracted by NH_4AC (pH 5.0, adjusted with HAC). Significant correlation was observed between Ca^{2+} and Mn^{2+} and no correlation between Ca^{2+} and Fe^{3+}/Fe^{2+}. The correlation coefficients ($n = 5$) for Ca^{2+} and Mn^{2+} were 0.9436 (T sediment) and 0.9677 (Y sediment), while for Ca^{2+} and Fe^{3+}/Fe^{2+} were 0.4164 (T sediment) and 0.5377 (Y sediment), respectively. The similar result was reported in the study of Span and Gaillard (1986), in determining the carbonate-bound trace elements in marine sediments, and they found that only Cd and Mn correlated well with Ca. According to Shan and Chen (1993), Mn^{2+} extracted with this reagent could come from the dissolution of Mg/Ca carbonates, as Mn^{2+} can substitute for Mg^{2+} as well as Ca^{2+} in carbonate minerals. It has also been reported that carbonate-bound Mn showed the same solubility as Ca at the same pH (Han and Banin 1996). The solubility products of pure $CaCO_3$ and $MnCO_3$ are $10^{-8.35}$ (Danen-Louwerse et al. 1995) and $10^{-9.47}$ (McBeath et al. 1998), which represents an approximately equal solubility of $CaCO_3$ and $MnCO_3$.

The effect of pH on carbonate-bound Ca, Fe and Mn fraction extraction. It was clearly dependent on pH with the greatest Ca extraction occurring at pH 4.0 and decreased with increases in solution pH for T sediments. While in the case of Y sediment (with high Ca content), Ca^{2+} extraction

