NUTRIENT ASSESSMENT OF TOGCHA RIVER, ESTUARY & BAY: USE OF DOMINANT SEDIMENTARY PHOSPHORUS (P) FRACTIONS TO IDENTIFY ANTHROPOGENIC P CONTRIBUTIONS & POTENTIAL IMPACTS

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Authors relaxing after water sampling for nutrient analysis (inset) over a daytime tidal cycle in the Togcha River estuary

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ABSTRACT

The Togcha River is the smallest of several rivers found in southern Guam. It is ~6 km long with a catchment area of ~18 sq km and drains into sea at Togcha Bay on the eastern side of the island. The river receives stormwater runoff from a nearby housing estate and effluent from a sewage treatment plant (STP) in the same area. It is also receives surface and subsurface drainage from two golf courses. To gain insight into the nutrient status of the waterway, phosphorous levels were examined in surface sediments from 9 sites in the river above the estuary, 14 sites in the estuary itself, and 15 sites in the bay. Sediment collections were made in 1999: at the end of the dry season in May and towards the end of the wet season in October. A sequential extraction technique was employed to isolate the following five P fractions from the sediments: loosely sorbed P, ferric-iron bound P, authigenic apatitic P (including calcium carbonate associated P), detrital apatitic P, and organic P. All samples were also analyzed for total organic carbon and reactive iron.

Average total P concentrations in river sediments ranged from 518-1030 µg/g (dry weight) over the study period. Mean levels in the estuary and bay ranged from 621-705 µg/g and 245-269 µg/g respectively. Overall, organic P was the dominant P fraction identified in the river and estuary and accounted for ~30-40% of total P. Ferric-iron bound P and detrital apatitic P ranked next in order of abundance followed by loosely sorbed P and authigenic apatitic P. In bay sediments, ferric-iron bound P was the dominant fraction in all samples with average levels representing close to 50% of the total P pool. Loosely sorbed P ranked second in order of abundance and averaged ~25% of the pool, followed by organic P and then the apatitic P fractions. Significant temporal differences between overall means were identified for each P fraction in at least one of the three locations studied. Several P fractions were also significantly correlated with one another. These findings are addressed and explained where possible in the text.

The P status of the region was evaluated by reference to reported P levels in aquatic sediments from elsewhere on Guam and other parts of the world. Comparative assessments based on total P, total inorganic P and organic P were found to be of limited use because of the inability to differentiate between biologically available and non-biologically available forms of P. Since ferric-iron bound P and loosely sorbed P are potentially available to the biota they were considered to be of much greater value as an assessment tool. Collectively these fractions are referred to as non-apatitic P and together represent less than 30% of total P in clean coastal sediments and upwards of 75% of total P in sediments from grossly polluted waters. Based on these figures it was concluded that the Togcha River and estuary are mildly to moderately enriched with P, depending on the season, while the immediately adjacent portions of Togcha Bay are grossly enriched year round. The implications of the data are discussed with respect to upstream discharges from the STP, dominant estuarine processes that liberate sediment bound P into the water column, and the periodic algal blooms that occur in the bay.

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INTRODUCTION

Phosphorus (P) is a necessary element for all life and is one of the major nutrients that affect productivity in freshwater and marine ecosystems. It is also recognized as a common limiting nutrient in both environments (Correll 1998, Nixon 1981, LaPointe 1985, 1987, 1989). Under deep ocean conditions the P cycle can take thousands of years to complete (Ruttenberg 1990). However, the activities of man have greatly increased the availability of this element to the biota via human waste, fertilizer, industrial waste, and phosphate mining. Domestic wastewater discharges, in particular, are known to have greatly accelerated the cycling of P (Andrews et al. 1996, Stumm 1973, Mackenthun 1968, Owens and Wood 1968).

The overabundance of P from such anthropogenic sources can cause eutrophication in aquatic environments (Pierzynski et al. 1994). This can result in the over production of algae and other autotrophs, such as cyanobacteria. Their bloom and subsequent decay increases bacterial populations and places increased demands on dissolved oxygen levels that ultimately cause hypoxia, or even anoxia, of the water and underlying sediments (Ketchum 1983, Pierzynski et al. 1994). Such dramatic changes in dissolved oxygen invariably result in the loss of eukaryotic species diversity within the ecosystem and play a significant role in determining the chemical form and biological availability of P from biotic and abiotic sources (Correll 1998).

P is one of the key elements examined when evaluating the nutrient status of any aquatic environment. Traditionally, soluble levels of inorganic P (orthophosphate-P) are monitored because this is the primary form of P that can be assimilated by microorganisms, algae, and plants (Correll 1998). However, aqueous orthophosphate-P determinations alone generally do not provide a reliable indication of background levels of available P. This is largely because orthophosphate-P, or reactive P as it is commonly called, is rapidly removed from the water column by biotic and abiotic processes. According to Correll et al. (1975), turnover times of reactive P in eutrophic waters are in the order of minutes. These authors further noted that P levels fluctuate considerably on a diurnal basis depending upon prevailing environmental conditions. Thus, water analysis provides little more than a snapshot that may or may not reflect the overall abundance and availability of P over longer periods of time.

Sediments, on the other hand, do not suffer from this deficiency. On the contrary, the particulate P pool found in sediments is reasonably stable because of the slower turnover rates of the phosphate anion. Sediments also serve as a major repository for several P fractions and represent a more permanent source of this nutrient in forms that are variably available to the biota (Reddy et al. 1999). In addition, levels are always much higher than those found in the overlying water which greatly reduces analytical problems associated with sample contamination. More importantly, particulate P plays a key role in regulating levels of soluble reactive P in the water column. This process is driven largely by the solubility product constant and buffers the system against P removal by biota, or any input from extraneous sources (Froelich 1988). For these reasons, sediments (or suspended particulates) are frequently the preferred medium of choice for P monitoring purposes.

P exists in various chemical forms and can be transformed from one to another by a variety of different mechanisms. Knowing which forms predominate in sediments can provide information on the availability of P to the biota. Furthermore, knowing their distribution and abundance can provide information on the primary source or sources of this element (Huanxin et al. 1997). Such information also provides insight into the possible interactions of P at the

sediment water interface and gives a better understanding of the dominant transport and transformation processes influencing the biological availability of this important nutrient to resident biota.

One way of determining P species in sediments is through sequential chemical fractionation. The methodology involved in this technique is based on the fact that certain chemical reagents can be used to preferentially extract different chemical forms of P from the sediment of interest. In recent years, the P fractions most commonly identified by sequential fractionation procedures include loosely-sorbed P, ferric iron-bound P, calcium-bound P, and organic P (Graetz and Nair 1999). Since these particular fractions were the focus of the current work, their physical characteristics and biological importance are briefly discussed below.

Loosely-sorbed P is reactive P (RP) that is weakly adsorbed onto particulates, e.g., inorganic minerals, organic matter, and metal oxyhydroxides and oxides. From an analytical standpoint, it also includes the P fraction in sediment porewaters that adsorbs to the sediment solids during the analytical drying process. This operationally defined fraction therefore contains P that is immediately available to the biota (Ruttenberg 1992).

Ferric iron-bound P is occluded in oxides and hydroxides of iron and is important with respect to the recycling of P between sediments and the overlying water. In an oxidizing environment, iron-bound P is biologically unavailable because of the insoluble nature of the ferric iron (Fe^{3+}) complex in which it is trapped. However, under hypoxic conditions, ferric iron is reduced to soluble ferrous iron (Fe^{2+}). This transformation apparently occurs when dissolved oxygen levels fall below 2 mg/L (Brezonik 1972). During this process, any occluded P is released into the surrounding pore waters and is immediately available for uptake by the biota (Krom and Berner 1980, Calmano 1981, Carreira and Wagener 1998). Because of the close association of P with iron, "reactive iron" was also examined during the current study to determine if this metal was limiting the formation of ferric iron-bound P.

Loosely-sorbed P and iron-bound P are collectively referred to as "non-apatitic inorganic P" (NAP). The presence and availability of this group in sediment is of primary importance in controlling algal growth since it is the principal source of reactive P to sediment porewaters and the overlying water column (Williams et al. 1976, McComb et al. 1998).

Calcium-bound P includes the sum of authigenic calcium phosphate, biogenic calcium phosphate, detrital calcium phosphate, and P associated with biogenic $CaCO_3$. Authigenic calcium phosphates are sedimentary minerals derived *in situ* in contrast to detrital calcium phosphates that originate from minerals of metamorphic and igneous origin. Biogenic calcium phosphate is also a form of authigenic calcium phosphate, but is produced exclusively by living organisms. Examples include bones, teeth, and scales (Ruttenberg 1990).

Calcium phosphates are commonly referred to as apatites. They have a general chemical formula of $Ca_5X(PO_4)_3$, where X can be OH, F, Mg, or CO_3. Apatitic P is tightly bound in the mineral matrix and not readily available for biological utilization. Therefore, large quantities of authigenic, detrital, and biogenic apatites in sediments will not generally provide sufficient quantities of P to the overlying water. P associated with $CaCO_3$ is also strongly bound to the calcium mineral and is not easily accessed by the biota (Ruttenberg 1990).

Organic P is associated with organic carbon molecules and forms C-O-P and C-P bonds. In sediments, organic P is derived from living organism, and includes such biopolymers as

phospholipids and nucleic acids. Generally, organic P is only directly available to the biota after decomposition and mineralization processes have converted it to the inorganic form; however, some studies have shown that algae and bacteria are capable of assimilating dissolved organic P (Huang and Hong 1999). These processes are largely microbiologically mediated and therefore proceed at rates dependent upon the physical and chemical properties of the aquatic environment in question. This P fraction is abundant at the sediment surface, and typically comprises one-third of the total P pool in most freshwater sediments (Wetzel 1999).

In the present study, an attempt was made to determine the abundance and distribution of total organic carbon, reactive iron, and the five P fractions described above, in sediments from the Togcha River, the Togcha Estuary, and the immediately adjacent coral reef flat waters of Togcha Bay, on the eastern side of Guam.

The Togcha River receives secondary treatment sewage effluent from the Baza Gardens Sewage Treatment Plant (BGSTP), located 2.7 km upstream. Approximately 600,000 gallons of effluent are discharged into the river each day (Public Utilities Authority of Guam 1993) and ultimately make their way downstream into the shallow waters of Togcha Bay. The full impact of this on the general ecology of the bay has yet to be determined. However, visible signs of nutrient enrichment are suggested at certain times of the year. For example, blooms of the filamentous green alga, *Enteromorpha clathrata*, appear around the river mouth and along the coastline to the immediate north and south during the dry season. Also, windrows of detached macroalgae periodically blow in from the outer bay area, along the old river channel, and wash ashore in and around the river mouth and adjacent coastline. The mass is a visible mixture of algal taxa, although the brown frondose algae (e.g., *Dictyota*, *Padina*, and *Sargassum*) predominate. Cyanobacteria (*Oscillatoria* spp.) and remnants of seagrass, (*Enhalus univernis*) are also present in varying proportions. As the mass decomposes, it frequently produces a foul-smelling odor not unlike that of raw sewage. Understandably, these algal blooms, and more importantly, the driving force behind them, are of considerable concern to local residents and others who frequent the area. Clearly then, a quantitative assessment of nutrient loadings into Togcha Bay is urgently needed together with a full evaluation of the ecological impact of any anthropogenic discharges in the area. The study described herein was seen as a first step towards achieving this goal and was designed to meet the following research objectives:

1. Determine spatial and temporal distribution and abundance of total organic matter, reactive iron, and five operationally-defined P fractions in surficial sediments from the upper, middle, and lower reaches of the Togcha River and immediately adjacent coastal waters to the north and south of the river mouth.
2. Identify any significant correlations between any of the parameters mentioned above and discuss their possible importance.
3. Compare P levels found with those reported for clean and polluted sediments from other parts of the world and make a preliminary assessment of the nutrient status of the study area.

As an adjunct to this study, water samples were collected for nutrient analyses from the lower reaches of the Togcha Estuary in an attempt to correlate aqueous orthophosphate levels with redox conditions at the sediment-water interface and identify important chemical processes that influence the export of biologically available P out into the bay.

MATERIALS AND METHODS

STUDY SITE DESCRIPTION

The Togcha River is the smallest of several rivers that drain southern Guam. It is approximately 6 km long with a catchment area of 18 sq. km (Figure 1), and enters the sea at Togcha Bay between the villages of Yona and Talofofo on the eastern side of the island. The headwaters of the river have several shallow, branching tributaries about 1-2 m deep. These eventually interconnect to form a swamp complex that converges to a single, large pond before flowing downstream towards the BGSTP. Approximately 275 m downstream from the BGSTP, the river drops rapidly in elevation towards the coast and forms a series of small pools connected by short waterfalls. These give way to a larger "swimming hole" about 50 m further on. Numerous ditches and gullies channel stormwater into the river along its way to Togcha Bay, with one permanent tributary that receives run-off from Baza Gardens, a nearby housing estate. In the dry season, no water flows beyond the base of the uplifted reef cliff approximately 700 m downstream of the BGSTP.

Nutrient inputs into the river are predominantly from rural and residential sources with BGSTP being a major contributor. Total N and P concentrations in filtered wastewater samples from this plant are around 10 mg/L and 0.5 mg/L respectively (Guam Waterworks Authority 2002, 2003). Such levels are orders of magnitude higher than those normally encountered in surface waters on Guam (Denton et al. 1998). The effluent also has an average biochemical oxygen demand of 37 mg/L, which is about 5-6 times higher than normally found in rivers and streams (Sawyer and McCarty 1978). Two other notable sources of nutrients in this area are the Talofofo Golf Course at the head of the Togcha River, and the Country Club of the Pacific Golf Course located further downstream near the estuary. Both golf courses are known to apply fertilizer to their property (Duenas and Swavely 1990, Sohbu Guam Development Co., Inc. 2002).

The river flows through a series of different geologic formations before reaching the beach deposits of the coast. In the upper catchment, the Bonya Limestone and volcanic rocks of the Umatac formation predominate, while alluvial deposits and Mariana Limestone are widespread throughout the lower half of the catchment (Tracy et al. 1992). The soils found on these formations range from fairly permeable Ritidian-rock outcrop to relatively impermeable Ylig clay (Young 1952). Soils from this region reportedly contain around 6-11 μg/g of extractable P (Motavalli et al. 1996). Total P levels are much higher and exceed 500 μg/g in Ylig clay (Demeterio et al. 1986). Preliminary analyses of sediments and soil upstream of the BGSTP during the early part of this investigation revealed total P concentrations of 291-546 μg/g. These samples were analyzed using methods described by Aspila et al. (1976).

Stream flows in the Togcha River are highly seasonal and largely reflect contributions from the BGSTP during the dry season. The effluent discharged from the plant has created a small, shallow pool at the point of entry into the river. This fills with fine, flocculent sedimentary material during low stream flow conditions of the dry season, and is scoured clean by flash flooding during the wet season. Under the latter conditions, the swollen waters inundate the coastal belt and transport large amounts of sediment and organic debris into estuary and bay. During the dry season, however, all surface flows are captured by insurgence about 2 km upstream and the riverbed below it dries out.

The deepest parts of the estuary are at the mouth of the river and under the Route 4 Bridge, approximately 175 m upstream. At high tide, water depths are approximately 1.5 m at each location. Sediments in these areas are organically enriched, fine-grained materials that become progressively more anoxic during the dryer months. The accompanying redox changes that follow this development undoubtedly play a significant role in the transport of nutrients from bottom deposits into the overlying water and out into the bay.

SAMPLE COLLECTION

Sediments

Surface sediments were taken on two occasions from 9 sites in the Togcha River, 14 sites in the estuary, and 15 sites in the bay within 750 m of the river mouth. The first set of samples was collected in May 1999, at the end of the dry season. The second set was collected in October 1999 after a period of prolonged, heavy rain. The site locations are shown in Figure 1. Sites R-1 to R-9 were freshwater locations in the upper and middle reaches of the river and included two relatively unimpacted reference sites. The first reference site (R-1) was located ~100 m upstream of BGSTP. The second (R-5) was just inside the mouth of the earlier described tributary that drains street runoff from the Baza Gardens housing area, ~400 m downstream of the treatment plant. Sites E-1 to E-8 represent estuarine sites in the narrower, upper reaches of the estuary where the shallow bed sediments were fairly well oxidized. Sites E-9 to E-14 were located in the lower section where the water was deeper and the sediments often distinctly anoxic. Bay sites, B-1 to B-15, are numbered in order of increasing distance from the river mouth.

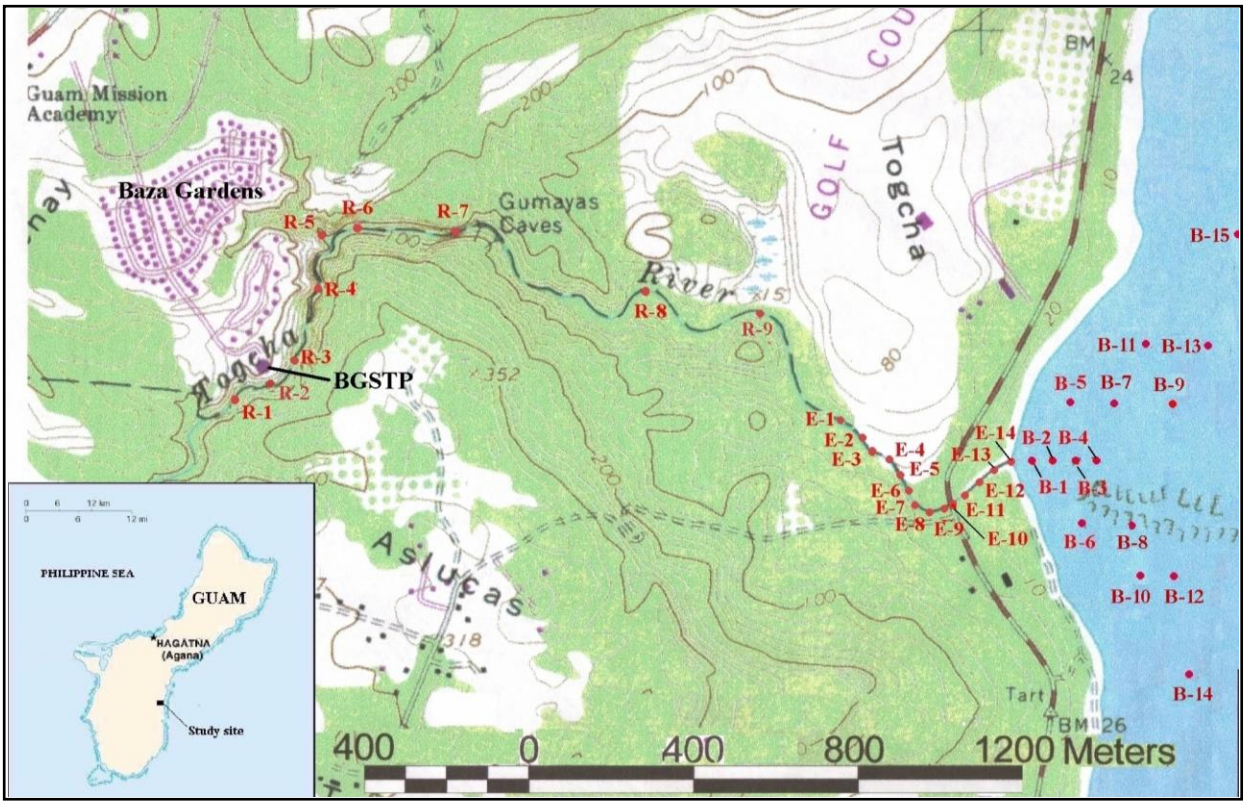

Figure 1: Map of study area showing sediment sampling sites in Togcha River (R-1to R-9), Togcha Estuary ((E-1 to E-14) and Togcha Bay (B-1-B15).

All samples were collected from submerged sites with the exception of those taken from sites R-8 and R-9 in May 1999. On this particular occasion the riverbed downstream of R-7 was completely dry.

Sampling was facilitated using a plastic box measuring 29x15x2cm (LxWxH) and cover. The box was pressed firmly into the sediment surface to a depth of 2 cm at each site. The cover was then carefully positioned underneath the inverted box to keep the sediments in place during the retrieval process. After draining off the excess water, the sediment sample was transferred to a Zip-lock plastic bag, labeled and immediately placed on ice. Multiple samples were collected in this way at each site and were subsequently pooled for analysis. Those taken from each river and estuary site were collected at ~1 m intervals across the riverbed. Bay sediments were taken within an area of ~1 m^2 at each site. Up to four samples per site were collected in this location depending on sediment availability.

In the laboratory, the bulk-wet sediments were transferred to aluminum pie dishes and dried to constant weight at 60 ^{0}C. The dried sediments were then placed in clean plastic bags and disaggregated prior to sieving. Only that fraction passing through a 125 μm stainless steel screen was subjected to the chemical analysis outlined below. Duplicate analysis was performed on approximately 10% of the samples.

Water

Surface, middle, and bottom water samples were collected on three occasions from the lower reaches of the Togcha River between April and May 2001. One set of samples was collected from site E-14, at the mouth of the river, and the other two were taken from site E-10, under the Route 4 Bridge. Both sites were sampled once during the day. The second set of samples from E-10 was collected at night. On all three occasions, sampling commenced at high tide and was repeated at approximately hourly intervals until low tide. Temperature, salinity, and dissolved oxygen measurements were taken by YSI (Yellow Spring Instruments) probes at all depths immediately prior to sample collection.

All samples were collected midstream in clean 50-ml polypropylene syringes. These were either hand-held for surface samples or clamped to an aluminum extension rod for those taken in deeper waters. Upon collection, each sample was transferred to another 50-ml syringe via a 0.45 μm inline filter (Sartorious). The syringe was then capped and sealed in a nitrogen-filled polyethylene bag to minimize sample oxidation and immediately placed on ice.

