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Sequential extraction and analysis of phosphorus in marine sediments: Streamlining of the SEDEX procedure

Abstract—We streamlined the five-step SEDEX (sedimentary extraction) procedure for characterizing sedimentary phosphorus to a four-step procedure. We combined extraction of adsorbed and oxide-associated pools into a single step, retaining steps for authigenic, detrital, and organic P. In addition, we used automated spectrophotometric flow injection analysis (FIA) to determine P concentrations, rather than traditional spectrophotometric techniques. We decreased our total extraction and analytical time from 12 d for 24 replicate samples to 5 d without sacrificing our geochemical objectives, detection limits, or analytical reproducibility.

The oceanic history of reactive phosphorus (P) (dissolved P available to promote oceanic primary productivity) is of interest because of the role of P as a biolimiting nutrient. Thus, knowledge of reactive P burial in marine sediments is a key to testing hypotheses about temporal changes in P input or output fluxes. In addition, geochemical understanding of P transformations provides critical insights into the diagenetic behavior of P that controls its retention in sediments. Thus, we are interested in distinguishing the reactive from the nonreactive P components in sedimentary burial and, within the reactive fraction, the authigenic from the organic and oxide-sorbed P fractions.

The SEDEX (sedimentary extraction) procedure operationally defines five P components (adsorbed, oxide-associated, authigenic, detrital, and organic), and was extensively tested for use in marine sediments with analogs for naturally occurring phosphatic phases (Ruttenberg 1992). The procedure allowed critical insights into the transition of organic, adsorbed, and oxide-associated P to authigenic P (Sink-swapping, Ruttenberg and Berner 1993). SEDEX has now been applied to a variety of oceanic sediments, adding evidence for P sink-swapping in deep ocean sediments and allowing the quantification of reac-

tive P burial (e.g., Filippelli and Delaney 1996; Delaney and Anderson 1997).

In this paper, we propose the removal of the operationally defined adsorbed step from the SEDEX procedure (renamed, four-step procedure). It is important to note that analogue phases are not available for the adsorbed and oxide-associated steps as sorptive surfaces are not pure phases (Ruttenberg 1992; Coston et al. 1995). We deleted the adsorption step on the assumption that most sorbed (combination of adsorbed and coprecipitated) phosphate associates with aluminum, iron, and mixed oxides (e.g., Turner et al. 1981; Coston et al. 1995; Slomp et al. 1996). Although there will be some adsorptive sites available on clays, the alkaline character and high ionic strength of seawater and interstitial waters means that few positive sorptive sites are likely to be available (e.g., Sposito 1984). Thermodynamic gains are typically much greater in the sorption of phosphate on oxides than they are on clays, and thus, as long as oxide surfaces are available, P will sorb to them (e.g., Sposito 1984). Furthermore, with the advent of techniques that allow observations on the binding characteristics of elements on surfaces, investigators have been able to observe how oxyanions such as P bind to metal surfaces. In work on the chemically analogous oxyanion arsenate, investigators have found that arsenate is not incorporated into the crystalline structure of oxide precipitates, but rather is adsorbed on the internal surfaces of the less organized oxide precipitates. As the oxides become more crystalline, arsenate is bumped out of the crystal structure (Fuller et al. 1993; Waychunas et al. 1993). Similar trends have been noted with phosphate (Fuller pers. comm.). Thus, the distinction between adsorbed and oxide-associated P in the SEDEX procedure may be in and of itself rather arbitrary, as most of the phosphate may be adsorbed on oxides. Thus, the four-step procedure may better define an operational sorbed fraction.

Table 1. Site characteristics.