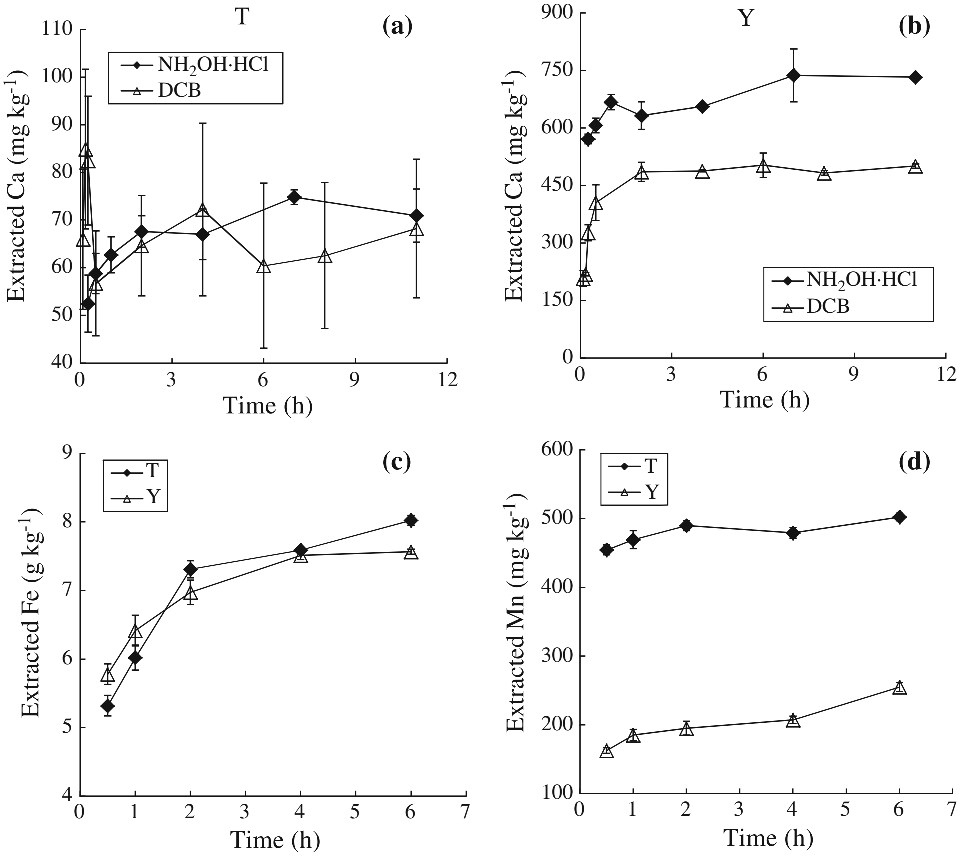

Fig. 7 Effect of shaking time with $NH_2OH·HCl$ (0.4 mol L^{-1}, 50 °C) or DCB (85 °C) on the extraction of Ca by *T* sediment (**a**) and *Y* sediment (**b**), with $NH_2OH·HCl$ (0.4 mol L^{-1}, 50 °C) on the extraction of Fe (**c**) and Mn (**d**) by two sediments previously extracted with NH_4AC (1 mol L^{-1}, pH 7.0) and NH_4AC (1 mol L^{-1}, pH 5.0)

increased with the increasing solution pH and reached a maximum at a pH of 4.5. As shown in Fig. 4 ($CaCO_3$), $CaCO_3$ was dissolved completely at pH 5.0. The lowest setting for pH is not recommended because large amount of Fe^{3+}/Fe^{2+} (6.2 g kg^{-1} for T sediment and 4.2 g kg^{-1} for Y sediment) and Mn^{2+} (235 mg kg^{-1} for T sediment and 310 mg kg^{-1} for Y sediment) was detected at pH 4.0, but not at pH 5.0, that much less amount of Fe^{3+}/Fe^{2+} (0.9 g kg^{-1} for T sediment and 0.5 g kg^{-1} for Y sediment) and Mn^{2+} (125 mg kg^{-1} for T sediment and 190 mg kg^{-1} for Y sediment) was extracted. For these reasons, the recommend setting for carbonate-bound fraction based on the tests would be 1 mol L^{-1} NH_4AC (pH 5.0) for 5 h.

Selection of extracting conditions for Fe/Mn oxides bound Ca extraction

This fraction of metals represents the contents of metal bound to iron and manganese oxides that would be released if the substrate is subjected to more reductive conditions. The citrate–bicarbonate–dithionite (CBD) method has been employed for decades due to its high selectivity in dissolving free Fe oxides (Kim and McBride 2006). Acidified hydroxylamine hydrochloride ($NH_2OH·HCl$) and ammonium oxalate [$(NH_4)_2C_2O_4$] (Agbenin and Olojo 2004; Li et al. 2006) were also commonly used to remove Fe and Mn oxides. Taking into account the CaC_2O_4 formation, $(NH_4)_2C_2O_4$ was not in consideration for Ca extraction. Kim et al. (2003) used high temperature (50 °C) for dissolving the amorphous oxide, based on this finding, 50 °C was chosen as the setting for temperature in our study.

A kinetic study was made in $NH_2OH·HCl$ and DCB (Fig. 7). The samples were shaken for different time, from several min to 11 h. In the T sediment extracted with DCB, the experimental precision was unsatisfactory, with relative standard deviations up 15 % (Fig. 7a). Even a satisfied precision was found for Y sediment (Fig. 7b), DCB extracted less Ca^{2+} than $NH_2OH·HCl$. Thus, $NH_2OH·HCl$ was selected to leach Fe/Mn oxide-bound Ca fraction. From 7 h of shaking onward, slight change in the amount of Ca^{2+} released was observed in T sediment extracted with $NH_2OH·HCl$. For Y sediment, the optimum time was 7 h. The amounts of Mn^{2+} and Fe^{3+}/Fe^{2+} dissolved in the extraction with $NH_2OH·HCl$ were simultaneously measured, which could indicate the attack of Fe/Mn oxides. The amount of Fe^{3+}/Fe^{2+} extracted from T and Y sediment

Table 1 Comparison extracting conditions, such as extractant, sediment to solution ratio (*m*:*v*) and extracting time in sequential extraction by the Tessier procedure (Tessier) and the modified Tessier procedure (M-Tessier)