In the laboratory, the samples were transferred under nitrogen to clean 100-ml polyethylene vials. After capping, they were placed in nitrogen-filled bags and stored at 4 ^{0}C until required for analysis.

CHEMICAL ANALYSES

Sediments

The sediment samples were analyzed for the five P fractions described earlier using the sediment extraction (SEDEX) method developed by Ruttenburg (1992). These were separated out in order of their decreasing reactivity using progressively stronger chemical extractants.

A flow chart outlining the SEDEX procedure is shown in Figure 2 below and is followed by summaries of the extraction and analytical methods for each step along with the procedure adopted for estimating total organic carbon content (TOC).

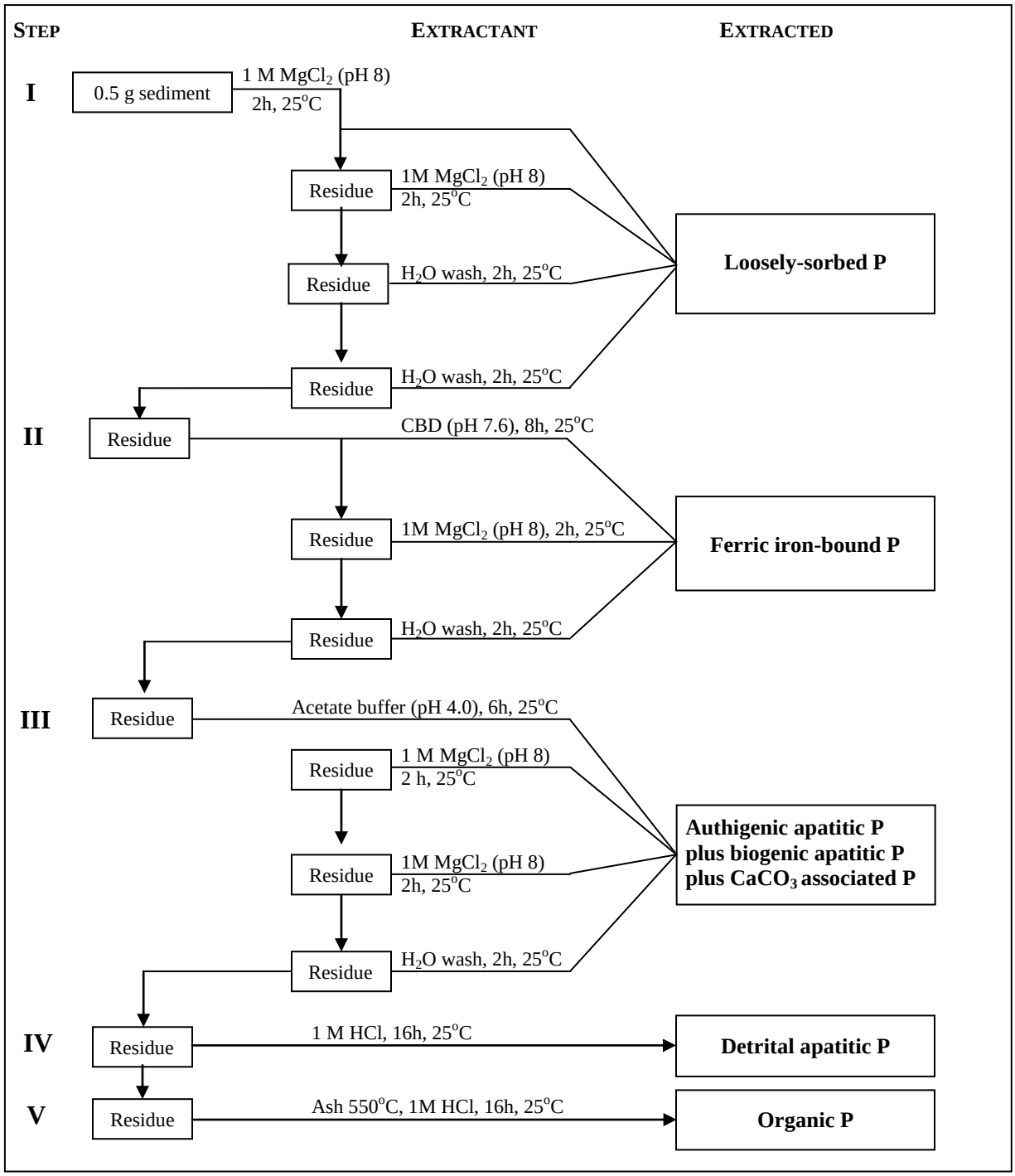

Figure 2: SEDEX chemical extraction scheme (after Ruttenberg 1992). CBD = citrate plus bicarbonate plus dithionite solution.

Total Organic Carbon (TOC)

TOC determinations were made by mass loss on ignition at a temperature below that is necessary to remove hydroxyl ions and bound water from the samples, or cause the degradation of any inorganic carbonate present (Leong and Tanner 1999). In this procedure, the sediment samples were rinsed with distilled water to remove excess salt and then dried in an oven overnight at 100^{o}C. The following day, about 0.5 g of dried sediment was accurately weighed into an ashing crucible and held in a muffle furnace at 360^{o}C for two hours. After cooling in a dessicator, the sample was quickly re-weighed. The difference in weight was assumed to represent the total organic matter (TOM) component of the sediment. TOC was estimated by multiplying TOM by a factor of 0.45 (Nelson and Sommers 1982).

Step I: Loosely-sorbed P Extraction

A half-gram (0.5 g) of sieved sediment sample was placed in an 80-ml Nalgene® polycarbonate centrifuge tube with 50 ml of 1 M $MgCl_2$ solution to remove loosely-sorbed P. This reaction formed the $MgPO_4^-$ complex by mass action displacement with Cl^-. The tube was placed on orbital shaker for 2 hours at a speed sufficient to maintain a suspension of the sample solids. After shaking, the sample was centrifuged for 10 minutes at 3900 x g in a Sigma 3K30 Centrifuge (Braun Biotech International). The supernatant was then passed through a Millipore® membrane filter (0.45 μm) into a 300-ml glass jar and set aside. The procedure was repeated and the filtered supernatant added to the jar. The sample residue was extracted twice more with 50 ml of distilled water to quantitatively remove any remaining extractant. The combined extractions were acidified to pH <1 with concentrated HCl, and P was determined colorimetrically at 885 nm using the ascorbic acid-molybdate blue method developed by Murphy and Riley (1962) cited in Strickland and Parsons (1968).

Step II: Ferric Iron-bound P and Reactive Iron Extraction

The residual sediment from Step I was extracted for 8 hours with 45 ml of a solution containing 0.3 M sodium citrate, 1.0 M $NaHCO_3$, and 1.125 g of sodium dithionite (abbreviated here as CBD). In this reaction, insoluble iron (Fe^{3+}) is reduced by dithionite to the soluble ferrous form (Fe^{2+}) thereby liberating any ferric-bound P into solution. Ferrous iron forms a chelate with citrate and is prevented from reverting to its oxidized state.

Following extraction, the sample was centrifuged and the supernatant filtered off and set aside as described earlier. The residual sediment was re-extracted with 50 ml of 1 M $MgCl_2$ followed by 50 ml of distilled water to remove any P that had re-adsorbed to the sample during the CBD extraction process. The three extracts were then combined and divided into two equal portions. One portion was analyzed for P at 667 nm in accordance with the colorimetric method described by Watanabe and Olsen (1962). The other was analyzed for iron using conventional flame atomic absorption spectroscopy.

Step III: Authigenic Apatitic P plus Biogenic Apatitic P plus $CaCO_3$ Associated P Extraction

In this step, the residual sediment from Step II was shaken for 6 hours with 50 ml of 1 M sodium acetate. This resulted in the acid dissolution and chelation of Ca^{2+} by acetate thereby releasing any P incorporated in the calcareous matrix. The initial extraction was subsequently followed by two 50 ml extractions with 1 M $MgCl_2$ and one 50 ml distilled water extraction as described above. The combined extracts were acidified to pH <1 prior to colorimetric analysis at 885 nm (Murphy and Riley 1968).

Step IV: Detrital Apatitic P Extraction

This single step extraction procedure involved shaking the residual sediments from Step III with 50 ml of 1 M HCl for 16 hours to liberate P from the more refractory calcareous components. After centrifugation and filtration, the supernatant was analyzed directly for P at 885 nm with no further pH adjustment necessary.

Step V: Organic P Extraction

The residual sediment remaining from Step IV was transferred to an ashing crucible using the smallest amount of distilled water possible, and placed in a drying oven at 60 ^{0}C overnight. The dried sample was then heated in a muffle furnace at 550 ^{0}C for two hours to liberate P associated with organic matter. Upon cooling, the resulting ash was gently washed into an 80-ml centrifuge tube with 50 ml of 1 M HCl. Any ash adhering to the side of the crucible was carefully dislodged using a disposable glass pipette. After capping, the tube was shaken for 16 hours and the contents centrifuged. The supernatant was filtered and analyzed directly for P at 885 nm without further pH adjustment.

Water

All water samples were analyzed by the WERI Water Quality Laboratory for reactive P, nitrate-N, nitrite-N, and ammonium-N using a Quickchem 800 Flow Injection Analyzer (Lachat Instruments) equipped with four analytical channels. The analytical methods were those recommended by the manufacturer and are essentially the same as those described in Standard Methods, Part 4500 (APHA 1992) with modifications specifically intended for flow injection analysis. They are listed below.

Reactive P:	Quickchem Method 31-115-01-3-A (ascorbic acid method)
Nitrate-N:	Quickchem Method 31-107-04-3-A (cadmium reduction method)
Nitrite-N:	Quickchem Method 31-107-05-1-A (diazotization method)
Ammonium-N:	Quickchem Method 31-107-06-1-A (phenate method)

All chemical analyses were performed on chilled samples under nitrogen to minimize oxidative interferences in analyte content. All samples were analyzed within 24 hours of collection.

RELIABILITY OF ANALYTICAL AND SAMPLING PROTOCOLS

Simple statistics were used to describe the analytical precision for each P fraction determined by the SEDEX procedure, and the intra-site sample variability encountered in the field. These tests are described below.

Analytical Precision

Ten replicates of a single river sediment sample were analyzed by the SEDEX procedure to determine the analytical variability associated with the methods. The results are listed in Table 1. The coefficient of variation (CV) is commonly used to determine analytical precision and is simply the standard deviation expressed as a percentage of the mean. A CV of 10% or less is generally considered to be acceptable for analytical purposes (Csuros 1994). The CVs obtained during the present study ranged from 2.8% to 10.4%.

Table 1: Analytical Variability for Phosphorus Fractions in Togcha River Surface Sediments.

Replicate Number	Phosphorus Fractions (µg/g dry wt.)[a]				
	LP	FeP	AAP+	DAP	OP
1	77.7	173	5.45	86.5	158
2	70.8	173	5.89	71.2	158
3	73.1	143	5.89	78.8	162
4	74.6	143	5.45	78.8	169
5	70.8	146	6.15	82.7	167
6	73.1	186	5.72	82.7	167
7	70.8	189	5.98	80.8	162
8	70.8	170	6.15	88.5	158
9	71.5	192	5.54	73.1	155
10	74.6	175	5.28	75.0	158
Average	72.8	169	5.75	79.8	161
SD	2.21	17.6	0.29	5.32	4.51
CV	3.0	10.4	5.1	6.7	2.8

[a]LP = loosely-sorbed P, FeP = ferric iron-bound P, AAP+ = authigenic apatitic P plus biogenic apatitic P plus $CaCO_3$ associated P, DAP = detrital apatitic P, OP = organic P; SD = standard deviation; CV = coefficient of variation

Intra-site Variability

Sample variability was determined by analyzing sediments from seven discrete points within a single site in the river, estuary, and bay. To maximize potential intra-site differences, samples were taken across the entire bed of the river and estuary. In the bay, they were collected from within an area of approximately 3 square meters. The results are listed in Table 2 and indicate a reasonable degree of agreement between samples from within the same site. Overall, the CVs ranged from 5.8%-26.9% and were mostly <20%. CVs varied between P fractions and locations with no consistent trends immediately obvious. The ratio of highest to lowest CV for each P fraction measured ranged from 1.7 for detrital apatitic P to 5.2 for organic P.

DATA ANALYSIS

Statistical analyses were performed separately on data sets from each of the three locations sampled. Non-parametric tests were used throughout to accommodate departures from normality and equality of variance assumptions. Thus, temporal differences between data sets from within each sampling location were determined using the Mann-Whitney two-sample test (Zar 1974). Simple correlation analysis between the various parameters analyzed was carried out using the rank test described by Spearman (Zar 1974).

Table 2: Intra-site Variability for Phosphorus Fractions in Surface Sediments from Togcha River, Togcha Estuary, and Togcha Bay.

Replicate Number	Phosphorus Fractions (µg/g dry wt.)[a]				
	LP	FeP	AAP+	DAP	OP
River					
1	10.8	421	1.55	125	198
2	14.5	388	1.98	187	225
3	13.0	372	2.16	156	220
4	17.5	470	1.55	160	240
5	10.0	388	1.55	160	226
6	10.0	405	1.28	138	214
7	lost	lost	lost	lost	lost
Average	12.6	407	1.68	154	221
SD	2.7	31.9	0.30	19.4	12.8
CV	21.6	7.8	17.7	12.6	5.8
Estuary					
1	lost	lost	lost	lost	lost
2	99.3	796	4.52	192	191
3	97.1	959	5.22	237	248
4	85.2	551	4.96	212	194
5	111	665	5.40	196	242
6	96.4	926	3.65	210	245
7	98.6	910	7.67	194	223
Average	97.9	801	5.24	207	224
SD	7.51	149	1.23	15.5	23.6
CV	7.7	18.6	23.5	7.5	10.5
Bay					
1	51.7	551	2.16	21.2	29.5
2	29.4	356	1.72	21.2	21.8
3	53.9	698	2.07	26.9	48.1
4	52.5	682	1.90	25.0	35.7
5	68.8	730	2.07	23.1	48.1
6	54.7	698	2.07	26.9	54.3
7	42.8	600	1.90	26.9	46.5
Average	50.5	616	1.98	24.5	40.6
SD	11.2	121	0.14	2.43	10.9
CV	22.1	19.7	7.0	9.9	26.9

[a]LP = loosely-sorbed P, FeP = ferric iron-bound P, AAP+ = authigenic apatitic P plus biogenic apatitic P plus $CaCO_3$ associated P, DAP = detrital apatitic P, OP = organic P; SD = standard deviation; CV = coefficient of variation

RESULTS AND DISCUSSION

SEDIMENTS

The analytical data for sediments collected over the entire study period are presented in Table 3 and graphically displayed in Figures 3-9. All data are expressed on a dry weight basis. Total P tabulations were determined by the summation of all five fractions. Location averages for all components were calculated as geometric means to accommodate outliers in some of the data sets. The pie charts shown in Figure 10 summarize the relative abundance on each P fraction in the river, estuary, and bay and were constructed using the location averages listed in Table 3. The results of the Mann-Whitney two-sample tests and Spearman rank correlation analyses are summarized in Tables 4 and 5 respectively. Scattergrams for all variable pairs from all data sets are shown in Appendices 1 through 6.

The data for each component analyzed are reviewed and discussed separately below. Spatial differences and temporal trends are identified as appropriate. Significant correlations between variable pairs are explained where possible.

Total Organic Compounds (TOC)

Sedimentary TOC levels in Togcha River and Togcha Bay are derived from biotic communities in the area as well as from terrestrial sources washed down the watershed during periods of heavy rain. Contributions from the BGSTP are also clearly evident from the data and reflect the generally high organic matter loading typical of sewage effluent (Lester 1990)

Relative Abundance in Study Area

TOC was the most abundant component measured in sediments during the present study, and accounted for 1-5% of the sample dry weight in the great majority of cases (Table 3).

Spatial & Temporal Differences

River: The reference site (R1 and R5) data suggests that normal background levels of TOC in this part of the watershed are around 3% during the dry season and 1-2% during the wet season. The significant temporal difference ($P<0.01$; see Table 4) most likely reflects the scouring effects of faster flows encountered during wet weather, or a dilution effect associated with the increased deposition of soil of low organic matter content in the river following major storm events.

TOC levels in sediments at the BGSTP point of discharge were close to 13% during the low stream flow conditions encountered in May and an order of magnitude lower in October following a bout of wet weather. In this particular instance, the marked change in sediment characteristics, from a predominantly fine, flocculent material in May to a shallower, coarser grained deposit in October, suggests that much of the organic material that had accumulated here during the dry season had been displaced and washed further downstream during the wet season. The same seasonal trend was apparent at most other sites in the river with TOC levels ranging from around 1-3% in May and 0.5-2% in October.

Estuary: The river widens appreciably in the lower reaches of the estuary between sites E-8 and the E-14 (mouth). The reduction in flow along this length of the waterway encourages the deposition of suspended sediments and other particulate material transported down river. Dissolved organic carbon also precipitates out of solution in this section as a result of

progressive increases in salinity. The net effect of these two processes is a gradual increase in TOC from the upper reaches of the estuary towards the mouth as shown in Figure 3.

Table 3: Concentrations of TOC, Reactive Fe, and Isolated P Fractions in Surface Sediments from Togcha River, Togcha Estuary, and Togcha Bay in May and October 1999.

Site	TOC (%)		Reactive Fe		Phosphorus Fractions (µg/g dry wt.)[a]										Total P	
					LP		FeP		AAP+		DAP		OP			
	May	Oct	May	Oct	May	Oct	May	Oct	May	Oct	May	Oct	May	Oct	May	Oct
River																
R-1	2.61	1.71	1398	3495	16.9	17.6	65.9	66.1	61.1	21.8	129	119	364	238	637	463
R-1D[b]	-	-	-	-	16.1	-	65.9	-	52.9	-	135	-	362	-	632	-
R-2	12.7	1.44	2738	3767	1764	40.2	1036	62.9	1939	16.2	391	102	4065	180	9195	401
R-3	2.70	1.71	2587	4527	184	58.3	339	234	90.0	35.0	136	163	337	211	1086	701
R-4	1.71	0.27	1763	2787	240	98.2	317	274	148	64.3	160	188	309	193	1174	818
R-4D[b]	-	-	-	-	234	-	267	-	153	-	159	-	316	-	1129	-
R-5	3.20	1.13	812	1507	26.0	24.4	50.2	59.6	94.0	35.0	74.0	112	259	178	503	409
R-6	2.97	2.03	974	1652	163	46.2	160	29.9	168	70.3	120	127	307	197	918	470
R-6D[b]	-	-	-	-	165	-	176	-	168	-	117	-	285	-	911	-
R-7	3.02	1.31	1183	1763	222	68.8	179	29.9	158	62.1	135	134	340	197	1034	492
R-8	1.40	1.98	667	1676	110	73.3	144	26.6	148	49.9	148	123	271	190	821	463
R-9	2.75	0.59	853	2201	143	65.8	97.3	135	121	35.0	116	123	273	218	750	577
Mean[c]:	2.9	1.2	1281	2405	123.1	48.61	166.6	71.85	146.3	39.07	140	130	383.3	199.4	1030	518.1
Estuary																
E-1	2.30	0.68	1630	2445	49.2	43.2	126	142	61.1	28.9	117	164	328	204	681	582
E-2	2.79	2.16	1952	3529	50.7	44.0	116	142	81.7	38.9	123	172	311	218	682	615
E-3	3.02	0.90	2764	2816	70.0	47.7	173	145	98.1	35.6	141	191	316	240	798	659
E-4	2.43	1.94	1517	3495	64.0	52.3	122	152	92.0	40.5	176	191	350	203	804	639
E-4D[b]	-	-	-	-	-	52.3	-	152	-	41.1	-	187	-	207	-	639
E-5	3.02	1.58	1653	4077	71.1	64.3	104	139	106	44.4	185	172	335	189	801	609
E-6	3.38	1.08	3144	4170	60.5	58.3	166	172	108	59.3	162	196	364	200	861	686
E-7	3.24	1.26	2387	4449	68.1	56.0	148	155	98.1	69.8	124	193	443	172	881	646
E-8	2.57	2.61	3176	4411	74.8	64.3	157	155	108	55.4	141	193	350	212	831	680
E-9	2.84	1.67	4536	3863	120	109	242	92.5	96.1	67.6	57.6	188	194	220	710	677
E-10	2.70	2.34	5284	5762	75.6	75.8	204	86.0	104	68.1	94.8	122	177	176	655	528
E-10D[b]	-	-	-	-	77.1	-	213	-	100	-	91.8	-	171	-	653	-
E-11	4.14	1.58	3964	5382	139	75.6	232	106	115	79.2	82.9	204	238	224	807	689
E-11D[b]	-	-	-	-	-	75.6	-	119	-	80.3	-	210	-	212	-	697
E-12	3.60	2.66	3144	4834	103	143	220	79.3	59.1	60.9	29.4	160	83.6	217	495	660
E-13	6.35	1.89	3312	6290	149	73.3	235	122	121	76.4	33.8	168	144	167	683	607
E-14	2.75	3.38	3196	6612	77.1	77.1	182	26.6	48.8	41.1	27.9	90.0	92.2	172	428	407
Mean[c]:	3.1	1.7	2782	4276	78.82	65.94	169.9	115.5	90.38	52.93	90.28	172	233.3	201	705.5	621.4
Bay																
B-1	1.485	1.71	1578	2067	47.0	80.8	104	106	51.4	37.8	62.1	93.5	113	125	378	443
B-2	1.26	1.40	188	2115	47.7	69.6	122	102	20.9	19.0	50.2	41.4	50.9	104	292	336
B-3	1.44	1.40	1154	1010	48.5	56.0	87.9	116	15.1	13.5	19.0	17.7	33.7	41.8	204	245
B-4	1.755	1.215	1032	1110	69.6	62.8	144	159	14.4	13.5	17.5	13.0	45.8	24.8	291	273
B-5	0.855	1.215	1380	1437	31.9	44.0	94.2	129	15.1	12.4	22.0	16.2	37.2	44.9	200	247
B-6	1.53	1.26	882	1150	47.7	78.6	107	152	22.4	19.6	19.0	16.2	40.6	29.4	237	296
B-6D[b]	-	-	-	-	-	78.6	-	139	-	21.8	-	17.8	-	27.9	-	285
B-7	1.665	1.035	545	843	69.6	61.3	129	142	15.8	14.6	19.0	11.4	47.5	32.5	281	262
B-7D[b]	-	-	-	-	-	67.3	-	139	-	12.4	-	13.0	-	31.0	-	263
B-8	1.4	0.90	766	735	59.8	74.1	75.3	155	21.7	18.5	19.0	14.6	25.1	27.9	201	290
B-9	1.575	1.125	650	797	66.6	68.1	141	129	16.5	12.9	14.5	9.86	32.0	21.7	271	242
B-10	1.17	0.99	568	619	46.2	67.3	119	119	15.1	14.0	19.0	11.4	23.4	24.8	223	237
B-11	1.215	0.945	679	924	51.5	52.3	113	112	15.8	16.8	16.0	11.4	28.6	27.9	225	220
B-12	1.215	0.63	429	649	53.8	164	113	109	15.1	16.8	16.0	11.4	32.0	49.5	230	351
B-13	1.575	1.035	661	437	74.8	49.2	126	69.4	17.3	16.8	14.5	8.28	20.0	12.4	253	156
B-14	1.26	0.675	35	636	56.8	96.7	100	152	18.0	12.9	19.0	9.86	33.7	29.4	228	301
B-15	1.40	1.26	493	706	44.7	77.8	116	119	15.1	15.1	16.0	9.86	28.6	20.1	220	242
Mean[c]:	1.4	1.1	570	921	53	70	111	124	18	16	21	15.1	36	33	245	269