Site	Latitude (° ')	Longitude (° ')	Water depth (m)	Deepest sample depth (mbsf)	Sediment characteristics					Interstitial water characteristics		
					Organic carbon (wt%)	Calcium carbonate (wt%)	Biogenic silica (wt%)	Detrital (wt%)	Phosphate		Sulfate	
									Maximum [PO ₄] (μM)	Depth to max. (m)	Depth [SO ₄] = 0 (m)	
1011	31 16.8 N	117 38 W	2043	135	0.6–2.6	1–15	1–2	80–90	50	25	45	
1012	32 16.9 N	118 23 W	1773	28	1.6–6.5	7–31	2–3	62–81	120	25	20	
1014	32 50.0 N	119 59 W	1164	80	3.1–7.0	17–57	0.7–1.5	25–69	200	150	10	

The goals of our study were to reduce time needed for the extraction procedure while retaining useful geochemical information and to improve analytical precision while increasing sample throughput. We investigated the geochemical consequences of removing the initial ion-exchange step, reducing the number of steps from five to four. We streamlined the authigenic-P step. We developed and applied flow injection analysis (FIA) techniques for the chemical determination of P in the procedure extracts. Flow injection methodologies are based on the integration of a timed portion of a spectrum generated by the kinetic reaction of analyte and reagents as the mixture flows past the detector. They differ from standard spectrophotometric techniques, which require

the analyst to wait for completion of color-producing reactions prior to sample analysis, and sample introduction is not generally automated as it is for FIA.

Samples and methods—Two composite solid standards of different sedimentary composition were routinely run by both the four-step and SEDEX procedures to allow comparison of techniques and evaluation of long-term analytical variability: a high-carbonate (89%), low-detrital (10%), and low organic (0.2%) composite (HCLDO), and a moderate-carbonate (11%), high-detrital (82%), and moderate-organic (1.65%) composite (MCDO). HCLDO is a composite sample of sediments from the Ceara Rise in the Western Equatorial Atlantic (Ocean Drill-

Table 2. Summary and comparison of SEDEX five-step procedure and four-step extraction procedure.

SEDEX five-step procedure (Ruttenberg 1992)		Four-step procedure (this study)		
Step Name (step number)	Chemical treatment	New step name (new step number)	Changes in chemical treatment	Comments
Adsorbed (step 1)	1 M MgCl ₂ (pH = 8), 10 ml, 2 hr mass action competition by chloride		Eliminated initial ion exchange steps	“Adsorbed” extracted with “oxide-associated.”
Oxide-associated (step 2)	0.22 M sodium citrate, 0.14 M sodium dithionite, 1.0 M sodium bicarbonate (pH = 7.6), 10 ml, 6 hr 1 M MgCl ₂ (pH = 8), 10 ml, 2 hr Distilled water, 10 ml, 2 hr	Oxide-associated or “adsorbed + oxide associated” (step 1)	Decreased concentration of sodium dithionite to 0.033 M	Estimated maximum concentration needed to reduce all Fe oxides if total sample was Fe oxides. Lower dithionite concentration resulted in decreased analytical background.
Authigenic (step 3)	1 M sodium acetate buffered (pH = 4), 10 ml, 2 hr 1 M MgCl ₂ (pH = 8), 10 ml, 2 hr 1 M MgCl ₂ (pH = 8), 10 ml, 2 hr Distilled water, 10 ml, 2 hr	Authigenic (step 2)	Decreased times for second ion exchange step and distilled water rinses to 1 hr each	Decreased times allow completion of step 2, start of step 3 on same day, decreasing working days required.
Detrital (step 4)	1 N HCl, 13 ml, 16 hr acid dissolution	Detrital (step 3)		
Organic (step 5)	50% (wv ⁻¹) MgNO ₃ , 1 ml—dry in oven at 80°C, ash at 550°C 1 N HCl, 13 ml, 24 hr acid dissolution	Organic (step 4)		

Table 3. Sample dilutions and automated spectrophotometric flow injection analysis instrument parameters for the four-step procedure (this study).