Step	Fraction	Extractant		Sediment to solution		Extracting time	
		Tessier	M-Tessier	Tessier	M-Tessier	Tessier (h)	M-Tessier (h)
1	Exchangeable	1 mol L^{-1} $MgCl_2$ pH 7.0	1 mol L^{-1} NH_4AC pH 7.0	1:8	1:25	1	3
2	Carbonate bound	1 mol L^{-1} NaAC pH 5.0	1 mol L^{-1} NH_4AC pH 5.0	1:8	1:25	5	5
3	Fe/Mn oxides bound	0.04 mol L^{-1} $NH_2OH{\cdot}HCl$ in 25 % HAC, 85 °C	0.5 mol L^{-1} $NH_2OH{\cdot}HCl$ pH 1.5 50 °C	1:8	1:30	6	6

increased with time and became slightly after 2 and 4 h (Fig. 7), respectively. After 30 min of leaching, only a small increase of dissolved Mn^{2+} was observed in both T and Y sediments. This was in accordance with the study of Suda et al. (2011). They investigated the extraction of Mn and Fe oxides from non-volcanic-ash soil and found Mn oxides could be semi-completely upon extraction for 30 min, while Fe oxides gradually dissolved throughout 4 h of extraction. Figure 7 indicated that for both sediments, extraction of reducible Fe/Mn was essentially complete after 6 h. This protocol was considered sufficient for Fe and Mn extraction in this fraction. Tessier et al. (1979) also demonstrated on sediments that the total dissolve of the iron-reducible fraction was achieved within 6 h.

The amount of Ca^{2+} extracted differed with the change of sediment to solution ratio from 48 mg kg^{-1} (1:15) to 75 mg kg^{-1} (1:30) for T sediment. Increasing sediment to solution ratio increased the extraction amount of Ca^{2+} for both sediments and got a maximum with 1:30 sediment to solution ratio. Rao et al. (2008) described that $NH_2OH{\cdot}HCl$ of 0.1 mol L^{-1} release metals mainly from amorphous manganese oxide phase with little attack on iron oxide phases. It was found that an increase in the concentration of $NH_2OH{\cdot}HCl$ without reducing the pH of the reagent might not significantly enhance the recovery of metals (Nemati et al. 2009b). However, in this study, by increasing the concentration of $NH_2OH{\cdot}HCl$ from 0.5 to 0.8 mol L^{-1} at pH 1.5, the amount metals released from T sediment were increased from 104 to 116 mg kg^{-1} for Ca^{2+}, 1,878 to 1,904 mg kg^{-1} for Fe^{3+}/Fe^{2+} and decreased from 912 to 890 mg kg^{-1} for Mn^{2+}. When lowering the pH of $NH_2OH{\cdot}HCl$ solution from 1.5 to 1.0 with concentration of 0.5 mol L^{-1}, the amount metals released from T sediment were increased from 104 to 122 mg kg^{-1} for Ca^{2+}, 1,878 to 1,940 mg kg^{-1} for Fe and 912 to 937 mg kg^{-1} for Mn. Increasing in the concentration of $NH_2OH{\cdot}HCl$ enhanced the amount of Ca^{2+}, Fe^{3+}/Fe^{2+}, Mn^{2+} more significantly than lowering the pH of $NH_2OH{\cdot}HCl$. In the case of Y sediment, increasing the concentration of $NH_2OH{\cdot}HCl$ caused a decrease in the metals extraction and an increase was found when lowering the pH. Taking into account both of sediments, we selected concentration of 0.5 mol L^{-1} and pH at 1.5, with which little organic matter could be attack and considerably large amount of Ca, Fe and Mn could be extracted. Rao et al. (2008) and Nemati et al. (2011) also conclude that increasing the concentration of $NH_2OH{\cdot}HCl$ from 0.1 to 0.5 mol L^{-1} and decreasing the pH from 2 to 1.5 provided effective attack on the iron oxide phases.

Comparison of the modified Tessier procedure with Tessier procedure

The optimized extractant, sediment to solution ratio and extracting time for each extraction in the first three steps of Tessier procedure were shown in Table 1. In the Tessier procedure, exchangeable metal was extracted with 1 mol L^{-1} $MgCl_2$ (pH 7.0), while we recommend extracting with 1 mol L^{-1} NH_4AC (pH 7.0), and more extractant volume and longer extracting time, with sediment to solution ratio of 1:25 and extracting time of 3 h, were suggested. In the modified Tessier procedure, 1 mol L^{-1} NH_4AC (pH 5.0) replaced 1 mol L^{-1} NaAC (pH 5.0) and sediment to solution ratio was from 1:8 to 1:25 with the same extracting time of 5 h for the extraction of carbonate-bound Ca. As for Fe/Mn oxide-bound Ca, the same extractant $NH_2OH{\cdot}HCl$ was adopted, but with