[a]LP = loosely-sorbed P, FeP = ferric iron-bound P, AAP+ = authigenic apatitic P plus biogenic apatitic P plus $CaCO_3$ associated P, DAP = detrital apatitic P, OP = organic P; [b]duplicate; [c]geometric mean. Dashes indicate no data

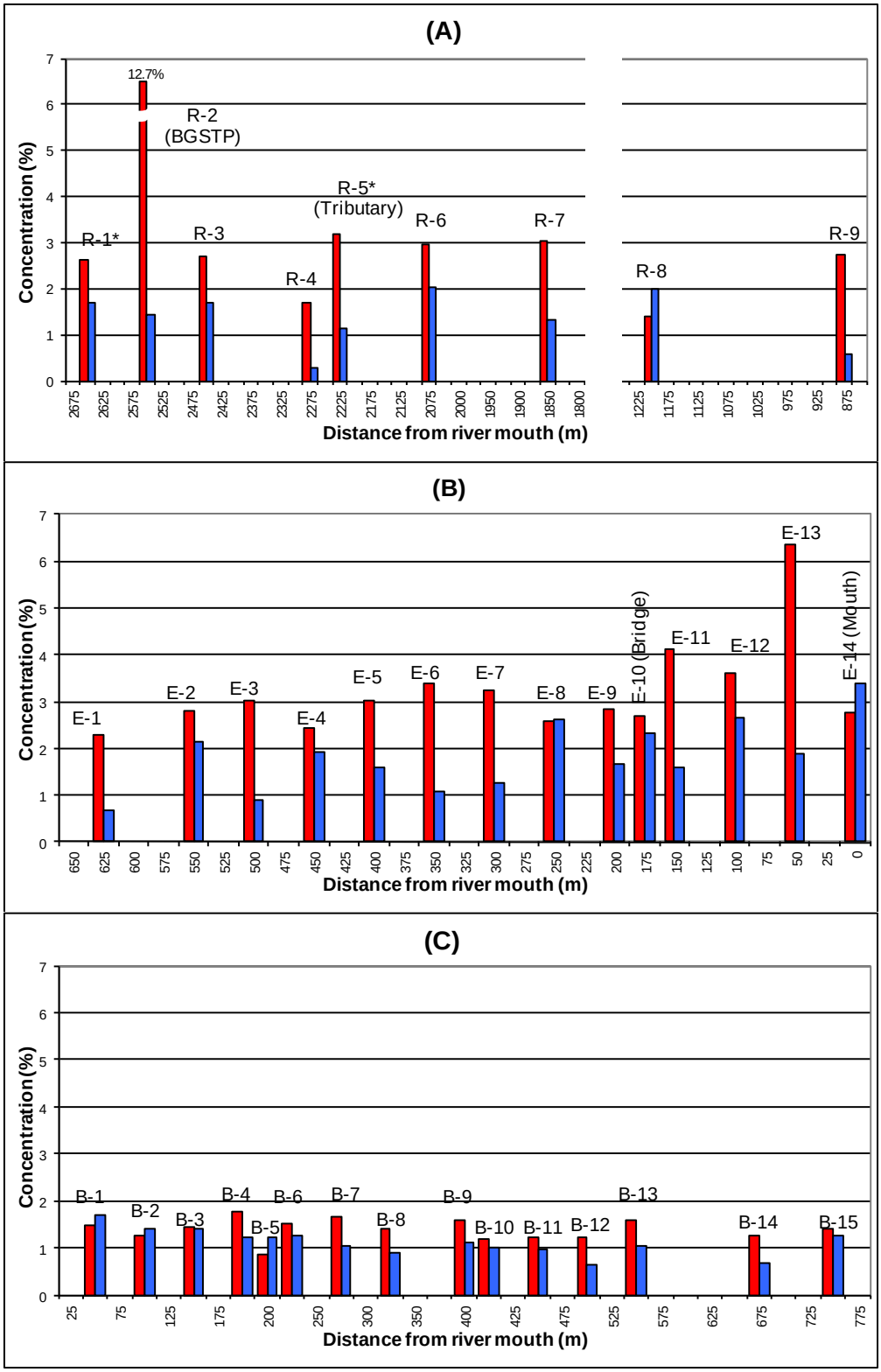

Figure 3: TOC in sediments from (A) Togcha River, (B) Togcha Estuary, and (C) Togcha Bay. Asterisk = reference sites, red bars = May 99 samples, blue bars = October 1999 samples

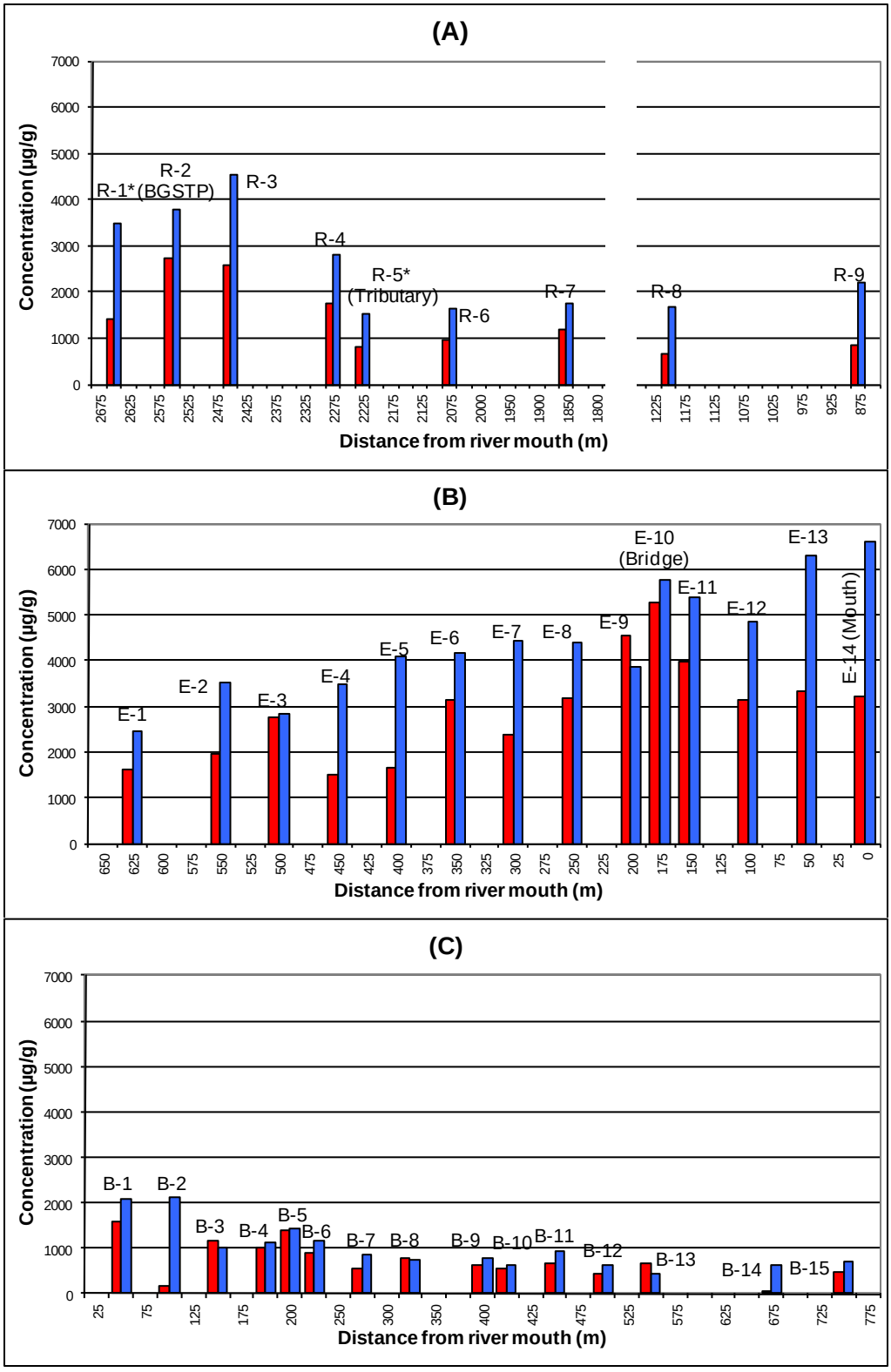

Figure 4: Reactive Fe (R-Fe) in sediments from (A) Togcha River, (B) Togcha Estuary, and (C) Togcha Bay. Asterisk = reference sites, red bars = May 99 samples, blue bars = October 1999 samples.

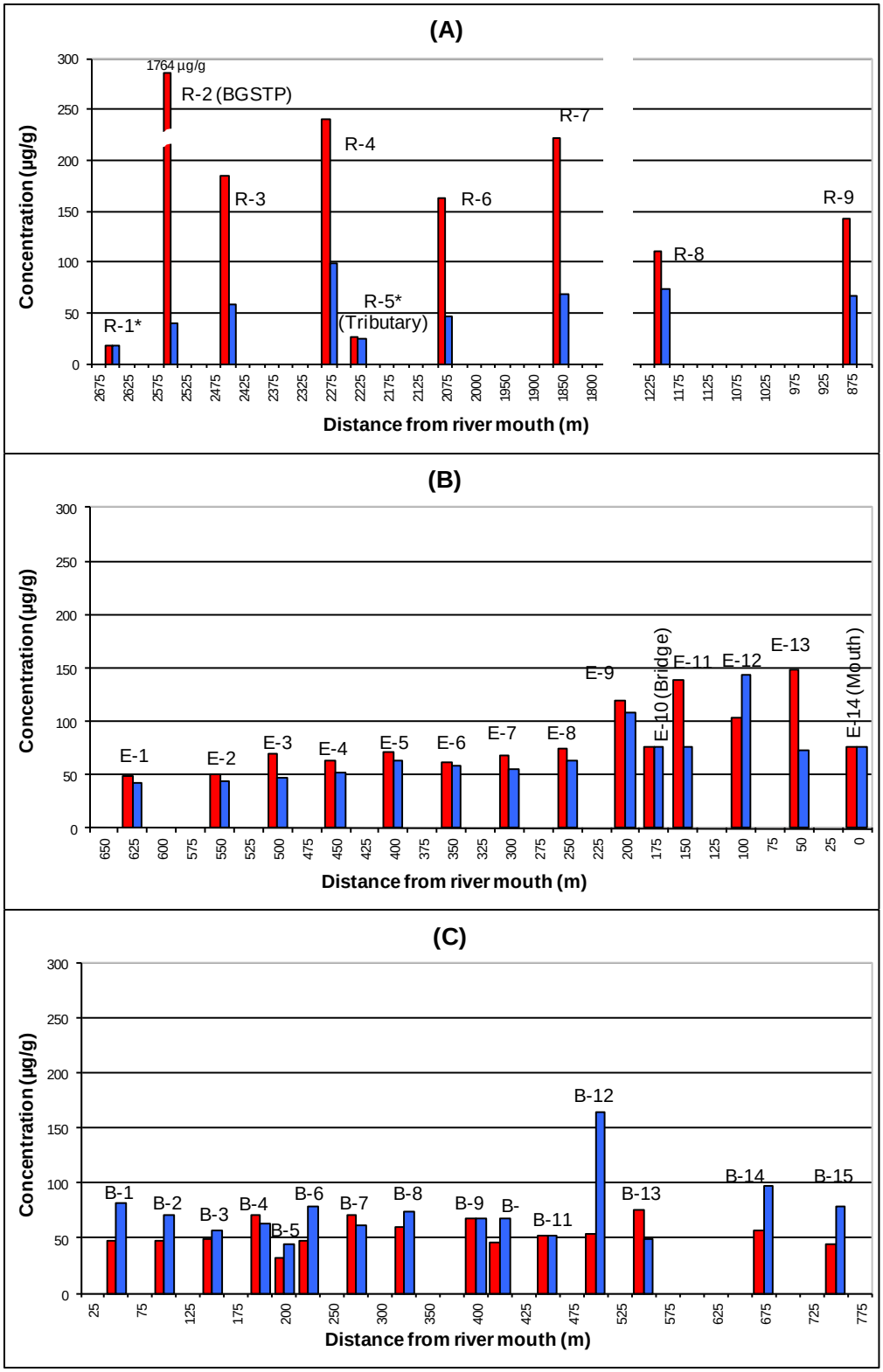

Figure 5: Loosely-sorbed P (LP) in sediments from (A) Togcha River, (B) Togcha Estuary, and (C) Togcha Bay. Asterisk = reference sites, red bars = May 99 samples, blue bars = October 1999 samples.

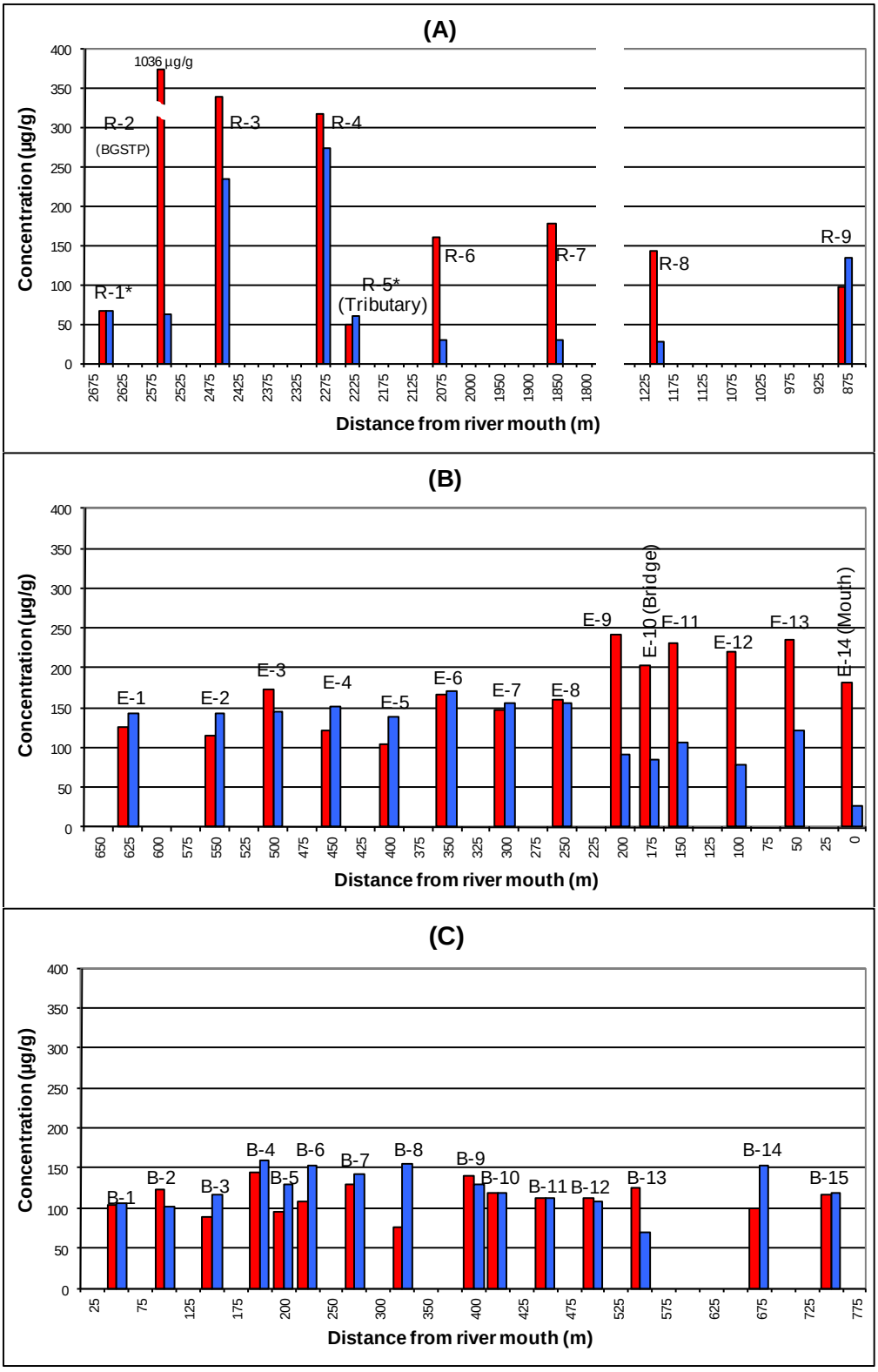

Figure 6: Reactive Iron-bound P (FeP) in sediments from (A) Togcha River, (B) Togcha Estuary, and (C) Togcha Bay. Asterisk = reference sites, red bars = May 99 samples, blue bars = October 1999 samples.

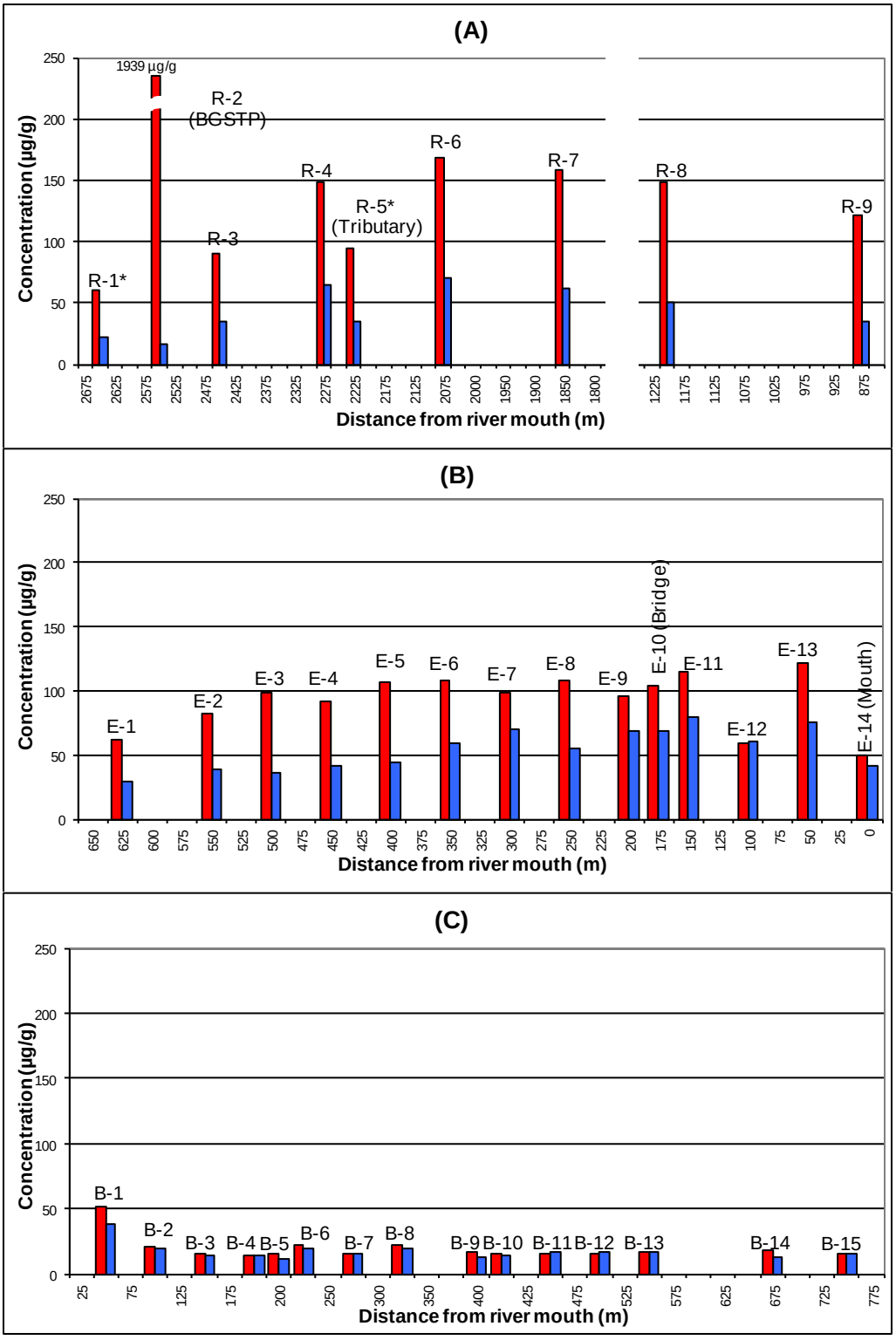

Figure 7: Authigenic apatitic P plus biogenic apatitic P plus $CaCO_3$ associated P (AAP+) in sediments from (A) Togcha River, (B) Togcha Estuary, and (C) Togcha Bay. Asterisk = reference sites, red bars = May 99 samples, blue bars = October 1999 samples.