Step name	Dilution volumes (sample : water)	Pump speed	Sample loop (cm × mm)	Temper- ature (°C)	Heater coil (cm × mm)	Baseline timing		Integration timing	
						Start (s)	End (s)	Start (s)	End (s)
Oxide-associated	1 : 6	35	150 × 45	37	650 × 0.8	19	110	51	53
Authigenic	0.5 : 6 or 0.25 : 6	35	150 × 45	37	175 × 0.8	2	65	26	29
Detrital	1 : 6 or 0.5 : 6	35	150 × 45	37	175 × 0.8	2	65	26	29
Organic	1 : 6	35	150 × 45	37	175 × 0.8	2	65	26	29

ling Program [ODP], leg 154 sites) and is typical of many high-carbonate, open ocean sediments. MCDO is a composite of sediments from California Margin sites in the Eastern Pacific (ODP leg 167 sites) and is typical of sediments from margin settings with higher detrital and organic carbon contents. We routinely ran these two composite standards, with differing amounts and proportions of calcium carbonate, organic carbon, and detrital components. The composite standards are not meant to be model phases but are excellent for monitoring reproducibility for typical samples. We also did a cross comparison of California Margin sediment samples from several leg 167 sites (Table 1). These samples were chosen because we wanted a range in concentration for each of the P components. We focused on samples from shallower sediment depths where the most significant diagenetic P transformations are likely. These sediments have variable detrital components and calcium carbonate, are generally organic carbon rich (up to 7 weight % organic carbon), and have sulfate-reducing interstitial waters with elevated dissolved phosphate concentrations at depth (Table 1). We did not explicitly measure estuarine and near-shore sediments, and thus caution must be maintained in applying this methodology to these sediments. However, the

range of detrital, carbonate, and organic carbon contents encompasses ranges typical of these sediments.

The SEDEX procedure follows Ruttenberg (1992) as modified for smaller total volumes by our laboratory (Filippelli and Delaney 1995; Delaney and Anderson 1997). The four-step procedure starts with the reductive, metal-complexation step (Table 2). We also ran total hydrofluoric-nitric acid sediment digests on all of the samples and the composite standards to evaluate incomplete extraction or losses due to sample handling (Murray and Leinen 1996). For all procedures, splits of samples were freeze-dried and lightly ground. Weighed samples (0.1 gram each) were run in replicate.

We made three basic changes to the SEDEX procedure. (1) We combined the adsorbed and oxide-associated steps. (2) In the oxide-associated step, we reduced the concentration of sodium thiosulfite added from 0.14 M to 0.033 M. The concentration we used was based on a conservative estimate of how much reductant would be necessary to reduce a sample that was all iron oxide. We confirmed this by comparing the oxide step run at both dithionite concentrations. Extracted P concentrations were identical within analytical error (intercept = 0.006, slope = 1.05 ± 0.07 , $r^2 = 0.94$, $N = 24$). (3) For the authigenic-P extraction, we decreased the length of the second $MgCl_2$ and of the glass-distilled water rinses to 1 h each (Table 2). This allowed us to extract the authigenic fraction and begin the time-intensive detrital fraction extraction in the same day. The rationale behind the $MgCl_2$ rinses is to remove by mass action of a competing anion any superficially re-adsorbed P. In streamlining this step, we wanted to maximize the concentration gradient and give sufficient time for the reaction to occur, but decrease the total time of this step by several hours. Thus we kept two $MgCl_2$ rinses but decreased the second rinse time to 1 h. Kinetic constraints on desorption of P internal to particles should not be a major issue because the rinses are supposed to remove any P that has been re-adsorbed after the dissolution of authigenic P. Comparisons of the composite standards run both ways were the same within analytical error.