Table 2 Calcium recovery of different lake sediments and the change of pH (ΔpH) in extraction solution after extraction by the Tessier procedure (Tessier) and the modified Tessier procedure (M-Tessier)

Method	T-Sed		D-Sed		Y-Sed		N-Sed	
	Tessier	M-Tessier	Tessier	M-Tessier	Tessier	M-Tessier	Tessier	M-Tessier
Recovery[a] (%)	47.43 ± 10.91	65.13 ± 18.39	63.17 ± 1.10	82.97 ± 5.03	69.47 ± 2.25	69.13 ± 3.47	55.70 ± 11.45	70.37 ± 11.82
ΔpH								
Step 1	−1.03	−0.11	−0.12	0.00	0.09	0.11	−0.10	0.03
Step 2	0.00	0.01	0.04	0.01	0.10	−0.02	0.03	0.00
Step 3	0.17	0.39	0.27	0.63	0.26	0.70	0.19	0.54

[a] The mean value of the recovery of three sediment samples in the same lake, e.g., the recovery of T-Sed was calculated by the mean value of the recovery of T1, T2 and T3

different concentration and pH. The selected setting in the modified Tessier procedure was 0.5 mol L^{-1} with pH 1.5, while in the Tessier procedure was 0.04 mol L^{-1} with pH about 2.0, and sediment to solution of 1: 30 was selected in the modified Tessier procedure.

The sediment samples were subjected to the two different sequential extraction schemes. The Ca recovery of lake sediment was expressed with the mean recovery of three sediment samples in the same lake. For example, the Ca recovery of Tangxunhu Lake sediment (T-Sed) was calculated by the average recovery of T1, T2 and T3, and the same as Donghu Lake sediment (D-Sed), Yuehu Lake sediment (Y-Sed) and Nanhu Lake sediment (N-Sed). An internal check was performed on the results of the sequential extraction by comparing the total amount of Ca recovered in the procedure with the results of the pseudo-total digestion. For all the sediment samples, the recoveries (Table 2) were in the range of 47.43–69.47 % for the Tessier procedure and a higher recovery 65.13–82.97 % for the modified Tessier procedure. Cappuyns et al. (2007) also observed the recovery was too low for Ca by optimized BCR procedure (Rauret et al. 1999). They inferred a poor recovery could be explained by the washing with water between two extraction steps. Another reason for inferior extraction variability and recovery could relate to heterogeneity of samples (Herreweghe et al. 2003).

The pH of the extracts was measured after each extraction step to compare the change of pH by Tessier and modified Tessier procedure (Table 2). In both of the procedures, the original pH of the reagent in exchangeable fraction was 7.0. For all the sediment samples, extracted with $MgCl_2$ by the Tessier procedure except for Y-Sed a decreasing of pH was noticed, going from 0.1 pH unit for D-Sed and N-Sed to 1.0 pH unit for T-Sed. In comparison, the modified procedure extracted with NH_4AC had a slight change of pH after step 1. All the samples had little pH change and had pH almost at 7.0. An increase of 0.1 pH unit by Tessier and modified Tessier method was observed for Y-Sed. In carbonate-bound fraction, the pH of final extracts is next to the pH of the extractants (pH 5.0) added for both the Tessier procedure extracted with NaAC and the modified Tessier procedure extracted with NH_4AC. Both of these reagents had buffering capacity. In Tessier procedure, the pH of the reagent in Fe/Mn oxide-bound fraction was next to 2.0, and in modified Tessier procedure, the pH of the reagent was 1.5. A significant increase was shown in the two procedures. The modified Tessier procedure had a change of 0.39–0.70, while slight pH change of 0.17–0.27 was observed in Tessier procedure, and this means the modified procedure dissolved more Fe and Mn oxides and could extracted more Ca than Tessier procedure.