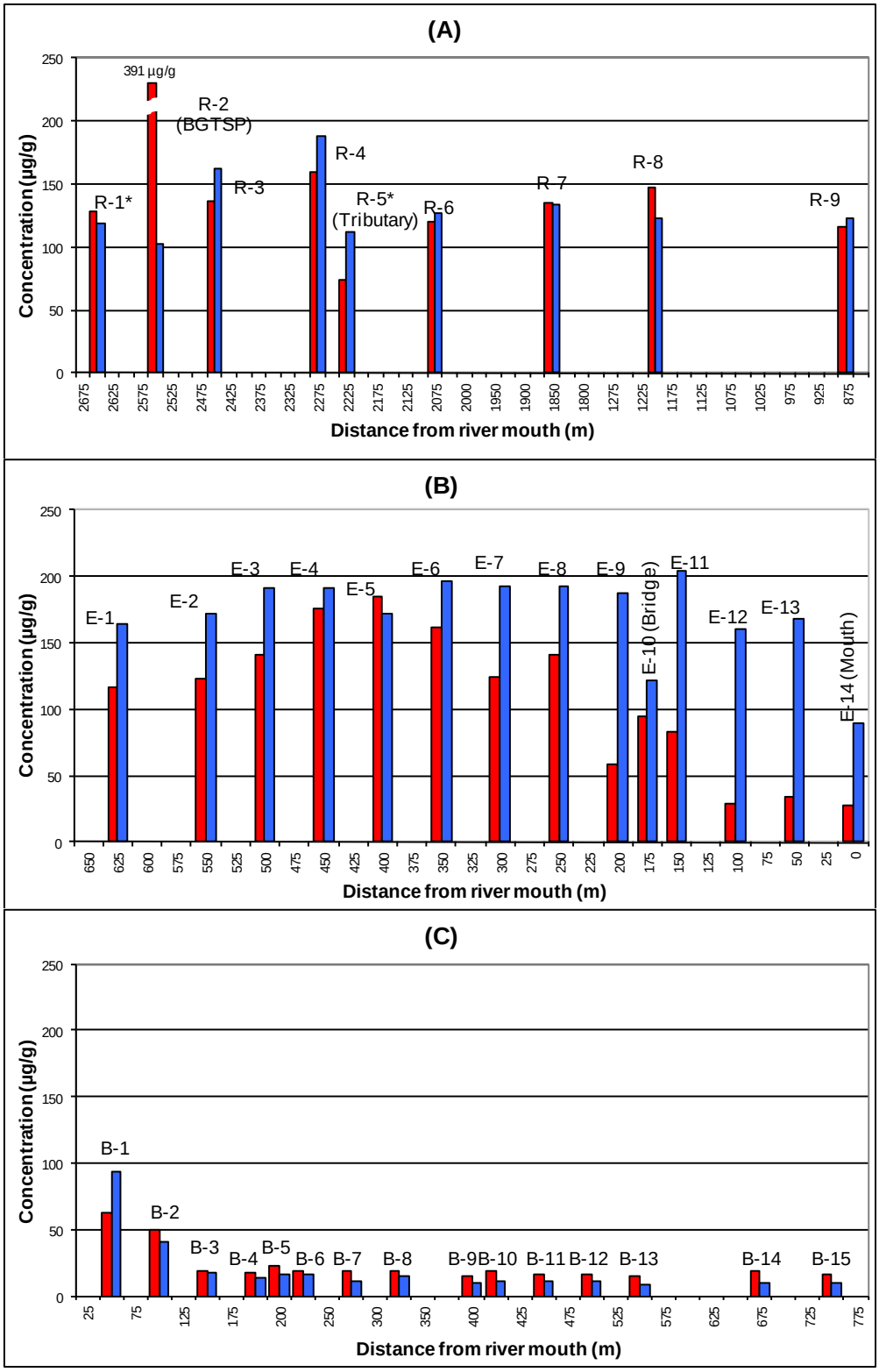

Figure 8: Detrital apatitic P (DAP) in sediments from (A) Togcha River, (B) Togcha Estuary, and (C) Togcha Bay. Asterisk = reference sites, red bars = May 99 samples, blue bars = October 1999 samples.

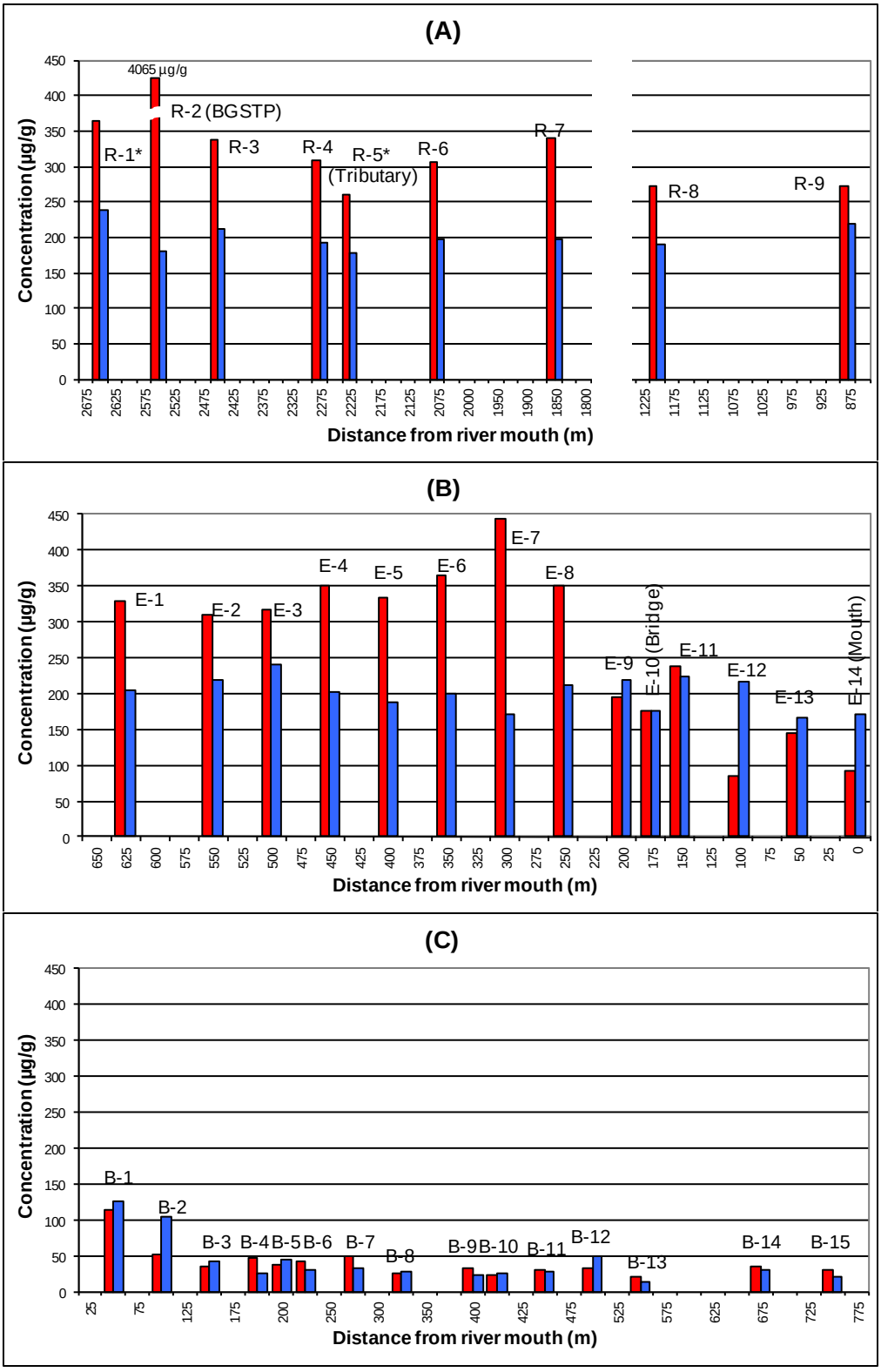

Figure 9: Organic P (OP) in sediments from (A) Togcha River, (B) Togcha Estuary, and (C) Togcha Bay. Asterisk = reference sites, red bars = May 99 samples, blue bars = October 1999 samples.

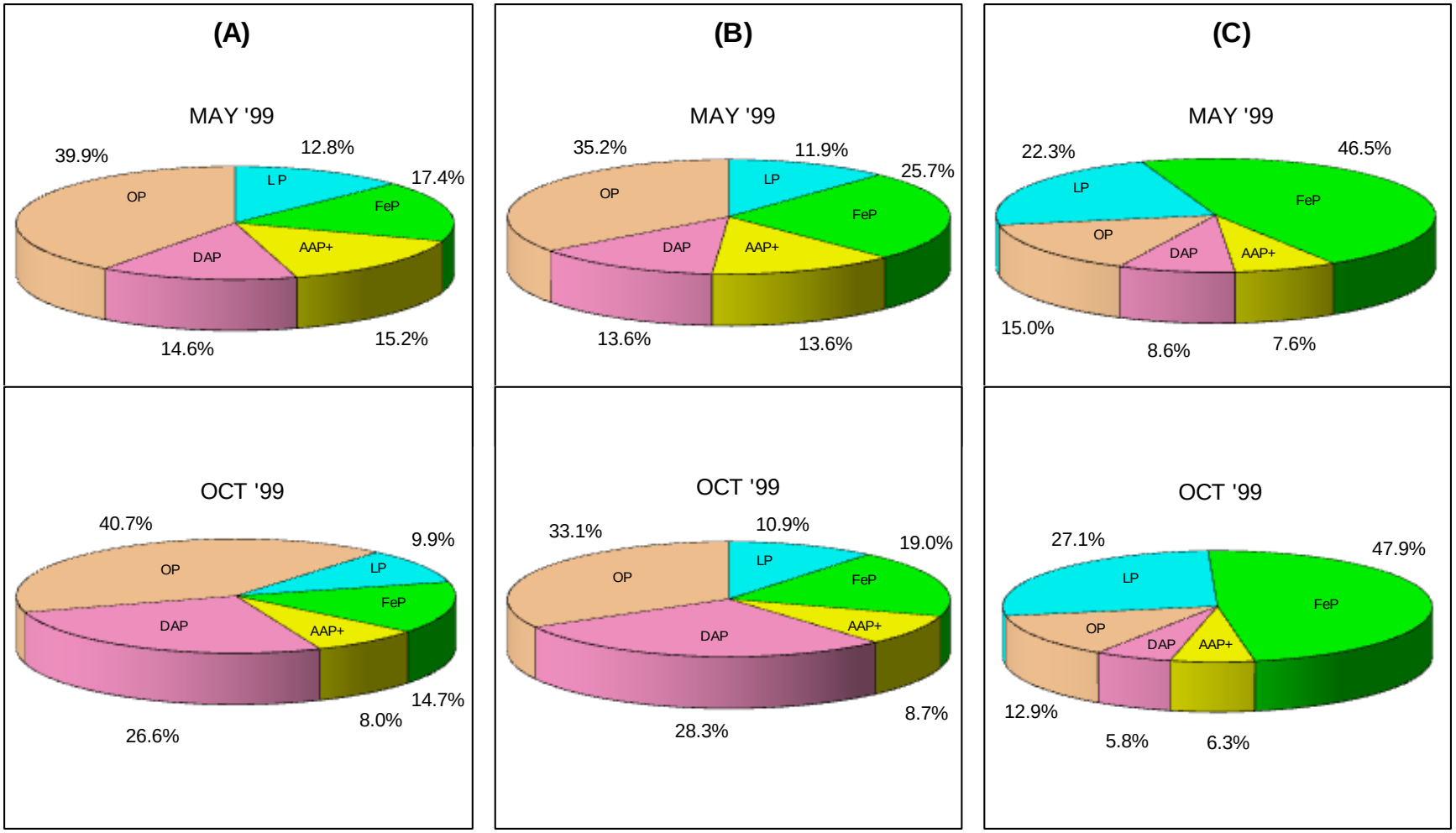

Figure 10: Relative abundance of five phosphorus fractions in sediments from (A) Togcha River, (B) Togcha Estuary, and (C) Togcha Bay. LP = loosely-sorbed P; FeP = ferric iron-bound P; AAP+ = authigenic apatitic P plus biogenic apatitic P plus $CaCO_3$ associated P; DAP = detrital apatitic P; and OP = organic P. Values for each fraction are based on geometric mean concentrations of all site data within each location.

Table 4: Mann-Whitney Two-sample Test for Differences between May and October Data Sets.

Fraction	Sites	Higher Monthly Mean	U-Statistic	Significance
Total Organic Carbon (TOC)	River	May	73	**
	Estuary	May	179	**
	Bay	May	174	**
Reactive iron (R-Fe)	River	Oct	67.5	*
	Estuary	Oct	161	**
	Bay	Oct	149	ns
Loosely-sorbed P (LP)	River	May	65	*
	Estuary	May	124	ns
	Bay	Oct	177	*
Ferric iron-bound P (FP)	River	May	62	ns
	Estuary	May	155	**
	Bay	Oct	148	ns
Authigenic/biogenic apatitic P + $CaCO_3$ P (APP+)	River	May	78	**
	Estuary	May	176	**
	Bay	May	134	ns
Detrital apatitic P (DAP)	River	May	48	ns
	Estuary	Oct	169	**
	Bay	May	179	**
Organic P (OP)	River	May	81	**
	Estuary	May	134	ns
	Bay	May	122	ns

* = P<0.05, ** = P<0.01, ns = not signficant

Dead and decaying algae provide another major source of organic matter to the lower reaches of the estuary, especially during the dry season. These periodically wash ashore from the outer bay region and accumulate in and around the river mouth and adjacent coastline following bouts of rough weather. Overexposure to the sun during the daytime low tides that start in April and continue through August is also a contributing factor in their demise. The higher TOC levels of up to 6% noted inside the estuary mouth during May were considered to be a direct result of such events.

During the height of the wet season, the swollen, silt-laden river purges this area of organic detrital material and dumps large amounts of sediment in the nearshore waters. Over time these deposits have accumulated at the mouth of the river to form a conspicuous cross-mouth bar that helps confine any detrital flotsam entering the estuary. Being of terrigenous origin, and therefore of relatively low organic matter content, the freshly deposited sediments effectively dilute out existing TOC levels in the surface layers, as indicated by the data. As the wet season recedes and stream flows abate, the suspended sediments are deposited further up the estuary resulting in diminished TOC levels here also. It is therefore not surprising that sedimentary levels of TOC were found to be significantly lower in October than May ($P<0.01$; see Table 4).

Bay: TOC levels in bay sediments were fairly stable between sites and ranged from 1-2% over the entire study period. Concentrations were marginally lower at most sites during October, largely as a result of the increased silt discharges described above. Statistical analysis revealed the difference between the two data sets to be highly significant ($P<0.01$).

Table 5: Spearman Rank Correlation Analysis for all Variable Pairs from all Data Sets.

Location	Dry Season (May 1999)						Wet Season (Oct 1999)					
	R-Fe	LP	FeP	AAP+	DAP	OP	R-Fe	LP	FeP	AAP+	DAP	OP
River												
TOC	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
R-Fe		ns	+*	ns	ns	+**		ns	ns	ns	ns	ns
LP			+**	ns	ns	ns			ns	ns	+*	ns
FeP				ns	+*	ns				ns	ns	ns
AAP+					ns	ns					+*	ns
DAP						ns						ns
Estuary												
TOC	ns	ns	ns	ns	ns	ns	+*	+*	ns	ns	ns	ns
R-Fe		+**	+***	ns	-*	-*		+**	ns	+**	ns	ns
LP			+***	ns	-*	-*			-**	+*	ns	ns
FeP				ns	-**	-*				ns	+**	ns
AAP+						ns					ns	ns
DAP						+***						ns
Bay												
TOC	ns	+*	ns	ns	ns	ns	+**	ns	ns	ns	+*	ns
R-Fe		ns	ns	ns	ns	ns		ns	ns	ns	+***	+*
LP			ns	ns	ns	ns			ns	ns	ns	ns
FeP					ns	ns				ns	ns	ns
AAP+						ns						ns
DAP						+**						+**

*P<0.05, **P<0.01, ***P<0.001, ns = not significant, TOC = total organic carbon, R-Fe = reactive iron, LP = loosely-sorbed P, FeP = ferric iron-bound P, AAP+ = authigenic apatitic P plus biogenic apatitic P plus $CaCO_3$ associated P, DAP = detrital apatitic P, OP = organic P.

Reactive Iron (R-Fe)

The R-Fe fraction obtained during the current study was derived from amorphic and crystalline forms of oxidic iron such as ferrihydrite, goethite, lepidocrocite and hematite (Ruttenberg 1992). These secondary minerals are normal components of soils and sediments and are formed, in the presence of water, by natural precipitation and transformation processes under conditions that favor the oxidation of soluble ferrous iron (Fe^{2+}) to insoluble ferric iron (Fe^{3+}). P can be occluded in the matrix of these minerals during their formation, as well as adsorbed onto positively charged binding sites on their surface (Solomons and Forstner 1984). Thus, these minerals are key players in determining the fate and transport of inorganic P in aquatic environments and are largely responsible for sequestering the P fractions identified in Steps I and II of the SEDEX procedure outlined above.

Relative Abundance in Study Area

R-Fe was the second most abundant component measured in sediments behind TOC with concentrations exceeding 5000 μg/g at some sites (Table 3). Such high concentrations are not surprising considering that total iron in soils from this part of Guam frequently exceeds 80,000 μg/g (Demeterio et al. 1986).

Spatial & Temporal Differences

River: Data from the two reference sites (R-1 and R-5) suggest that background levels of R-Fe in sediments from the upper watershed are in the order of 800-1400 μg/g during the dry season. This range approximately triples (2800-3500 μg/g) during the wet season, supporting

earlier suspicions of soil deposition from runoff and riverbank erosion during major storm events. The significantly higher levels of R-Fe determined in October ($P<0.05$) sediments from the river lend additional support to this hypothesis (Table 4).

R-Fe contributions from the BGSTP are evident from the data, particularly in sediments collected during the low stream flow conditions encountered in May. This is to be expected considering that crude sewage typically contains Fe concentrations in the order of 10 mg/L (James 1990). Presumably then, the hypoxic effluent leaving the plant gradually improves in dissolved oxygen content as it cascades down the shallow embankment into the river. This change in redox conditions facilitates the oxidation of soluble ferrous Fe, which precipitates out of solution as the hydrated ferric oxide, forming colloids and surface coatings on bed sediments and detrital material in the water.

Hydrous oxides in colloidal form are carried downstream and settle out in the sediments at rates determined by stream flow and local topography. Between sites R-4 and R-6, the river drops rapidly in elevation and becomes increasingly turbulent as it makes its way to the coast. As a consequence, shallow water settlement of colloidal oxidic iron is somewhat restricted in this stretch of the river as shown by the data. The deeper pools in this region likely accumulate colloidal material but were not sampled during the study.

Estuary: The R-Fe levels of estuarine sediments increased dramatically in a downstream direction and were generally higher than elsewhere in this study area (Figure 4). During May, levels peaked under the Route 4 Bridge (E-10), where the river widened, but pushed towards the mouth (E-14) during October when the river was swollen. The two seasonal maxima measured were 5284 μg/g and 6612 μg/g in May and October respectively. With the exception of a single site, October levels of R-Fe in the estuary were greater than those identified in May. Statistical analysis showed a highly significant difference ($P<0.01$) between the two data sets (Table 4).

The estuarine R-Fe profiles reflect settlement of suspended sediments washed into the river from further upstream, in addition to the salinity induced flocculation and precipitation of hydrated iron oxides and colloidal clay material to which Fe is adsorbed. The *in situ* generation of oxidic iron from anoxic sediment in this region is also suspected. Significant temporal differences in R-Fe levels are therefore understandable in this region given the river's high silt loading during wet season conditions.

Bay: R-Fe concentrations in bay sediments were among the lowest in the study area and generally decreased in a seaward direction away from the estuary. For example, the majority of sites within 225 m of the mouth yielded sedimentary R-Fe levels between 1000-2000 μg/g while those beyond this distance gave values that were mostly between 400-900 μg/g. Although temporal differences in R-Fe were statistically insignificant (Table 4), it is noteworthy that levels were generally higher at most sites during October. Periodic discharges of highly turbid river waters into the bay at that time of the year undoubtedly accounted for this observation.

Correlation Analysis

A significant positive correlation was found between R-Fe and TOC in bay and estuarine sediments collected in October (Table 5). The simultaneous precipitation of iron and river-borne dissolved organic matter in the estuary at this time of the year most likely explains this relationship. The absence of a clear correlation between these two variables in the sediments during May reflects a disruption of these parallel processes. This is to be expected considering

very little freshwater flows into the estuary during the dry season plus the fact that almost all of the organic matter imported into the estuary at this time of the year is of marine origin.

The relationship between R-Fe and TOC in October sediments collected from both bay and estuary is shown in Figure 11. The similarity in slopes of the regression line for both data sets provides evidence that common estuarine processes, namely sedimentation and salinity-induced coagulation and precipitation, influence the abundance of each component in the estuary and bay during the wet season.