P concentrations were analyzed by standard spectrophotometric techniques in the SEDEX procedure. Color-developing reagents (ammonium molybdate tetrahydrate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$, 4.8 mM; potassium antimonyl tartrate hemihydrate $[K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O]$, 8.1 mM; and sodium citrate, 64 mM) were mixed with the samples. Color was allowed to develop for 30 min, and then absorbances were measured with a 1-cm (adsorbed, oxide-associated, and au-

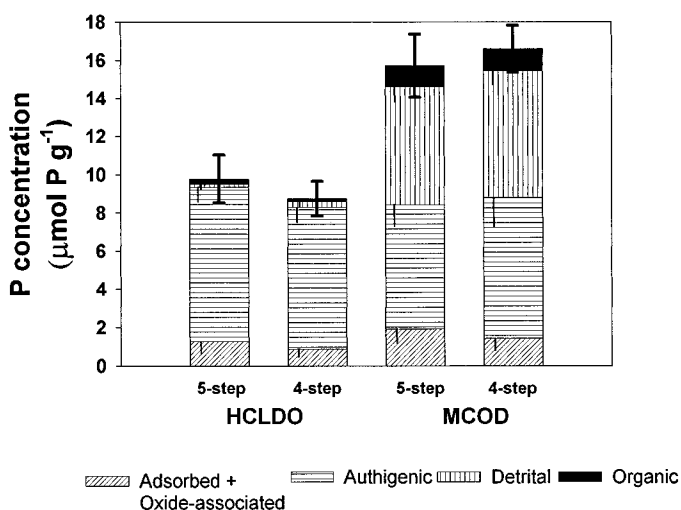


Fig. 1. Comparison of the principal P components and total P concentrations determined using the SEDEX and four-step procedures for the composite standards HCLDO (SEDEX $n = 15$; four-step $n = 15$) and MCDO (SEDEX $n = 4$; four-step $n = 5$). Large error bars and vertical lines represent ± 1 s on mean total values and each component. Analyses by FIA except for the adsorbed step.