It has been reported that the pH of the extract was clearly related to the original pH of the sediment, since a higher sediment pH resulted in a higher pH of the reagent (Cappuyns et al. 2007). In the study of Suda et al. (2011), the change of pH during extraction influenced the solubility of Fe oxides. Outola et al. (2009) had made effort to control the pH change by readjusting, but they found better results were achieved by choosing settings that would avoid a significant increase in the final pH during the extraction process. Ross (2009) also noted that buffered extractants often yield higher exchangeable metals than methods featuring unbuffered solutions. In our study, NH_4AC (pH 7.0) had a better buffering capacity than $MgCl_2$ (pH 7.0), but the buffering capacity of $NH_2OH{\cdot}HCl$ was decreased with pH decreased from 2.0 to 1.5.

The results obtained by Tessier method are different from those found with the modified Tessier scheme. Fig. 8 showed the fractionation of Ca in four lake sediments by

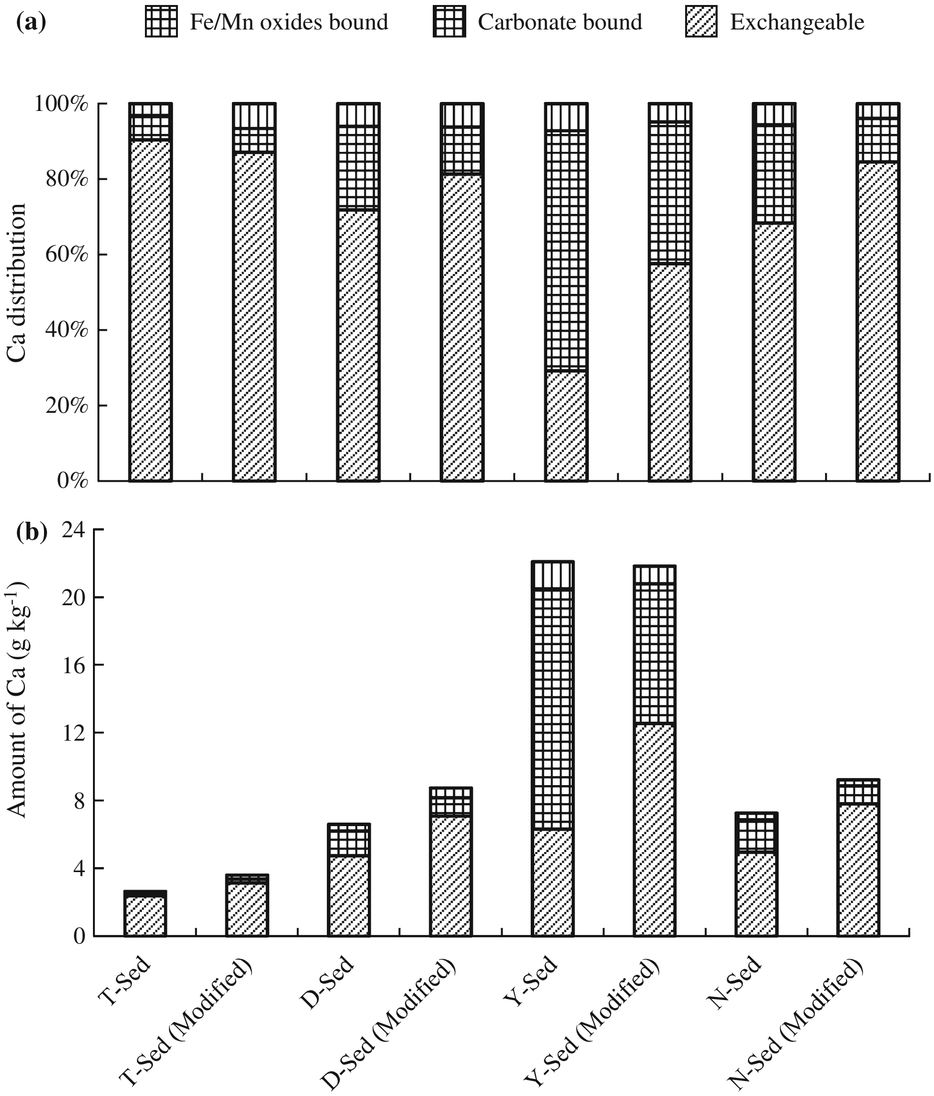

Fig. 8 Partition (**a**) and speciation (**b**) of calcium in different lake sediments extracted by the Tessier procedure and the modified Tessier procedure (modified)