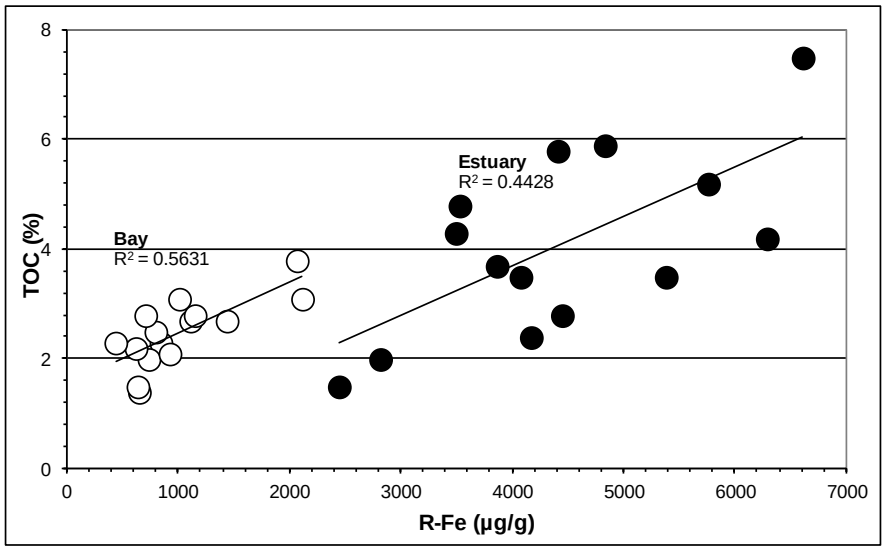

Figure 11: October data sets for total organic carbon (TOC) plotted against reactive iron (R-Fe) in sediments from Togcha Estuary and Togcha Bay.

Loosely-sorbed P (LP)

The LP fraction measured in this study represents P that is weakly bound to the surface of sediment solids, particularly iron oxyhydroxides. According to Ruttenberg (1990), it also includes P released from the lyophilization of bacteria and planktonic organisms in the sediment at the time of collection, in addition to that released into sediment pore waters by redox processes. This fraction is particularly important because it represents that portion of the total P pool that is readily available for biotic use.

Relative Abundance in Study Area

The relative abundance of LP in sediments varied between sites and between collection times, as did all of the P fractions measured. However, the location averages (Table 3) accounted for approximately 9-13% of the total P pool in the river and estuary and 22-27% of that found in the bay over the study period (Figure 10).

Spatial & Temporal Differences

River: Levels of LP in sediments from both reference sites (R-1 and R-5) in the upper reaches of the river were lower than at any other site in the study area and varied little between sampling excursions. The marginally higher level from the tributary site (R-5) likely reflects runoff from the Baza Gardens housing estate. Thus, baseline LP levels for natural waters in this part of the watershed are considered to be somewhere between 15-25 µg/g (Table 3).

LP levels in sediments from the upper section of the Togcha River were clearly influenced by the BGSTP (Figure 5). This was evident during the low flow conditions encountered in May when 1764 μg/g was determined in the fine, flocculent sedimentary material taken from the small shallow pool at the point of discharge (R-2). No doubt the high LP concentration at this site reflects the biological and chemical sequestration of dissolved P present in the wastewater stream. From here, LP concentrations dropped sharply and were an order of magnitude lower in sediments 100 m downstream. Levels thereafter generally diminished in a more gradual fashion in the direction of the estuary as flow rates increased in line with changing topography and elevation.

Levels determined between the outfall and the estuary was significantly lower in October than in May (Table 4). This suggests that much of the LP associated with the fine material observed at the outfall also settled out in the less turbulent parts of the river during the dry season, only to be resuspended and transported further downstream during the high stream flow conditions that preceded the October sampling.

Estuary: LP concentrations in the estuarine sediments collected showed a well-defined trend with levels gradually increasing towards the river mouth on both sampling occasions (Figure 5). The range of values recorded here in May and October were remarkably similar although marginally lower levels were found at most sites during the latter month. Levels were mostly between 50-150 μg/g with the vast majority below 80 μg/g. Statistical analysis (Table 4) revealed no significant difference between the two data sets ($P>0.05$).

It seems likely that the reduction and solubilization of hydrated iron oxides in the anaerobic sediments of the estuary is the dominant mechanism responsible for the generally higher levels of LP in this part of the river when stream flow is interrupted. This process is driven by the decomposition of organic matter largely derived from decaying algae imported into the estuary by the prevailing northeast trade winds and the tides during the dry season, and from the deposition of particulate organic materials and precipitating dissolved organic matter that are flushed downstream during the wet season.

Bay: Bay sediments contained relatively stable LP concentrations that mostly ranged between 40-80 μg/g on both sampling occasions. Most of the sites here had LP levels that were marginally higher in October in direct contrast to that observed elsewhere in the study area. No doubt this was associated with the flushing of fine LP enriched sediments from the river and estuary into the bay during the wet season. The overall difference between the May and October data sets (Table 4) was found to be highly significant ($P<0.01$).

Correlation Analysis

There was a positive correlation between LP and TOC in the bay and estuary in May and October respectively ($P<0.05$), and between LP and R-Fe in both estuarine data sets ($P<0.05$). These relationships imply a connection between all three components in the recycling and sequestration of soluble P in sediment pore waters.

Ferric Iron-bound P (FeP)

FeP is associated with secondary minerals of oxidic iron. These are formed in the porewaters of soil and sediments, and their importance in the fate and transport of P in aqueous environments was mentioned earlier. During the formation of these minerals, inorganic P and certain trace elements are occluded in the hydrated iron oxide matrix and co-precipitate along with them. In this form, P is essentially non-available; however, under anoxic conditions many

such secondary minerals are solubilized and release P back into the surrounding water. Thus, they provide a P sink that is readily transformed back to a biologically available form when certain redox conditions prevail.

Relative Abundance in Study Area

When expressed as a percentage of the total P pool (Figure 10), the average concentrations of FeP listed in Table 3 show a progressive increase in relative abundance as one moves from the river (~16%) to the estuary (~22%) and out into the bay (~47%). Clearly the formation of FeP was not limited by the availability of iron in any of these regions since R-Fe concentrations were substantially higher than those for FeP at all sites throughout the study area.

Spatial & Temporal Differences

River: Sedimentary levels of FeP were similar at both reference sites and changed little over the study period. This suggests that baseline levels in this part of the watershed are somewhere between 50-70 µg/g, which is 2-4 times higher than for LP.

The river distribution profile for FeP was generally similar to that of LP, reflecting major contributions from the BGSTP (Figure 6). The highest concentration (1036 µg/g) was found at the point of discharge during the low stream flow conditions encountered in May. The *in situ* formation of FeP is largely a redox driven process here, as described earlier.

FeP concentrations at most river sites downstream of the outfall were appreciably lower during the wet season. However, while the overall average for October was less than half that determined in May, the identification of a significant difference between the two data sets was obscured by the relatively large number of overlapping values in the statistical matrix.

Estuary: Individual site concentrations of FeP in estuarine sediments ranged from a high of 242 µg/g in May to a low of 27 µg/g in October (Table 3). Although data set averages for both months were significantly different from one another ($P<0.01$), concentration changes in the lower half of the estuary were greater than those occurring further upstream (Figure 6).

In May, levels generally showed a progressive increase along the estuary towards the mouth where stream-flow rates were noticeably slower. Such changes in the hydrodynamic conditions tend to favor the increased deposition of suspended particulate FeP and could account for this trend. Redox driven interactions between Fe and P at the sediment-water interface is also considered to be a major contributing factor in view of the anoxic conditions that often prevail in this region.

The pronounced decrease in FeP concentrations in the lower part of the estuary in October was attributed to the influx of FeP depleted soil into the river during the wet season. Such material, while similar in Fe content to the existing sediments, generally contains much lower concentrations of extractable P (Demeterio et al. 1986a and b). On settling out in the estuary, the imported soil thus tends to dilute out existing FeP concentrations without appreciably changing sedimentary iron levels. The data for R-Fe from these sites lends support to this hypothesis.

Bay: FeP was the dominant P fraction determined in bay sediments and accounted for almost half of the total P pool measured (Figure 10**)**. Levels were also relatively stable in this environment and showed comparatively little spatial and temporal variability. Almost all sites yielded data that fell between 75-150 µg/g and most were above 100 µg/g.

Correlation Analysis

Examination of the scatterplots shown in Figure 12 clearly indicates a positive relationship between LP, FeP, and R-Fe in river and estuarine sediments during May. This is to be expected considering their redox related interactions with one another. However, due to the limited database, significant correlations between all three variable pairs were only identified in the estuary on this sampling occasion (Table 4). In October, the same positive association between all three components may have been obscured by the relatively high concentrations of R-Fe in the river as a result of bank erosion and terrestrial runoff. No significant correlations were identified between these variables in bay sediments in either month, a factor presumably related to the redistribution and reorganization of dominant P fractions in this region.

Authigenic Apatitic P plus Biogenic Apatitic P plus $CaCO_3$ associated P (AAP+)

Step III of the SEDEX procedure extracts P from several calcium-bound sources. These include authigenic apatites that are formed in marine sediments by diagenetic processes; biogenic apatites, which are found, for example, in fish skeletons, scales and teeth; and calcite and aragonite structures like coral skeletons, mollusk shells, stromatolites, coccolithophore, and foraminifera. Some P contributions can also be expected from certain clays present in the sample, particularly smectite (Ruttenberg 1990). It is noteworthy here that smectite, also known as montmorillinite, is common throughout the Togcha River watershed (Siegrist et al. 1996), along with limestone.

Carbonate fluorapatite (francolite) is the most stable form of authigenic apatite in seawater and is also the most abundant (Balson 1990). It forms slowly in undisturbed, anoxic sediments when porewaters become super-saturated with P (and fluoride) ions. This process is intimately linked to the microbial decomposition of organic matter and the dissolution of hydrated iron oxides at oxidation-reduction boundaries (Howarth et al. 1995).

Although apatites can potentially release soluble P to the surrounding water, dissolution rates are very slow under normal conditions (Calmano 1981). Both authigenic and biogenic apatites can therefore be regarded as a permanent sinks for P (Ruttenberg 1990). Calcite and aragonite bound P are also relatively unavailable although carbonate dissolution can occur in the porewaters of anoxic sediments, facilitating the release of biologically available P back into the water column (Howarth et al. 1995).

Relative Abundance in Study Area

A review of the pie charts shown in Figure 10 indicates that AAP+ was not a dominant component of the sedimentary P pool in the study area. In fact, it was generally the least abundant fraction noted in the October samples representing around 6-9% of the total P pool. Proportionately higher amounts of AAP+ were noted in the May sediment collections, especially from the river and estuary where average levels accounted for approximately 13-15% of the total P pool.

Spatial & Temporal Differences

River: Background concentrations of AAP+ in sediments from the reference sites ranged from about 20-100 μg/g and appear to be seasonally dependent. Soil imported into the river during the wet season diluted out existing sediment concentrations of AAP+ and accounted for the lower levels found here and elsewhere in the river during October. The difference between the May and October data sets for this region was found to be highly significant ($P<0.01$).

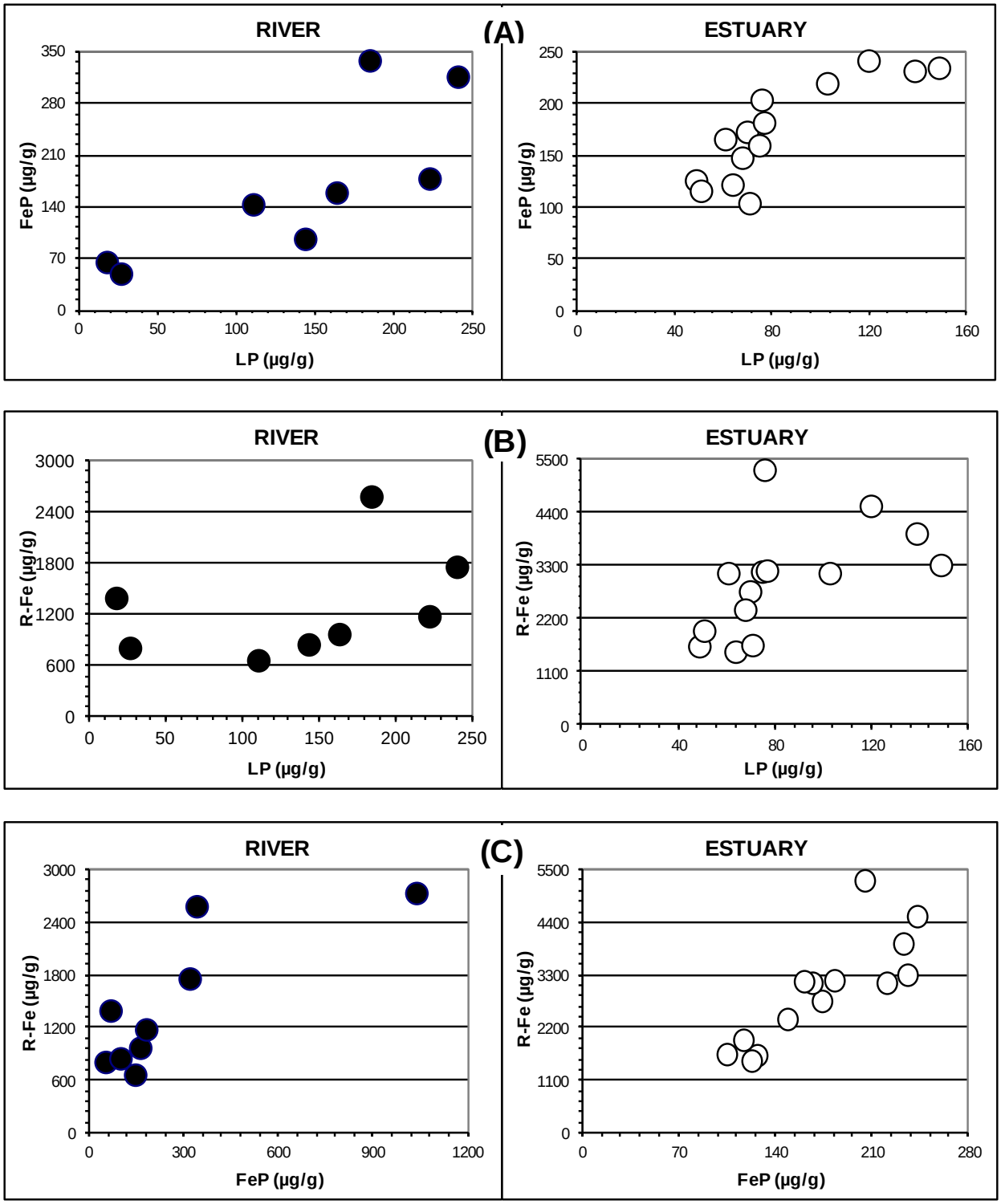

Figure 12: May data sets for loosely-sorbed P (LP) plotted against **(A)** ferric iron-bound P (FeP) and **(B)** reactive iron (R-Fe), and **(C)** FeP plotted against R-Fe, in sediments from Togcha River and Togcha Estuary.

The May data clearly identify the BGSTP as a major contributor of AAP+ to the watershed (Table 3). Contributions from this source explain why AAP+ levels downstream of the reference sites were all well above baseline at this time of the year.

The high AAP+ output from the BGSTP is interesting and leads one to speculate on possible sources of this P fraction. Certainly, the formation of amorphous calcium phosphate and other authigenic apatite precursors in the plant itself seems unlikely given the slow nucleation of P and the absence of supersaturated conditions necessary to promote such reactions (House 2000). Likewise, the formation of calcite (and associated P) is likely to be prevented by the high dissolved organic matter content acting to inhibit calcite nucleation (Neal 2001). Thus, contributions from biogenic apatites (fish bones and scales) and other refractory P components present in human wastes, in addition to clay materials found in laundry wastewater, are the most likely explanation for much of AAP+ present in the BGSTP effluent.

Carbonates derived from the various limestone formations in the watershed, smectite clays, and biological remnants of stream dwelling organisms are believed to be the primary sources of sedimentary AAP+ in riverine areas unimpacted by the BGSTP. Calcite precipitation associated with algal photosynthesis and stromatolite activity may also play an important role here.

Estuary: AAP+ levels in estuarine sediments ranged from 30-120 μg/g and were generally lower than those found in the upper part of the watershed. The significantly lower levels recorded here during October ($P<0.01$) are attributed to dilution by the mass fall-out of suspended soil particles during flood conditions. The recovery noted in May implies that much of the particulate AAP+ found in the estuary actually comes from the bay and is imported into the estuary by tidal activity under low to no stream flow conditions. Possible sources of AAP+ transported back into the estuary are authigenic and biogenic carbonates of marine origin and terrigenous clay deposits resuspended from the cross-mouth bar. Indeed, analysis of the muddy, scum-like substance washed into the Togcha estuary on a rising tide revealed a fine-grained material that was 50-60% carbonate, 20-30% clay, and 10-25% organic matter. Contributions specifically from authigenic apatite seem unlikely because the high instability and deposition rates of sediments in the estuary and bay do not favor the formation of this particular mineral (Ruttenberg 1990).

Bay: The AAP+ levels in bay sediments were low and extremely stable, the great majority being less than 20 μg/g. Such low values cast doubt on the significance of imported marine carbonates in elevating AAP+ levels in the estuary during the dry season. Thus, contributions from resuspended clay and mud scums lifted off the bottom and transported back into the estuary on rising tides seem the more likely explanation. There was no significant difference between the two temporal data sets ($P>0.05$) for this part of the study area.

Correlation Analysis

AAP+, LP, and R-Fe were all positively correlated with one another ($P<0.05$ or better) in October sediments from the estuary. It seems likely that all three fractions were predominantly associated with sediments and soil washed into the estuary from further upstream during the wet season, and that clay accounted for much of the AAP+ measured at this time. No significant correlations between AAP+ and any previously discussed components were identified anywhere else over the study period.

Detrital Apatitic P (DAP)

Detrital apatites are calcium phosphate minerals derived from the mechanical and chemical fragmentation of land-based igneous and metamorphic rocks. They are transported into rivers and streams in runoff from the land, and as a result, tend to be more concentrated in coastal sediments compared with those further offshore. Detrital apatites, unlike authigenic apatites, are not formed from reactive P. They do, however, represent a relatively permanent sink for P in much the same way as their authigenic counterparts.

Relative Abundance in Study Area

DAP was more abundant in the river and estuary than in the bay. This was particularly noticeable during the high stream flow conditions encountered in October when levels accounted for about 27-28% of the total P pool in both regions (Figure 10). In contrast, DAP levels in bay sediments represented only ~6-9% of the total P pool over the entire study period, and ranked among the least abundant P fractions measured (Figure 10).

Spatial & Temporal Differences

River: Background levels of DAP in river sediments were approximately 75-135 μg/g. Levels elsewhere in the watershed were all less than 200 μg/g except at the BGSTP outfall site (R-2) where close to 400 μg/g was recorded in May (Table 3). Elevated levels of DAP at this spot during the dryer months are clearly not associated with stormwater runoff from the land. More likely, they reflect contributions from domestic wastewaters entering the plant, and possibly from soil mobilized from the drainage ditch by the effluent stream as it makes its way down gradient into the river.

As expected, levels of DAP in river sediments were generally higher during the wet weather conditions encountered in October and were attributed largely to riverbank erosion and soil imported from the land during major rain events (Figure 8). However, the difference between seasonal data sets was marginal and not significant at the 95% confidence level (Table 4).

Estuary: In May, DAP levels rose sharply from ~120-180 μg/g in the upper portion of the estuary (sites E-1 to E-5) and then rapidly declined to a low of ~30 μg/g towards the mouth. The general displacement of this concentration profile towards the bay in October represented the influx of fresh terrigenous material into the estuary during high stream flow conditions. The difference between the two data sets was highly significant ($P<0.01$), as shown in Table 4. Such differences could reflect annual variations in storm duration and intensity in terms of soil mobilization rates within the watershed during the wet season. They could also point towards partial burial of DAP by marine deposits mobilized into the estuary by wind and tidal activity during the dry season (see below).

Bay: DAP concentrations in bay sediments dropped sharply from ~40-90 μg/g at sites within 100 m of the estuary mouth to ~10-20 μg/g in samples collected further afield. The higher levels found at most sites during May ($P<0.01$) suggest small amounts of DAP continue to be exported from the estuary into the bay during the dry season. This is contrary to that expected given the absence of any significant stream flow at this time of year. Another possibility is that DAP concentrations are artificially raised by the selective removal of lighter components from bay sediments during the dry season by wind and tidal activity. These are then imported into the estuary in suspension and as components of the surface films or "mud scums" described earlier.

Correlation Analysis

Correlation analysis revealed a number of significant relationships between DAP and the other fractions so far discussed (Table 5). However, since detrital apatite is chemically inert, such relationships are believed to be independently linked via common sources and transportation processes. These are briefly discussed below.

Scatterplots of the river sediment data suggested that DAP was positively correlated with LP, FeP, and AAP+ in the watershed and point towards common terrigenous sources for all four fractions (Figure 13). However, statistical analysis failed to identify a significant correlation between the variable pairs DAP:LP and DAP:AAP+ in May, and between DAP:FeP in October (Table 5). The analysis was hampered by the limited sample size.

The significantly negative correlations between DAP:LP and DAP:FeP in May sediments from the estuary contrast sharply to those found in the river. However, close inspection of the scattergrams for each variable pair clearly shows that this relationship reversal is due to the differential clustering of data sets in the upper and lower regions of the estuary (Figure 14). When the clusters were analyzed independently no significant correlations were identified between the variable pairs.