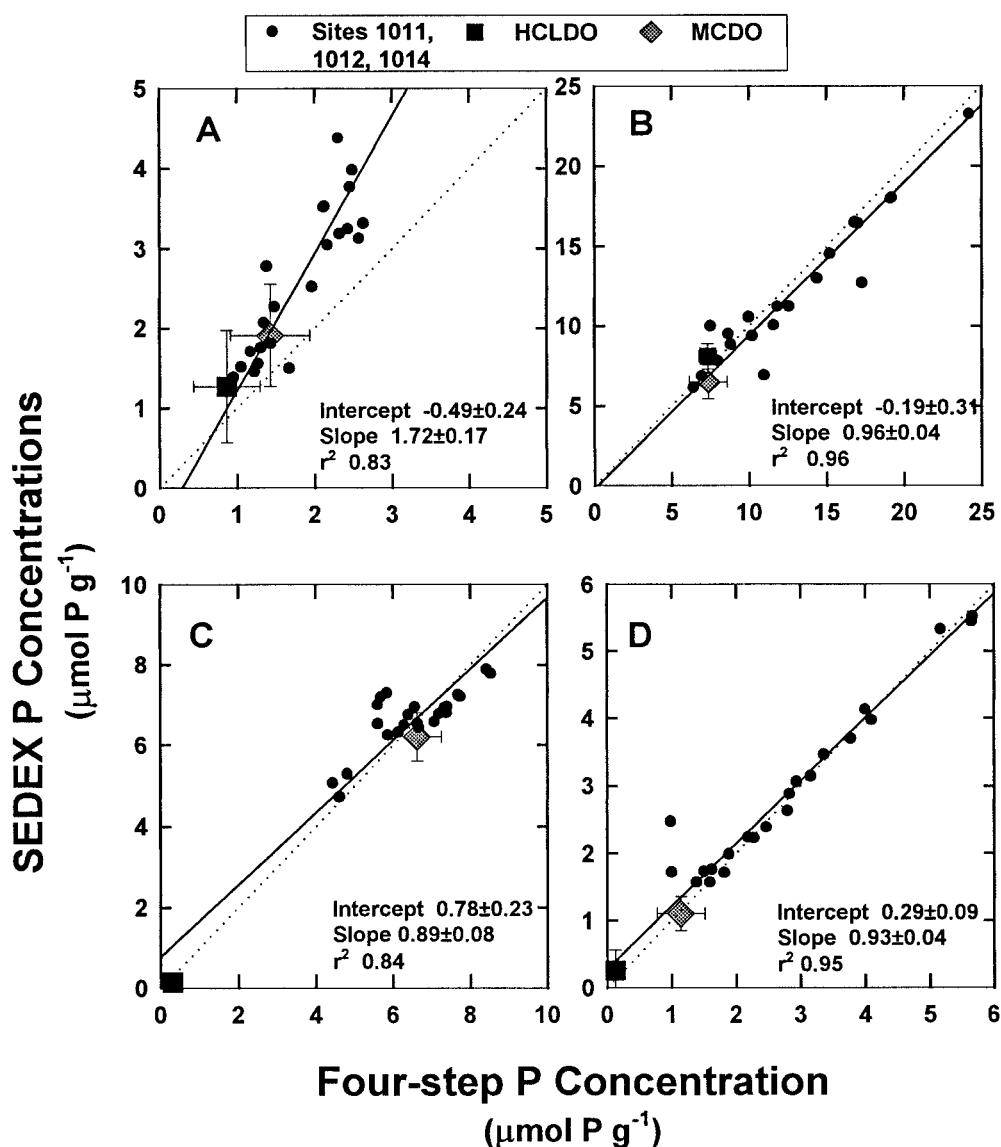


Fig. 2. Comparison of SEDEX and four-step procedure results for the different P components. Dotted line shows 1:1 relationship for reference. Linear regressions (model II type, major axis analysis) and statistics were run on 25 samples; t -test must be 1.72 for slope to be significantly different from one. (A) Adsorbed plus oxide-associated versus oxide-associated P (t -test = 4.56). (B) Authigenic P (t -test = 0.90). (C) Detrital P (t -test = 1.41). (D) Organic P (t -test = 1.66). Analyses by FIA except for the adsorbed step.

thigenic) or 10-cm cell (detrital and organic) with a spectrophotometer (Shimadzu, UV2101PC) at 880 nm. This required a liquid-liquid extraction procedure for the oxide-associated step to remove interference from citrate and hydrosulfite, which form a colored compound that absorbs at 880 nm (Ruttenberg 1992). This extraction step added handling time and decreased analytical reproducibility.

In this study, P concentrations were also determined using an automated spectrophotometric flow injection analysis (FIA) system (Lachat, Quikchem 8000) except for the adsorbed step (SEDEX step 1), which was run by standard spectrophotometric techniques. The high ionic strength and low concentrations typical of the adsorbed step make it analytically difficult to run by FIA. High ionic strength creates a refractive index response that significantly raises the de-

tection limits by this method. Dilution of the samples to deal with the refractive index problem makes the concentrations too low to measure. For P analyses by FIA, the samples and standards were mixed in line with a molybdate coloring agent composed of 6.8 mM ammonium molybdate tetrahydrate and 0.34 mM potassium antimonyl tartrate hemihydrate, with a reducing agent composed of 340 mM ascorbic acid. All fits for standard curves were first order. Dilutions for each step's extractants (Table 3) were chosen to maintain solution concentrations within the linear working range of the instrument (10 μ M). For each extraction step, a set of standards was matrix-matched for the same reagents. Analyses were run by standard brackish techniques outlined by Lachat (Table 3; Lachat instruments, QuikChem method 31-115-01-3-A), which means that a selected portion of the