Tessier and modified Tessier procedure. The Ca association with different fractions followed the order: exchangeable Ca (F1) > carbonate-bound Ca (F2) > Fe/Mn oxide-bound Ca (F3) (Fig. 8a) in all the sediment samples except for Y-Sed. The highest percentage of Ca in sediments was associated with the exchangeable fraction (F1) in both Tessier (29.0–89.7 %) and modified Tessier (56.6–86.8 %) procedures, which was supposed to be water soluble and exchangeable. Ca showed a marked presence in carbonate-bound fraction in Tessier (6.5–63.2 %) and modified Tessier (6.3–36.9 %) procedure. This was consistent with the findings of Gomes et al. (2012) in sludge.

The amount of Ca extracted by Tessier method in the exchangeable fraction is clearly lower than that found with Modified Tissre procedure (Fig. 8b). Differences ranged from 0.7 to 6.2 mg kg^{-1}. However, the original Tessier scheme recovered equal or significantly more carbonate-bound Ca from all sediments. Differences ranged from 0.1 to 5.9 mg kg^{-1}. This trend was opposite to that noted in the exchangeable fraction. This might be due to the incomplete dissolve of exchangeable Ca in Tessier method. Since after three steps, the total extracted Ca^{2+} (F1 + F2 + F3) in Tessier method was still less than Ca^{2+} extracted in the F1 fraction of the Modified method for all sediments except for Y-Sed. Therefore, the modified Tessier method extracted with 1 mol L^{-1} NH_4AC (pH 7.0) with a sediment to solution ratio of 1:25 is more complete than the $MgCl_2$ extraction of Tessier approach with a solid/solution ratio of 1:8. When the modified method was used, nearly 10 %

more Ca was recovered in the exchangeable fraction than that extracted with Tessier method.

Compared to the modified procedure, the first two fractions (F1 + F2) of the Tessier approach recovered lower concentration of Ca from all sediments except for Y-Sed. In the cases of Y-Sed, negligible difference was observed between the first two fractions (F1 + F2) for the two approaches. After two steps, the difference of extracted Ca^{2+} between two methods was reduced from 6.2 to 0.3 g kg^{-1} for Y-Sed. Stone and Droppo (1996) have reported that carbonate can be an important adsorbent for many metals when organic matter and Fe–Mn oxides are less abundant in the aquatic system. Leaching of Ca is strongly dependent on pH. Ca could be precipitated at alkaline pH. The observed pH (7.11) for Y-Sed in step 1 (Table 2) in our study could explain the considerable adsorption of Ca in the sediments. It was recognized that there might be significant adsorption of Ca^{2+} with $pH > 7.0$. When extracted with NH_4AC (pH 5.0) in carbonate-bound fraction, the adsorbed metals would be released (Gomez-Ariza et al. 2000).

Conclusion

Based on our selective test and comparison test, the modified Tessier procedure achieved more complete release of Ca from the samples without decreasing the selectivity of dissolution, i.e., without dissolving significant amounts of Fe oxides in exchangeable and carbonate-bound calcium fractions. The modified conditions for Ca extraction of the exchangeable fraction were: 1.0 mol L^{-1} NH_4AC pH 7.0, 25 °C, 3 h; for carbonate-bound fraction: 1.0 mol L^{-1} NH_4AC (pH 5.0 adjusted with HAC), 25 °C, 5 h; and for Fe/Mn oxide-bound fraction: 0.5 mol L^{-1} $NH_2OH{\cdot}HCl$, (pH 1.5 adjusted with HNO_3), 50 °C, 6 h.

All recoveries for sediments by the modified Tessier method were in the range 65.13–82.97 %. Washing between two extraction steps might cause the poor recoveries since part of calcium would be discarded with water. The modified Tessier procedure corresponding to sediment samples confirmed that Ca were mainly exchangeable and associated with carbonate; consequently, a high mobility was expected for Ca. The procedure to extract organic bound calcium and residual calcium was recommended to remove since scarce Ca was released in these two fractions and with lowest bioavailable.

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