The clustering indicates that sediments in the upper estuary (sites E-1 to E-8) were proportionately enriched with DAP while those from the lower region (sites E-9 toE-14) were proportionately higher in LP and FeP fractions. Such differences probably reflect differential sedimentation rates between fractions, with much of the heavier DAP settling out higher in the estuary during the wet season. Redox driven transformation process influencing iron recycling within the estuary, and the wind and tide driven importation of iron rich particulates from the bay, are also thought to contribute towards higher FeP and LP levels in the lower reaches of the estuary during the dry season.

DAP and R-Fe were positively correlated ($P<0.001$) in bay sediments collected in October after substantial quantities of silt were washed out from the river. The terrigenous connection between these two fractions is therefore highlighted once again.

Organic P (OP)

In unpolluted soils and sediments, extractable OP is largely a component of dead and decaying organic matter of plant origin (Schlesinger 1997). Dominant OP compounds include inositol phosphates and phosphomonoesters. Many other OP compounds remain to be identified. Inositol P can account for up to 50% of extractable OP in sediments. It is readily sorbed by iron oxides and clay materials, and forms complexes with humic and fulvic acids. Consequently, it is somewhat protected from enzymatic attack by microbial phosphatases and tends to be relatively persistent (Wetzel 1999).

Sediments impacted by domestic wastewater are nutrient and organic matter enriched and tend to support relatively high densities of microorganisms and some small invertebrates, like leaches and tubificid worms (Connell and Miller 1984). In such instances, higher proportions of OP from key cellular components like nucleic acids, phospholipids, phosphatidylcholine phosphodiesters, and phosphotriesters can be expected. In general, such compounds are rapidly mineralized and recycled supporting further biological growth (Wetzel 1999).

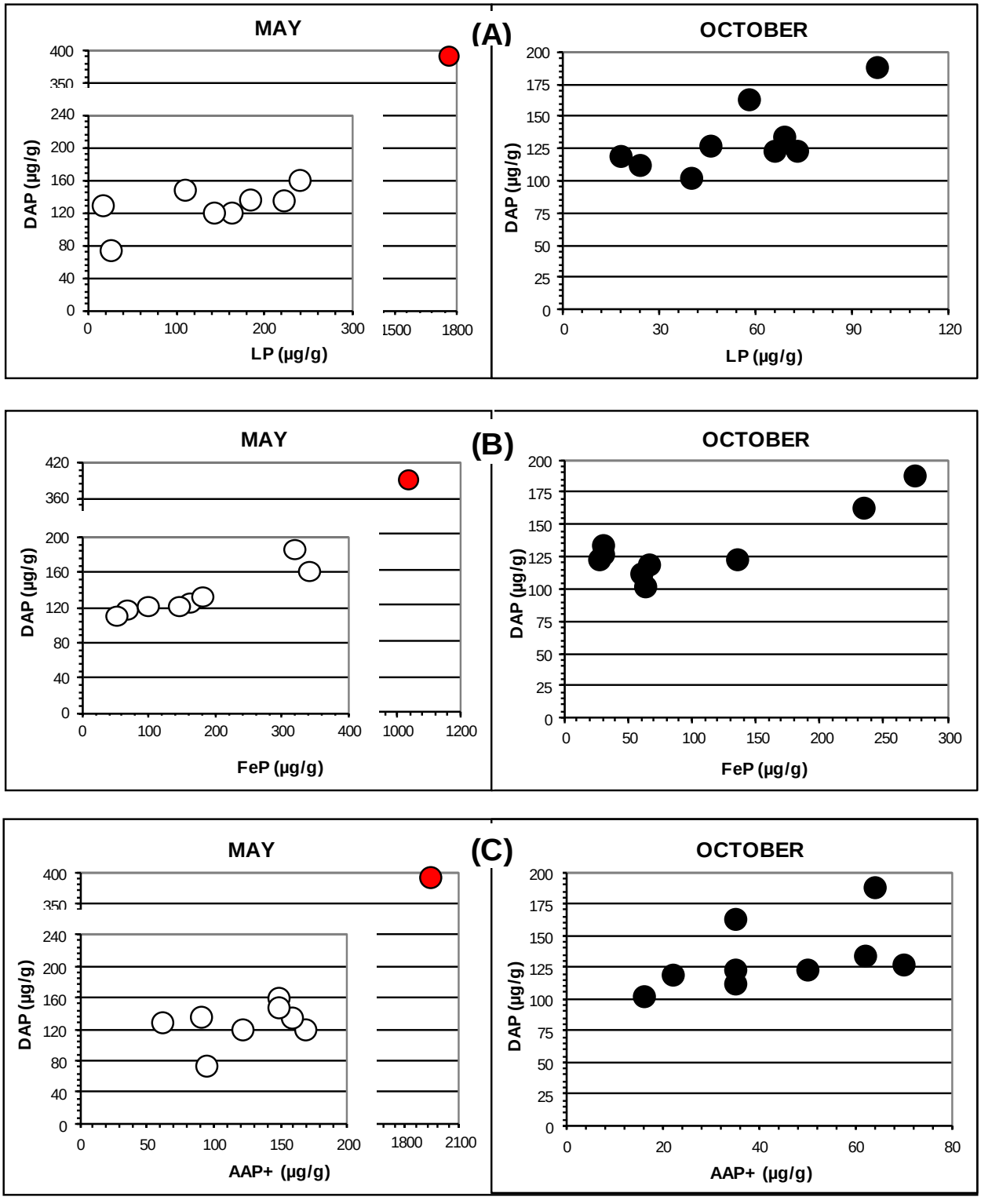

Figure 13: Detrital apatitic P (DAP) plotted against **(A)** loosely-sorbed P (LP), **(B)** ferric iron-bound P (FeP), and **(C)** authigenic apatitic P plus biogenic apatitic P plus $CaCO_3$ associated P (AAP+), in sediments from Togcha River on each sampling occasion. Red filled data point for BGSTP outfall site (R-2).

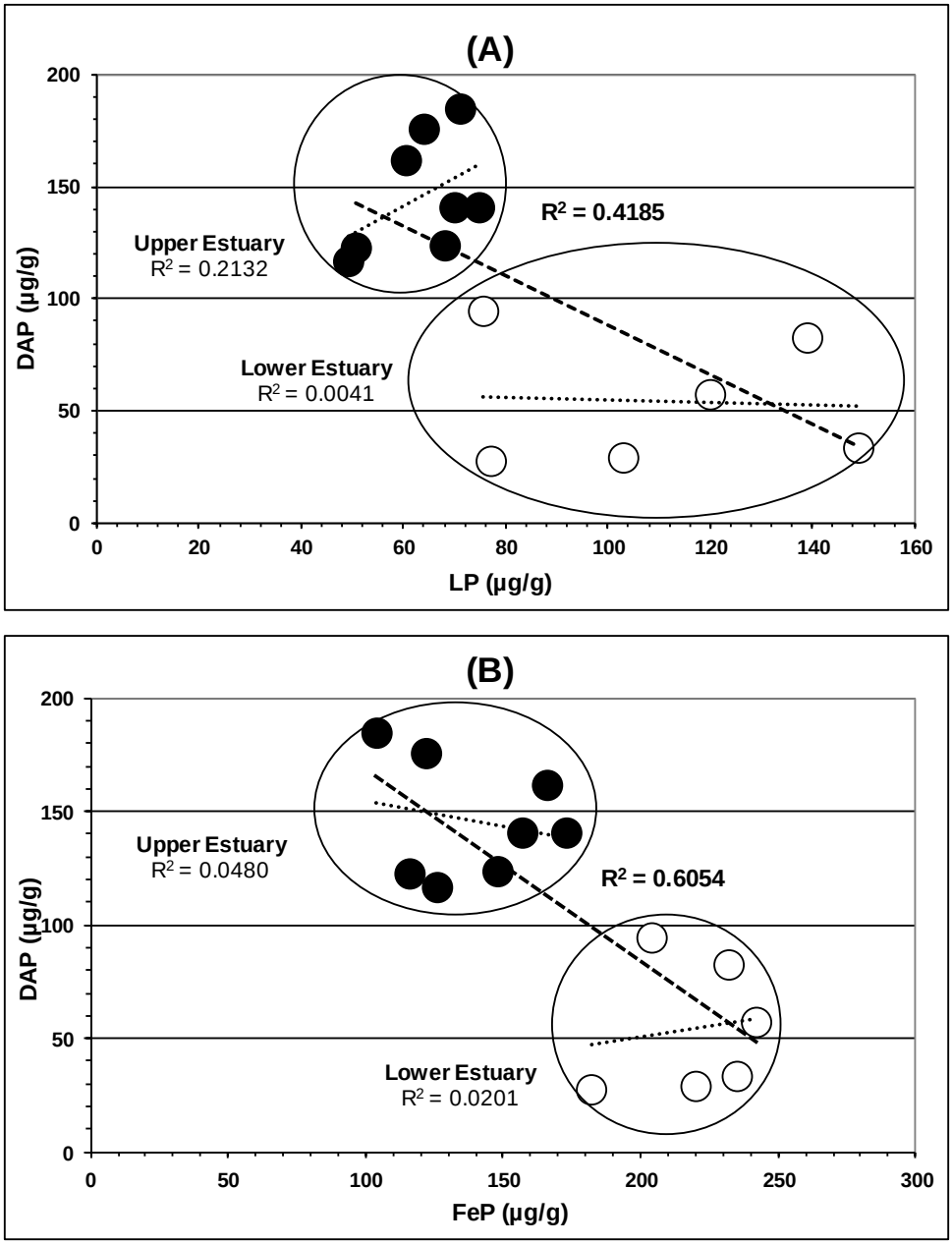

Figure 14. May data sets for detrital apatitic P (DAP) plotted against **(A)** loosely-sorbed P (LP) and **(B)** ferric iron-bound P (FeP) in sediments from the upper (E-1 to E-8) and lower (E-9 to E-14) halves of Togcha Estuary. Regression lines for data sets and sub-sets are shown by dashed and dotted lines, respectively.

Relative Abundance in Study Area

OP was consistently the most abundant P fraction analyzed in both river and estuarine sediments and accounted for 33-40% of the total P pool (Figure 10). In contrast, OP represented only 13-15% of the total P pool in bay sediments and ranked third behind FeP and LP in order of relative abundance (Figure 10).

Spatial & Temporal Differences

River: Reference site concentrations of sedimentary OP varied from 180-364 µg/g over the study period (Table 3). Levels downstream of the BGSTP outfall site (R-2) were all within this background range. At the outfall site itself, OP concentrations exceeded 4000 µg/g in May but had returned to background levels by October. Such pronounced seasonal disparity was only apparent at this river site and was undoubtedly related to the flushing of OP rich bottom deposits that had accumulated there over the dry season, during high stream flow conditions. These nutrient and organic matter enriched sediments were subsequently replaced with relatively depauperate terrigenous material washed into the river during major storm events. OP levels at all other sites declined by 20-40% during wet season conditions, presumably for the same reason. Differences between the May and October data sets were shown to be highly significant ($P<0.01$) as shown in Table 4.

The elevated concentrations of OP at the outfall site during the dry season could have originated from the BGSTP. However, information presented in GWA's Discharge Monitoring Reports for this treatment plant indicates otherwise (Guam Waterworks Authority 1999-2001). Indeed, their data generally show very little difference between RP and total P levels in the plant effluent, which means that OP levels in this medium are normally low. It should be mentioned however, that the GWA samples were all filtered (0.45µm) prior to analysis. This process could effectively remove fine particulate and colloidal OP from the sample, thus excluding it from analysis. Additionally, some labile forms of filterable OP are hydrolyzed to inorganic P during the acidification process necessary for ortho-P analysis (APHA 1992). Notwithstanding these constraints, the lack of OP enrichment in sediments immediately downstream of BGSTP tends to support the implications of the GWA data. The alternative hypothesis, then, is that the extremely high level of OP measured at the outfall site during the dry season was largely formed *in situ* and associated with the biotic components living in the soft muddy ooze. While the microbiological biomass of sediments at this site was never determined, tubificid worms were found here in abundance.

Estuary: OP concentrations in sediments from within the estuary varied from 83-443 µg/g over the course of the study (Table 3). Most were within, or close to, the range of values listed above for the river reference sites. Overall, no significant difference between data sets was shown (Table 4) although it is clear from the distribution profile shown in Figure 9 that levels were consistently higher in May at all sites upstream of the Route 4 Bridge (sites E-1 to E-8). Interestingly enough, these sites demonstrated a generally progressive increase in OP concentrations down the estuary at this time of the year. This trend is thought to reflect microbial population increases promoted by the flocculation and precipitation of dissolved organic matter in the upper estuary at the end of the previous wet season. Much of this organic matter probably originated from the BGSTP in view of the elevated BOD of the effluent (Guam Waterworks Authority 1999-2001). Upon precipitation it would therefore have provided a readily utilizable carbon and energy source to sediment dwelling microorganisms downstream.

The sharp decline in OP concentrations in the anaerobic sediments of the lower estuary (E-9 to E14) in May suggests major differences in the activity and relative importance of the biological and chemical transformation processes operating here for P. Certainly, the higher levels of FeP in May samples from the lower estuary strongly suggests that dissolved iron in sediment pore waters is much more effective in excluding mineralized P from the biota in this region compared with further upstream. Likewise, clays imported back into the estuary in the surface scums of rising tides may also compete with the biota for labile P within depositional zones.

During the wet season, such OP discrepancies between the upper and lower regions of the estuary disappear as the relatively enriched sediments at the former location are flushed out to sea and replaced by OP depleted particulates of terrigenous origin. Higher levels of R-Fe throughout the estuary, at this time, support this contention.

Bay: OP levels in bay sediments dropped rapidly within 100-150 m of the river mouth and were mostly between 25-50 µg/g outside the area of major deposition. Temporal differences between the two data sets were not significant ($P<0.05$) although increased levels around the mouth (B-1 and B-2) were apparent during the wet season and presumably reflect the mobilization of OP sources from within the watershed.

Correlation Analysis

A highly significant positive correlation was observed between OP and DAP in May sediments from the estuary ($P<0.001$) and in May and October sediments from the bay ($P<0.01$). The positive correlation between these P forms suggests a common link with terrestrial sources.

OP and R-Fe were positively correlated with one another in river sediments collected in May ($P<0.01$). A similar though non-significant trend between these two variables also occurred in October. The propensity of OP for clays and iron oxides could account for this relationship, at least in part. Certainly, microbial populations in the BGSTP effluent stream and sediments adjacent to the outfall provide a continuous and renewable source of OP for such interactions.

The significantly negative correlations between OP and R-Fe, LP and Fe-P in the May estuarine sediments are caused by the differential data clustering in the upper and lower regions of the estuary (Figure 15). When the data sets for the two regions were analyzed separately, all three variable pairs yielded weak positive relationships in the upper estuary. However, the relationships between them in the lower estuary were far more convincing, presumably as a result of their interactive participation in P transformation processes in the anoxic sediments at this location.

The absence of any significant relationship between TOC and OP anywhere in the study area was unexpected and suggests that much of the former is composed of P depleted refractory material. Likewise, the fact that OP and AAP+ were not correlated anywhere supports earlier claims that the AAP+ fraction measured during this study does not include authigenic apatite (carbonate fluorapatite) since the formation of the latter in marine sediments is dependent upon the presence and subsequent mineralization of OP (Ruttenberg 1990).

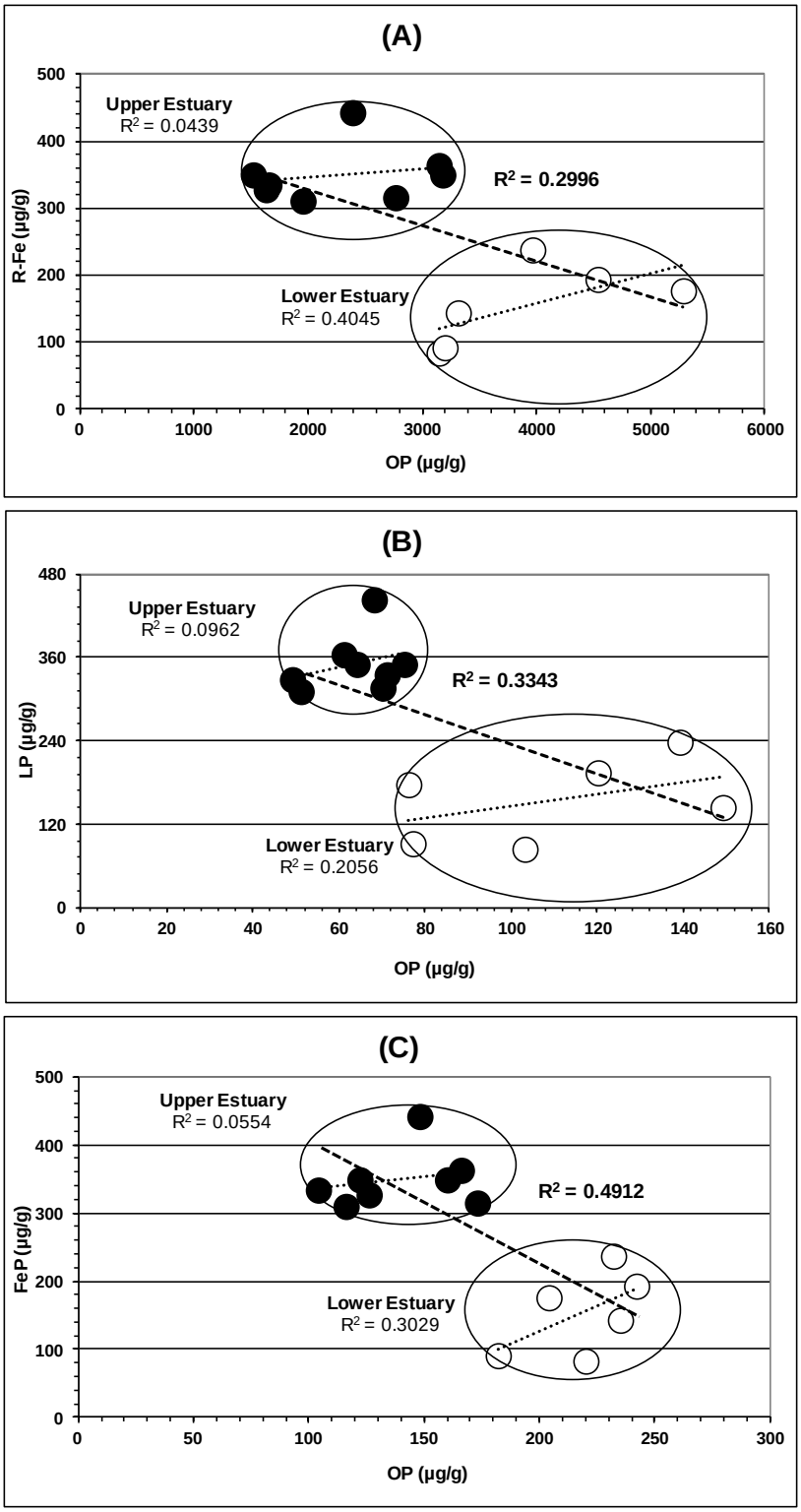

Figure 15: May data sets for organic P (OP) plotted against **(A)** reactive iron (R-Fe), **(B)** loosely-sorbed P (LP), and **(C)** ferric iron-bound P (FeP), in sediments from the upper (E-1 to E-8) and lower (E-9 to E-14) halves of Togcha Estuary. Regression lines for data sets and sub-sets are shown by dashed and dotted lines, respectively.

WATER

The analytical data for water samples collected from estuary sites E-10 and E-14 are presented in Table 6. Changes in water depths over the three sampling periods ranged from 0.3-0.5 m. No obvious stream flows were apparent in the river below site R-7. Other points of significance are discussed below for each parameter investigated.

Temperature

As expected, temperatures in the water column followed ambient air temperatures and gradually increased during the day and decreased at night (Figure 16). Overall, a range of 25.6-32.9 ^{0}C was noted. Depth-dependent temperature gradients were distinctive at the mid-estuary site with surface water being warmer than the underlying water after sunrise and cooler after sunset. This trend was not seen at the mouth, presumably because of lagoonal buffering.

Salinity

Salinity profiles were clearly depth-dependent at each site with bottom waters being the most saline (Figure 17). The progressive decline in surface water salinities over time was indicative of freshwater intrusion and was presumed to be associated with groundwater seepage within the estuary. Several small seeps and springs were identified at low tide along the shoreline immediately north of the river mouth.

Dissolved Oxygen (DO)

Photosynthetic and respiratory processes in the water column and underlying sediments influence dissolved oxygen (DO) levels in the estuary. Other factors of importance during this study were the continual influx of comparatively well-oxygenated water from the bay and efflux of oxygen-depleted groundwater from the land.

The implications of the data presented here for the mid-estuary are that DO levels rise from a night-time low of ~2.0 mg/L, about 4 hours after sunrise, to a daytime high of 5-6 mg/L sometime after midday (Figure 18). During evening hours, levels diminished slowly and return to 2.0 mg/L around midnight, some 5 hours after sunset. It is recalled that DO levels of 2.0 mg/L, or less, favor the reduction of insoluble ferric iron (Brezonik 1972) and facilitate the movement of dissolved P across the sediment-water interface.

Temporal DO profiles at the mouth of the estuary were somewhat noisier, presumably as a result of tidal mixing processes. Nevertheless, levels displayed the same general pattern of increase over time, during daylight hours, as that observed in the middle reaches of the estuary.

The relatively high DO levels noted in the bottom waters at this site are especially noteworthy and reflect wave-generated movement of denser bay water back and forth across the cross-mouth bar, even at low tide. Such movement would encourage mixing of stagnating bottom waters and help facilitate the export of sediment-released nutrients out into the bay.