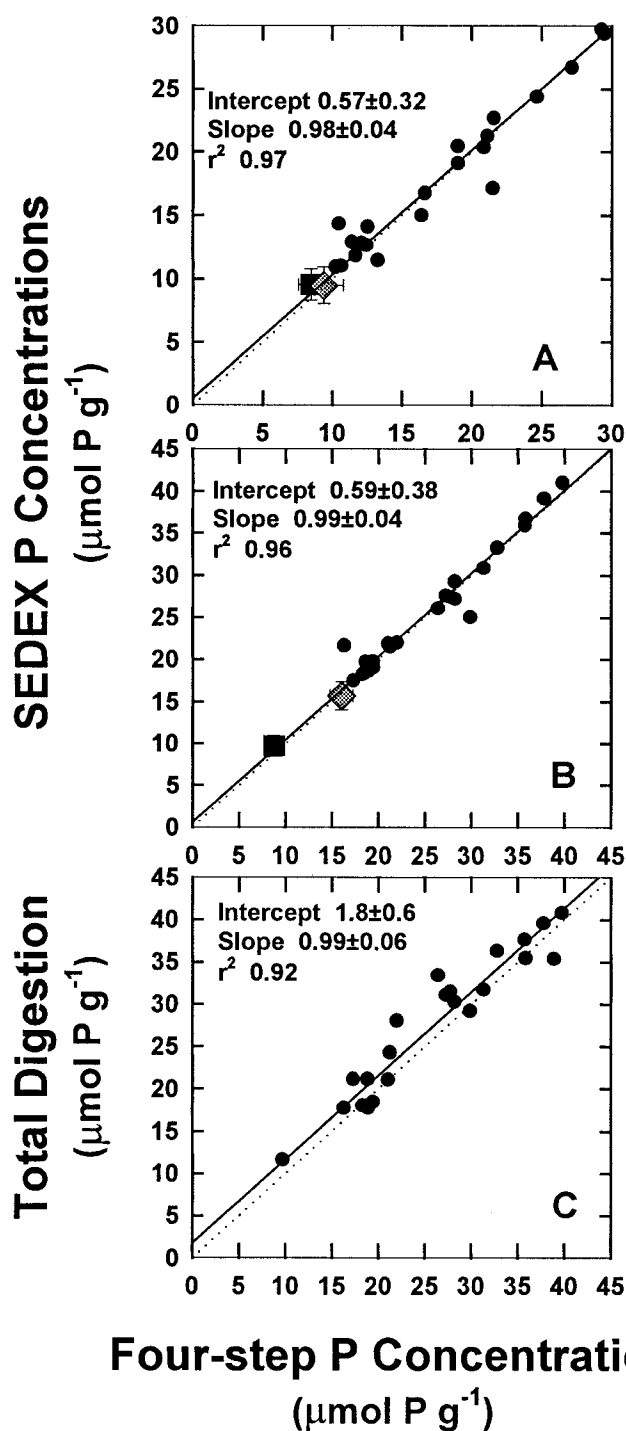


Fig. 3. Comparison of four-step procedure (A) with SEDEX for total reactive P, as sum of adsorbed plus oxide-associated, authigenic, and organic P components (t -test = 0.51) (B) with SEDEX for total P (t -test = 0.26). (C) with total digestion for total P (t -test = 0.15). Dotted lines show 1:1 relationship for reference. Linear regressions (model II type, major axis analysis) and statistics were run on 25 samples; t -test must be 1.72 for slope to be significantly different from one. Analyses by FIA except for the adsorbed step. See Fig. 2 for symbol definition.

curve is integrated (typical timing, Table 3), with spectrophotometric detection at 880 nm. Optimal results for the oxide-associated step resulted from an increase in the heating time by increasing the length of the heater coil. Note that spectra baseline and integration timings for the oxide-associated step are different (Table 3).

Results—P concentrations determined by the SEDEX and the four-step procedures are within error for the two composite standards analyzed over multiple sample runs, for both the P components and the total P (as defined by the sum of all the steps) concentrations (Fig. 1). The consistency of results from the two procedures is evaluated as well in the comparison for the California Margin sediment samples (Figs. 2, 3). Linear regression slopes of sedimentary P concentrations determined by the SEDEX method versus those by the four-step procedure were calculated using 23 California Margin samples and mean values for the two composite standards (total $n = 25$). A regression for the total digestions included California Margin samples and single measurements of the composite standards. Regressions were determined allowing errors in both the x and y variables using the standard axis method (Laws 1997). Slopes are compared to one using a standard t -test (Dowdy and Wearden 1985). The slopes for all steps except adsorbed plus oxide (SEDEX) versus oxide-associated (four-step) do not differ significantly from one (Figs. 2, 3). Furthermore, the P in combined four steps agrees within 6% of a total digestion with a slope indistinguishable from one (Fig. 3C).