Reactive P (RP)

Shoreline seepage samples (brackish), collected earlier from around the mouth of the river contained ~15-20 µg/L RP. Groundwater seeping into the estuary further upstream thus accounted for the elevated concentrations of RP in surface waters at both sites during the present work (Figure 19). The fact that all bottom water samples were consistently higher in RP than their mid-water counterparts clearly identifies the underlying sediments as a contributing source of P to the water column.

Table 6: Analytical data for water samples collected over receding high tides from Togcha River Estuary in April (Site E-10) and May 2001 (Site E-14).

Time	Sample[a]	Depth (m)	Temp. (^{0}C)	Salinity (ppt)	D.O.[b] (mg/L)	Ortho-P[c] (µg/L)	Nitrate-N (µg/L)	Nitrite-N (µg/L)	Ammonium-N (µg/L)
Site E-10: Daylight									
7:40 AM	S	0.15	27.0	29.6	2.00	8.25	149	1.71	41.9
	M	0.48	27.0	32.4	2.00	5.17	98.3	<1.00	42.8
	B	0.97	27.0	34.1	1.85	6.36	68.9	<1.00	58.0
8:40 AM	S	0.15	27.4	23.2	2.06	11.1	216	3.13	41.4
	M	0.48	25.8	31.0	1.72	6.23	81.9	<1.00	51.7
	B	0.97	25.6	32.7	1.74	7.52	78.3	<1.00	55.3
9:55 AM	S	0.15	27.8	21.5	2.24	16.5	312	4.31	44.5
	M	0.41	27.2	27.7	1.82	9.32	146.3	1.99	49.5
	B	0.81	27.4	30.7	2.2	10.4	70.1	<1.00	71.9
10:55 AM	S	0.15	28.2	15.8	3.31	18.4	498	3.83	41.7
	M	0.30	27.9	32.2	2.72	9.83	167	1.79	44.2
	B	0.61	28.0	35.9	3.45	18.0	68.2	<1.00	88.2
12:00 AM	S	0.15	28.8	14.2	4.01	20.2	451	4.29	42.8
	M	0.25	27.8	29.7	1.89	10.3	140	1.37	61.2
	B	0.48	27.8	35.4	3.41	16.1	69.2	1.55	113
Site E-10: Darkness									
7:00 AM	S	0.15	31.6	24.6	4.43	8.67	179.56	3.69	54.56
	M	0.51	32.4	30.1	5.40	6.06	82.24	2.02	80.11
	B	1.02	32.9	31.5	3.90	6.22	58.29	<1.00	98.32
7:30 AM	S	0.15	30.8	19.2	3.66	11.98	211.63	3.15	53.29
	M	0.44	32.5	26.5	4.48	6.59	100.93	3.88	69.49
	B	0.89	32.7	32.5	4.70	8.28	56.04	1.78	130.02
8:30 AM	S	0.15	30.0	15.6	3.39	15.42	243.05	4.37	43.78
	M	0.41	32.2	28.2	4.80	6.44	118.99	3.46	79.95
	B	0.81	32.5	31.2	4.32	8.51	55.72	2.34	147.52
9:25 AM	S	0.15	29.4	12.5	2.53	20.36	265.67	4.17	41.70
	M	0.38	32.3	29.4	4.32	5.67	79.30	1.14	90.90
	B	0.76	32.5	33.9	3.88	13.54	65.73	<1.00	204.48
11:00 AM	S	0.15	28.8	10.0	2.58	21.73	363.91	5.98	36.06
	M	0.36	31.9	27.0	2.88	10.44	93.59	6.16	126.46
	B	0.71	32.3	29.2	2.51	16.50	67.15	2.76	253.70
Site E-14: Daylight									
8:38 AM	S	0.15	27.2	34.4	2.99	<0.34	<1.34	<1.00	<2.49
	M	0.61	27.2	34.4	6.03	<0.34	<1.34	<1.00	<2.49
	B	1.22	27.2	34.4	5.99	<0.34	<1.34	<1.00	<2.49
9:30 AM	S	0.15	26.9	32.2	5.98	2.70	37.49	1.02	29.35
	M	0.62	27.5	33.7	4.82	0.60	15.16	<1.00	<2.49
	B	1.14	27.5	34.2	5.59	1.72	2.57	<1.00	5.55
10:30 AM	S	0.15	27.8	23.5	3.89	10.67	119.54	4.66	49.21
	M	0.33	28.3	31.6	6.64	1.72	17.96	<1.00	14.44
	B	0.66	28.3	32.9	6.63	2.84	9.48	<1.00	22.97
11:34 AM	S	0.15	29.1	21.6	4.90	12.75	147.48	5.56	68.25
	M	0.36	28.5	31.3	5.60	1.79	22.46	<1.00	14.18
	B	0.71	29.1	32.5	7.44	3.84	12.11	<1.00	26.02

[a]Sample 'S 'M' and 'B' from surface, mid and bottom depths respectively; [b]dissolved oxygen; [c]orthophosphate-P.

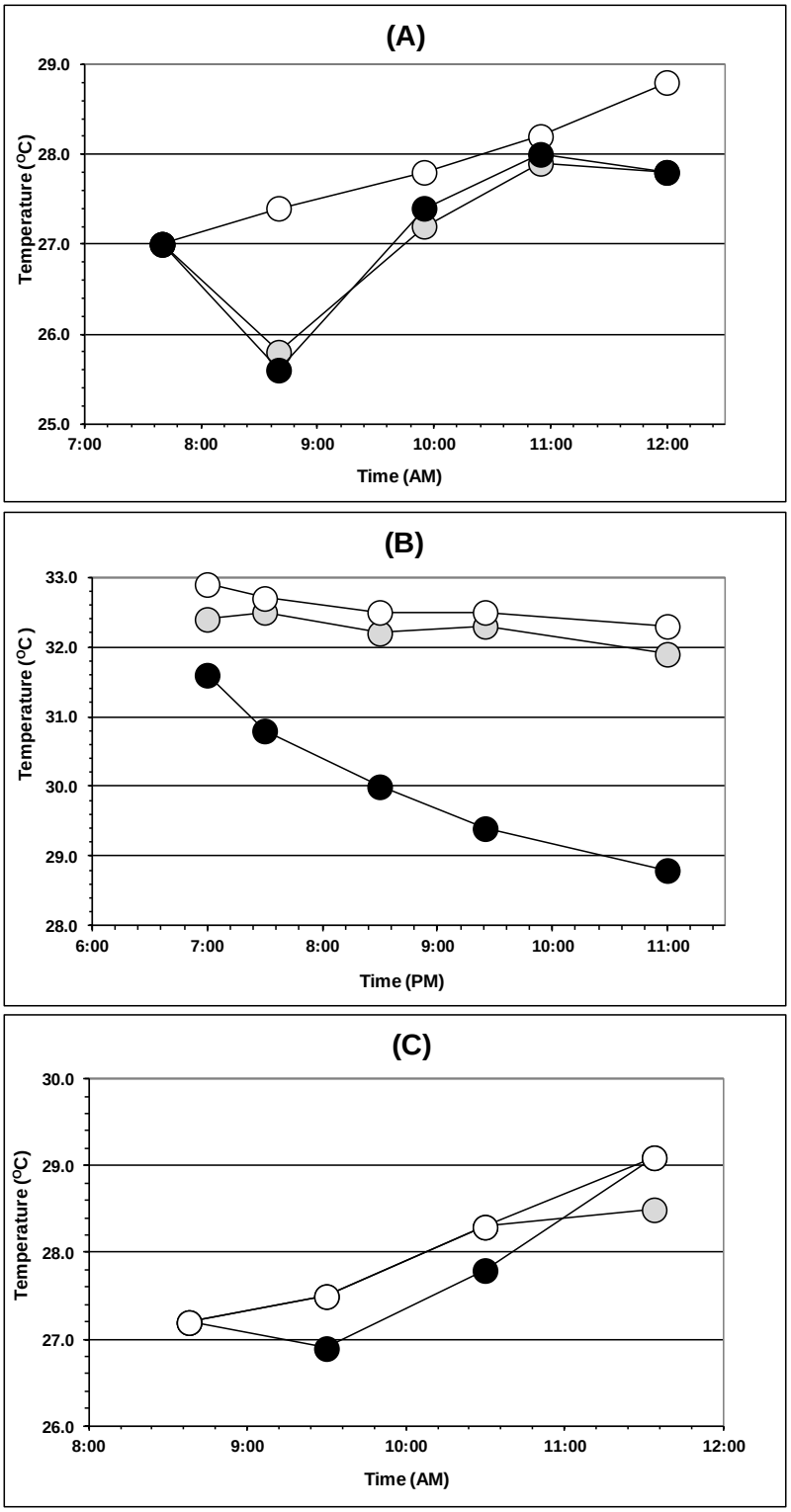

Figure 16: Temperature profiles at surface (white filled circles), mid (grey filled circles), and bottom (black filled circles) depths in the water column over receding high tides at Togcha Estuary sites E-10, during **(A)** daylight and **(B)** darkness, and **(C)** E-14 during daylight.

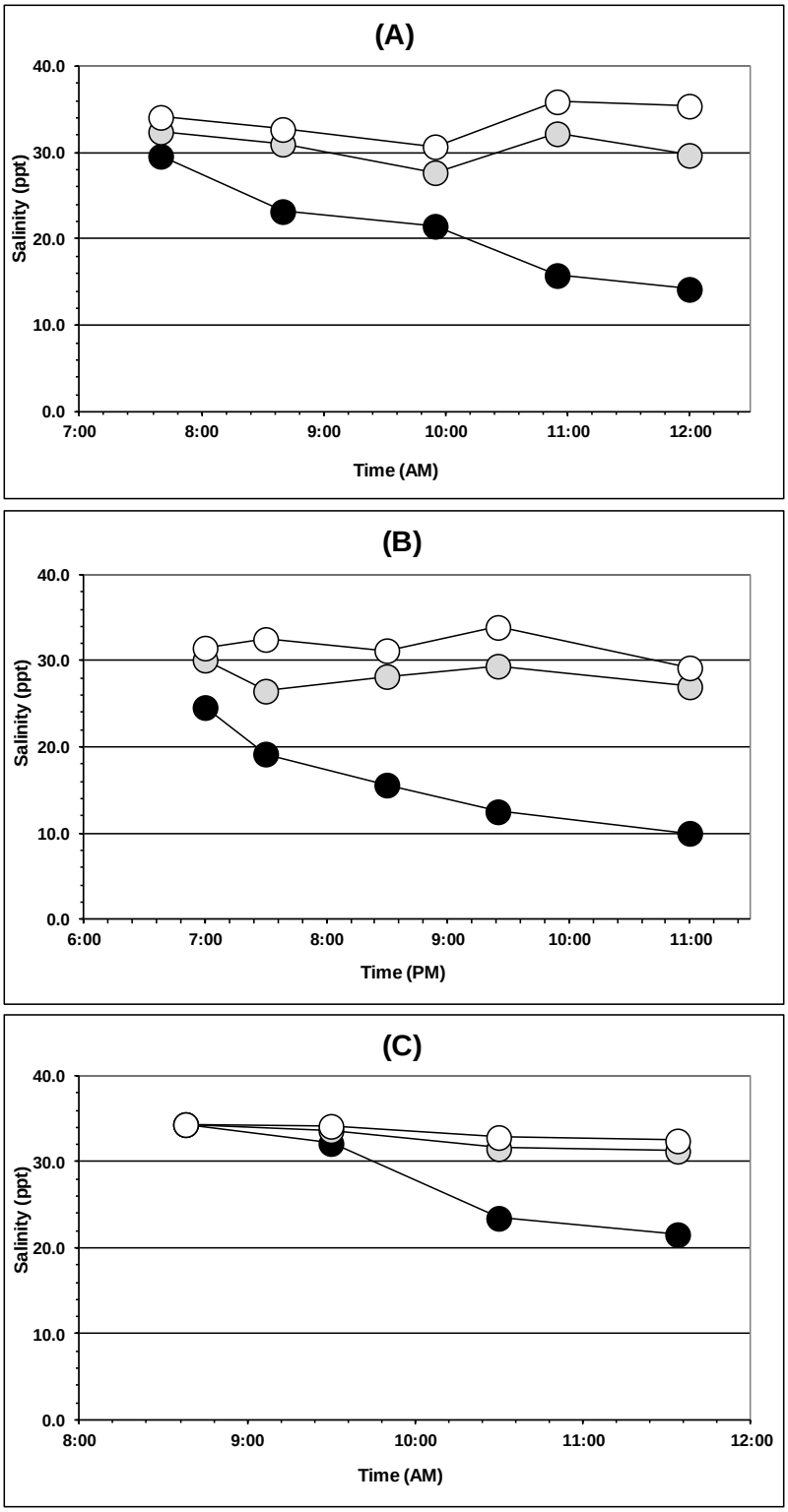

Figure 17: Salinity profiles at surface (white filled circles), mid (grey filled circles), and bottom (black filled circles) depths in the water column over receding high tides at Togcha Estuary sites E-10, during **(A)** daylight and **(B)** darkness, and **(C)** E-14 during daylight.

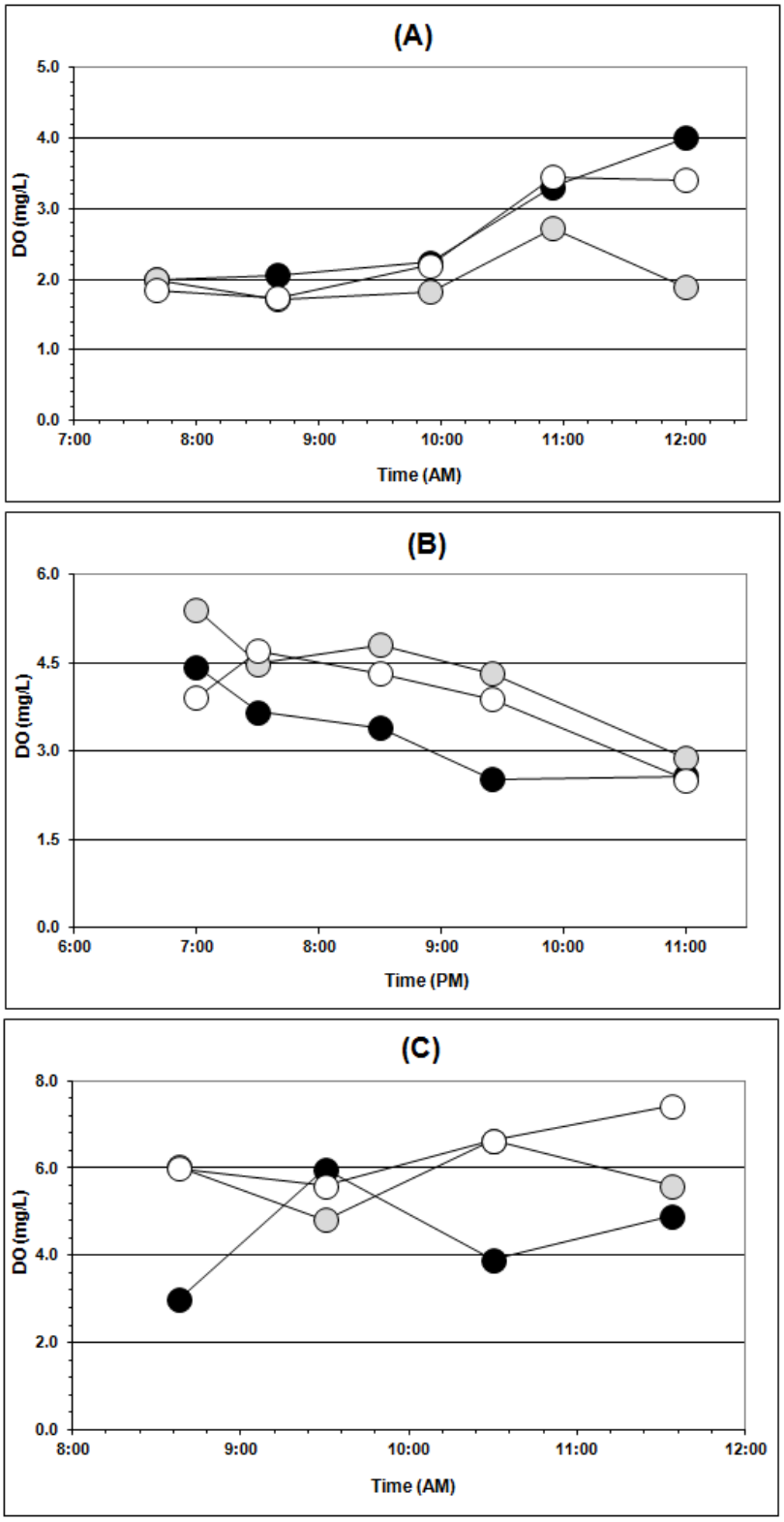

Figure 18: Dissolved oxygen (DO) profiles at surface (white filled circles), mid (grey filled circles), and bottom (black filled circles) depths in the water column over receding high tides at Togcha Estuary sites E-10, during **(A)** daylight and **(B)** darkness, and **(C)** E-14 during daylight.

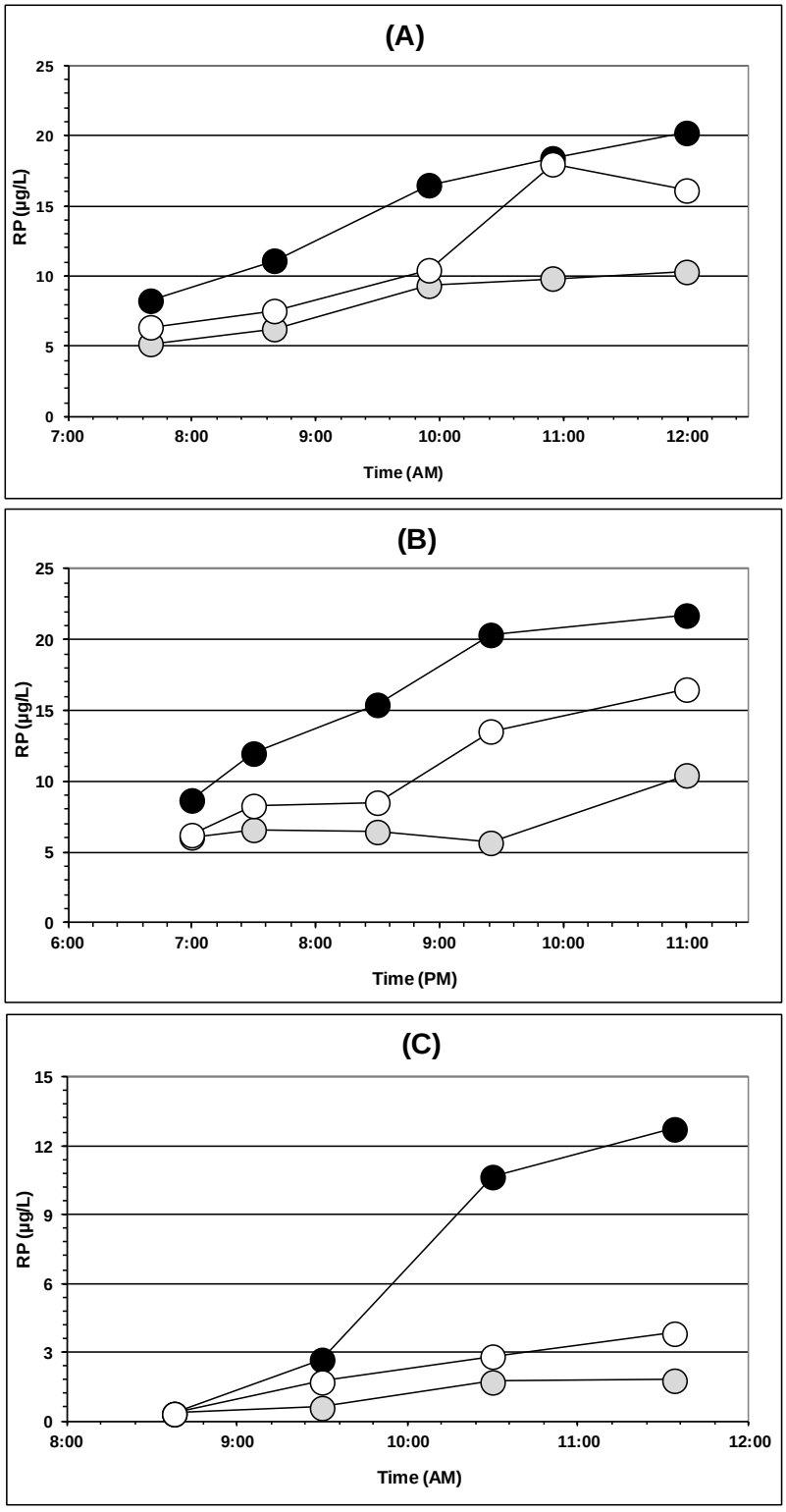

Figure 19: Reactive P (RP) profiles at surface (white filled circles), mid (grey filled circles), and bottom (black filled circles) depths in the water column over receding high tides at Togcha Estuary sites E-10, during **(A)** daylight and **(B)** darkness, and **(C)** E-14 during daylight.

Scatterplots of the pooled data sets for RP and salinity from both estuary sites are shown in Figure 20. The strong linear relationship between these two variables in surface and mid-water samples [(A)] confirms that conservative mixing of freshwater and saltwater largely influences RP levels in this portion of the water column. The significant departure from linearity noted when all bottom water data sets were superimposed on the graph [(B)] highlights the addition of P from sediments, a process commonly referred to as *benthic regeneration* (Nixon et al. 1980 and Pilson 1985).