We assessed the analytical figures of merit for FIA versus standard spectrophotometric techniques used in the SEDEX procedure using the HCLDO composite standard (Table 4). This composite, with low adsorbed, oxide-associated, detrital, and organic P concentration for these components, should give higher relative variability than samples with higher concentrations, and thus is a good test of reproducibility. Authigenic P and organic P components show no significant change in detection limits using the FIA rather than standard spectrophotometric analysis (Table 4). However, the oxide-associated component shows a fivefold decrease in the detection limit with the FIA strategy. We were able to decrease sample handling and analytical time from about 10 to 3 h by this change alone. There is an increase in the detection limit for the detrital P component, but sample concentrations are typically greater than three times the detection limit (equivalent to $0.3 \mu\text{mol P g}^{-1}$ sediment), so the loss in sensitivity is not significant for the samples in this study. FIA also decreased analyst time for the organic and detrital P steps by more than one-half. Because of low P concentrations in these two steps in many of our samples, along with the necessary 1:5 dilution to get sufficient color development, the analysis of these by standard spectrophotometric techniques required measurement using a 10-cm cell to get adequate sensitivity.

Relative standard deviations (RSD) of the HCLDO composite solid sample (run routinely as a sample, and thus including variability introduced by the sample and extraction procedure as well as the analysis) for FIA were comparable to those for spectrophotometric techniques (Table 4). These RSDs are high because the sample concentrations ap-

Table 4. Analytical figures of merit for automated spectrophotometric flow injection analysis (FIA) and traditional spectrophotometric analysis.

Analytical technique	P Component				
	Adsorbed P	Oxide-associated P	Authigenic P	Detrital P	Organic P
Detection limits ($\mu\text{M P}$ [$\mu\text{mol P g}^{-1}$ sediment])*					
FIA		0.68 [0.20]	0.63 [0.25]	0.70 [0.10]	0.25 [0.04]
Spectrophotometric		3.30 [1.00]	0.57 [0.23]	0.17 [0.02]	0.20 [0.03]
HCLDO (high carbonate, low detrital and organic) composite standard, replicate analyses ($\mu\text{mol P g}^{-1}$ sediment \pm RSD)†					
FIA‡	—	$0.87 \pm 45\%$	$7.3 \pm 10\%$	$0.30 \pm 62\%$	$0.20 \pm 53\%$
Spectrophotometric§	$0.53 \pm 43\%$	$1.03 \pm 80\%$	$8.3 \pm 8\%$	$0.13 \pm 44\%$	$0.18 \pm 50\%$

* Measured as three times the standard deviation of a reagent blank [calculated for 0.1 g sediment].

† Relative standard deviation in percent as $(1 \text{ standard deviation mean concentration}^{-1}) \times 100$.

‡ Mean of 14 separate extraction runs.

§ Mean of 10 separate extraction runs.

|| Concentrations for FIA technique from four-step procedure and for spectrophotometric, from SEDEX.

proached the detection limits (Table 4) for all but the authigenic fraction. Internal run variability dropped by one-half for the FIA technique relative to the spectrophotometric technique for oxide-associated (27% from 54%), detrital (13% from 34%), and organic P (19% from 33%) fractions and remained about the same for the authigenic fraction (5% vs. 8%).

Discussion—We expected the adsorbed plus oxide-associated in the SEDEX procedure to be equivalent to the four-step oxide-associated step. This was not the case (Fig. 2A). It could be argued that the four-step procedure does not extract phosphate from clays, which for some reason are not desorbed by competition from either citrate or the MgCl_2 in the oxide-associated step. However, as explained above, clays are unlikely to sorb much phosphate in the higher ionic strength, alkaline conditions typical of both seawater and interstitial waters. It is, however, logical that some organic P could be extracted while exposed (for 4 h) to the basic conditions of the MgCl_2 -ion-exchange step, resulting in an overestimation of the adsorbed component by the SEDEX procedure.

It is important to emphasize that the other steps and the reactive total and total P for both procedures are not statistically different. It is likely that small differences in the organic, detrital, or authigenic components account for the offset in the adsorbed plus oxide by the SEDEX procedure. However, the analytical variability in the adsorbed and oxide-associated SEDEX steps makes diagnosing the source difficult.

We assessed whether the increased extraction within the adsorbed and oxide-associated steps by the SEDEX procedure are correlated with decreases in the extraction within the other components by comparing the differences between the two procedures for all of the steps. If there was a simple relationship, then we expected to see the increased SEDEX extraction in the adsorbed plus oxide-associated balanced by a decrease in another step. For example, the relative slopes of the adsorbed-oxide associated steps (Fig. 2A) and the authigenic step (Fig. 2B) suggest that the increased extraction by the SEDEX in the first two steps may be accounted for by a decrease in the SEDEX authigenic step, suggesting dis-

solution of authigenic P in the first two SEDEX steps. We and others (Schenau pers. comm.) have observed dissolution of authigenic P during the reductive step. In our case, during methods testing of a lower concentration of bicarbonate buffer (0.1 M bicarbonate), dissolution occurred when the pH decreased due to inadequate buffering during the extraction. Furthermore, both the SEDEX and the four-step procedures use a dithionite reductive step, although our method has decreased the concentration added, which may make it less likely to exceed the buffering capacity. However, our comparison of the extractions at the two dithionite concentrations shows no pH change over the extraction interval at either dithionite concentration in 1 M bicarbonate solution.

When you look at individual samples, the increases in the SEDEX adsorbed plus oxide step are not accounted for by losses in the authigenic SEDEX step. None of the decreases in other SEDEX steps could account for the increased extraction in the first two SEDEX steps.

Several additional lines of evidence suggest that the adsorbed extraction step may complicate the operational definition of the total sorbed P fraction. Replicate sample RSDs (California Margin, leg 167) for the oxide-associated step decreased from 38% for the SEDEX procedure to 20% for the four-step procedure. All the P concentrations for the oxide-associated step were run by FIA, so the larger variability for the SEDEX extraction is not a function of the analytical technique. Additional variability within the adsorbed fraction (average 10% RSD) adds to the compounded error of the initial two steps of the SEDEX extraction. Also, the adsorbed step is difficult to ground truth as no good analogue components exist (Ruttenberg 1992). And finally, the combined steps (four step) compare to a total digestion to within error (an average of 94% of the total digestion with a range of 80 to 110%). Our extraction efficiencies for the four-step procedure are similar to those found by comparison of X-ray fluorescence totals to SEDEX totals (Filippelli and Delaney 1991).

Conclusions—Combining the adsorbed and oxide-associated steps into one extraction step is based on current understanding of phosphate adsorption on surfaces. The four-step procedure does not compromise our objectives of

characterizing the transformation of P from highly reactive oxide-associated and organic components to authigenic P or of quantifying total reactive P concentrations to calculate the mass accumulation rates of reactive P. The four-step procedure has significantly lower RSDs in a comparison of California Margin samples by both techniques in the oxide-associated and organic components (the other steps were not significantly different), indicating that this extraction procedure gives more reproducible results.

The change from standard spectrophotometric techniques with liquid-liquid extraction to FIA for the reductive, metal-complexation step (SEDEX, step 2; four-step, step 1) decreased the detection limit fivefold. Analysis by FIA for all steps decreased our analytical time from greater than 10 h to three unsupervised hours. (The time to dilute samples, run standard curves, and start the autosampler is about 1 h of the analyst's time.) We decreased our total extraction and analytical time from 12 to 5 d without sacrificing our geochemical objectives, detection limits, or analytical reproducibility.

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