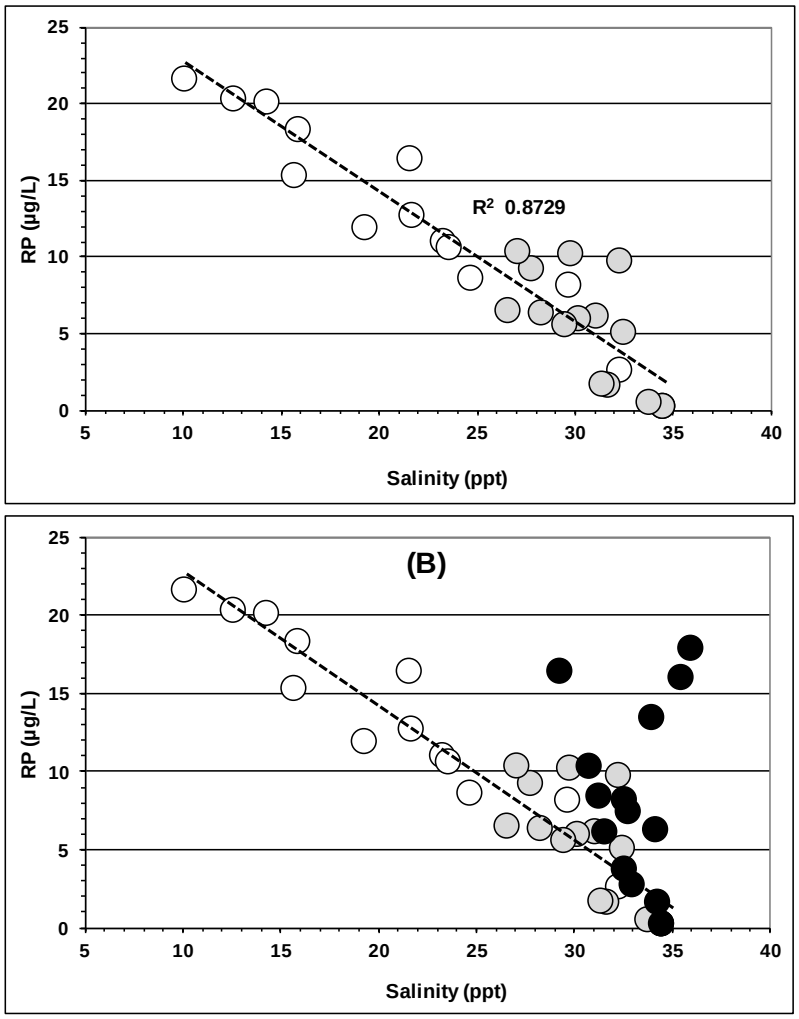

Figure 20: Reactive P (RP) plotted against salinity for surface (white filled circles), mid (grey filled circles), and bottom (black filled circles) water column depths of Togcha Estuary at sites E-10 and E-14. Graph **(A)** for surface and mid water depths only. Graph **(B)** for all three depths. Regression line for **(A)** reproduced in **(B)** for comparative purposes.

Such non-conservative mixing of RP in bottom waters is commonly encountered in estuaries, like that of the Togcha River, where oxygen is limiting. Additions of dissolved P in estuaries can also arise as result of P desorption from river-borne particulates (van Bennekom et

al. 1978, Sharp et al. 1982, and Froelich 1988). However, such sources were probably of little importance during the current work in view of the limited stream flow at the time of sampling.

Overall, the data clearly show that ocean water entering the estuary from the bay, on a rising tide, contains very low levels of RP (<0.3 μg/L). As this water body pushes up stream it undergoes progressive enrichment with RP from benthic regeneration and surface diffusion processes. Contributions from these sources gradually build up in the middle reaches of the estuary over the tidal cycle. The relatively low RP levels in the water column at the river mouth, at low tide, suggest that much of the RP is sequestered by precipitating iron and returned to the sediments as the waters recede out into the bay. This results in a net accumulation of FeP in surface deposits of the lower estuary with some spill over into the bay. Such events are certainly supported by the sediment data for FeP, as discussed earlier.

Dissolved Inorganic Nitrogen (DIN)

The naturally high levels of nitrate in Guam's groundwater[1] coupled with continuous seepage of groundwater into the Togcha River watershed undoubtedly amplified nitrate levels in surface waters of the estuary and caused the marked stratification illustrated in Figure 21. Diminished oxygen levels in the mid-estuary region promoted the reduction of nitrate to nitrite with both species showing reasonably similar depth dependant distributions throughout the water column (Figure 22). Oxygen replenishment associated with intruding bay water and tidal mixing made this less obvious in mid and bottom waters at the mouth. Nevertheless, nitrate and nitrite concentrations correlated fairly well with one another overall (r=0.672), with those of the former generally exceeding those of the latter by an order of magnitude or more. The marked absence of any relationship between dissolved nitrate and ammonium levels (r=0.065) is noteworthy and suggests that the bulk of this particular species in the water column is generated by anaerobic degradation of organic matter in the underlying sediments (Figure 23). The fact that only nitrate and nitrate behave conservatively in the estuary, i.e., are affected only by dilution with seawater (Figure 24), lends weight to this contention.

The data clearly indicates that inorganic nitrogen is exported from the river estuary out into the bay on ebb tides, and along with P, provides a significant source of nutrients to biotic components in the immediate vicinity. Further discussions of these data are confined to the final chapter of this report.

flourishes in the boulder strewn delta region of the river during the dryer months of the year when stream flow is minimal.

[1] DIN (NO_3^-+NO_2^-+NH_4^+) levels in karst limestone aquifers tend to be higher than those in more consolidated systems (Lapointe 2004) with nitrate normally being the dominant (>99%) nitrogen species (Matson 1993, Denton and Sian-Denton 2009, 2010). Such natural enrichment likely reflects rapid recharge rates and shorter residence times of water in the vadose zone. This in turn, limits exposure times of drainage water to microbial denitrification processes and results in relatively high levels of residual nitrate being transported into the underlying saturated zone.

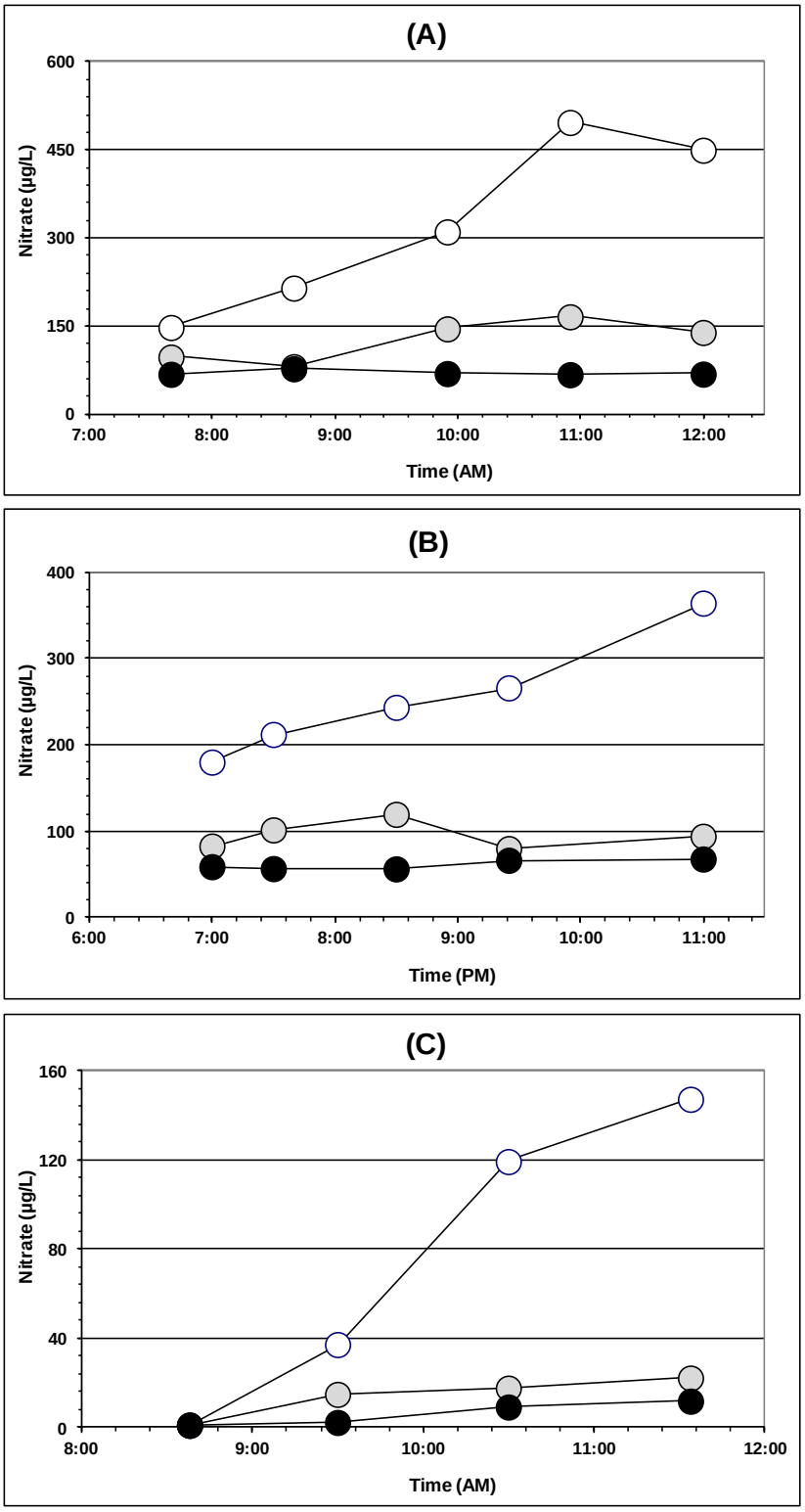

Figure 21: Nitrate profiles at surface (white filled circles), mid (grey filled circles), and bottom (black filled circles) depths in the water column over receding high tides at Togcha Estuary sites E-10, during **(A)** daylight and **(B)** darkness, and **(C)** E-14 during daylight.

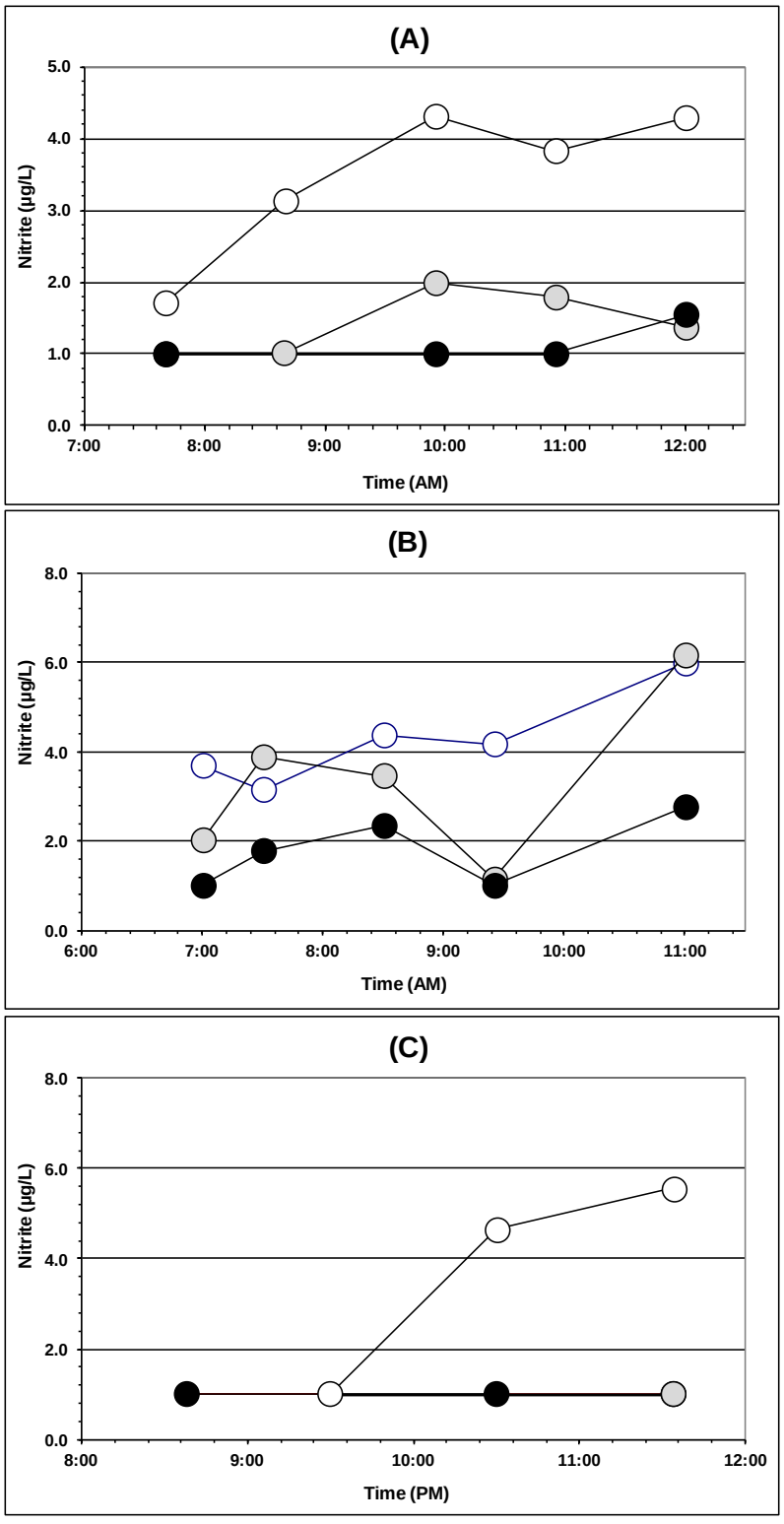

Figure 22: Nitrite profiles at surface (white filled circles), mid (grey filled circles), and bottom (black filled circles) depths in the water column over receding high tides at Togcha Estuary sites E-10, during **(A)** daylight and **(B)** darkness, and **(C)** E-14 during daylight.

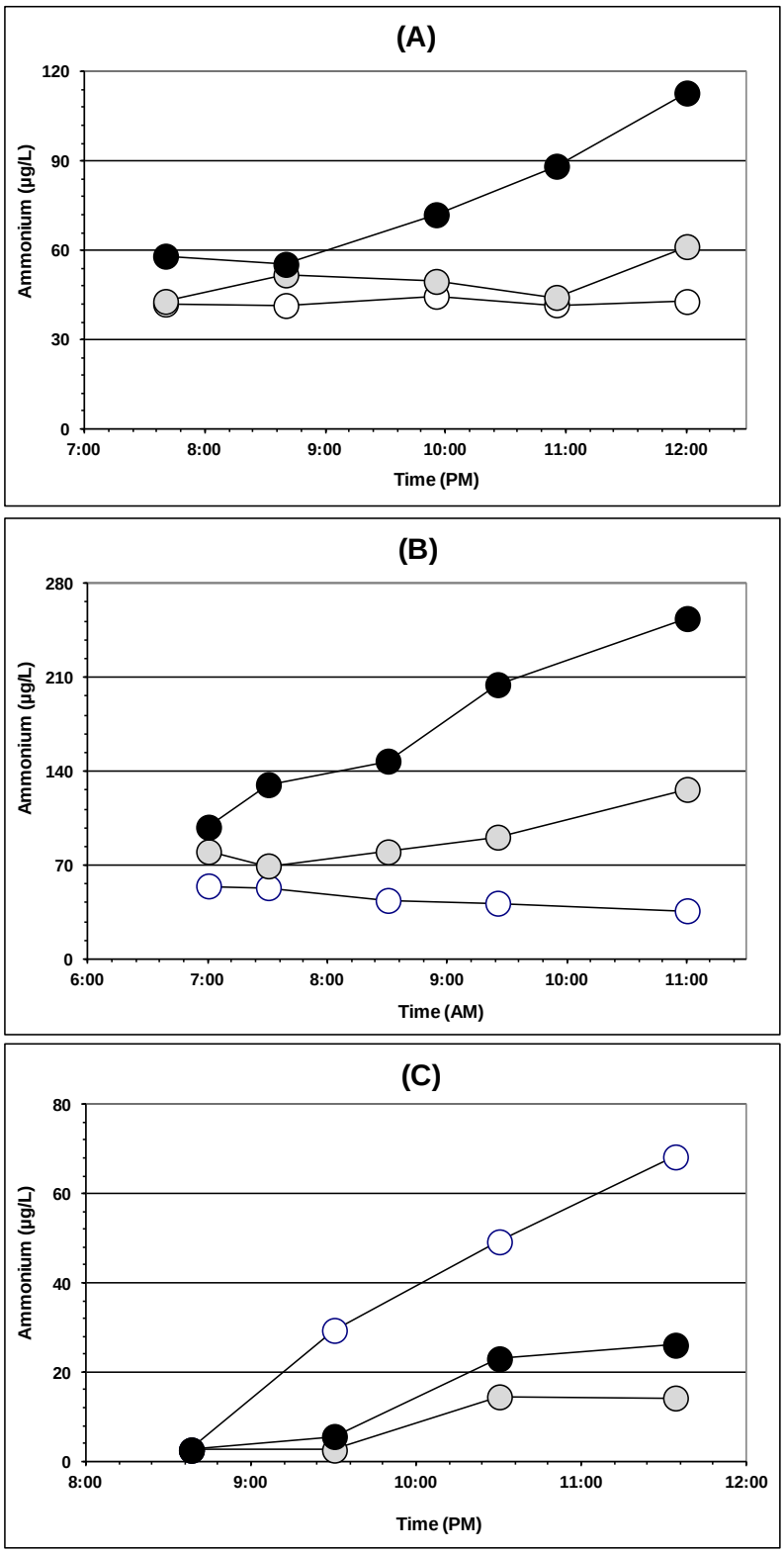

Figure 23: Ammonium profiles at surface (white filled circles), mid (grey filled circles), and bottom (black filled circles) depths in the water column over receding high tides at Togcha Estuary sites E-10, during **(A)** daylight and **(B)** darkness, and **(C)** E-14 during daylight.

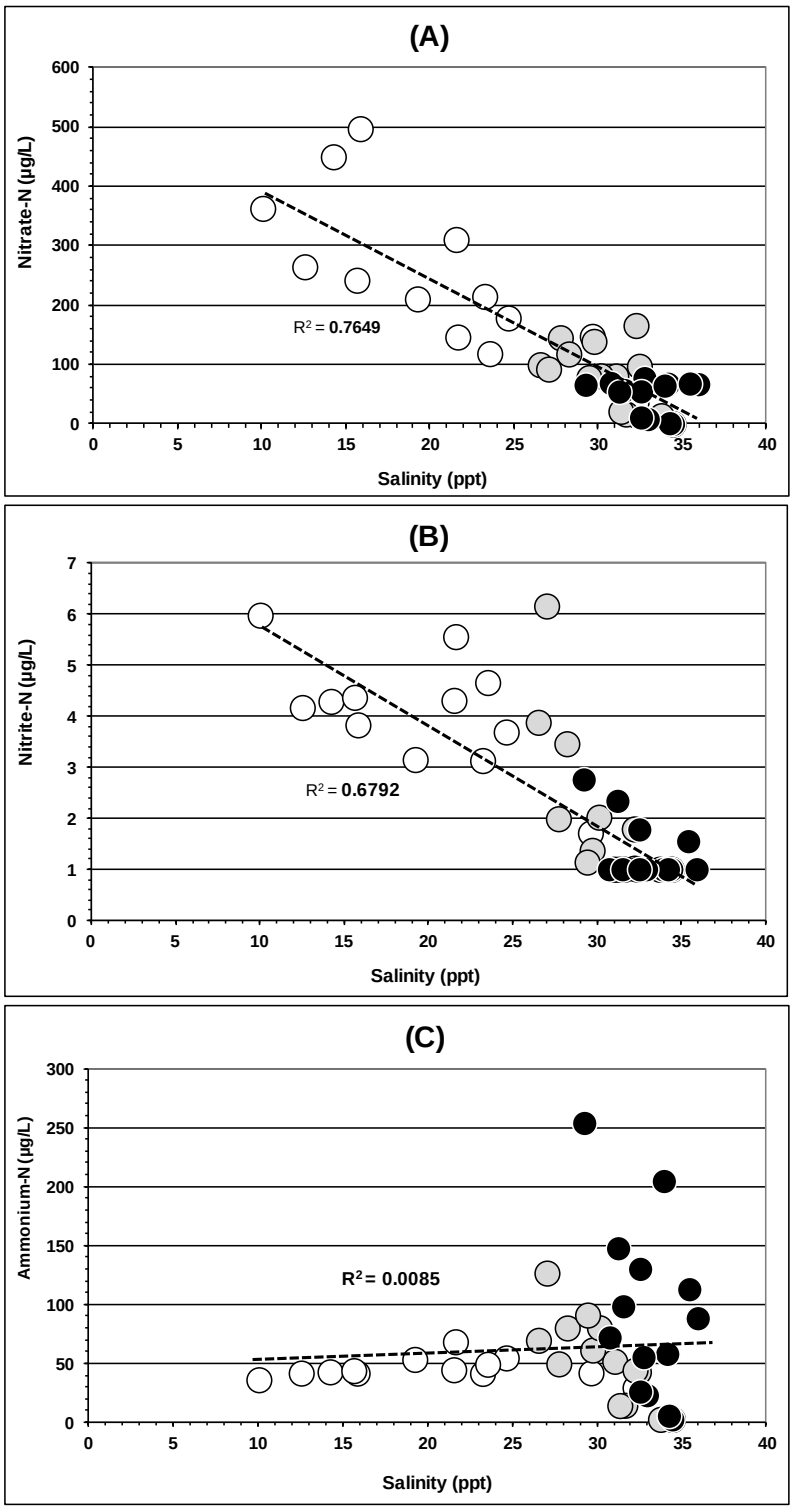

Figure 24: Dissolved inorganic nitrogen (DIN) species plotted against salinity for surface (white filled circles), mid (grey filled circles), and bottom (black filled circles) water column depths of Togcha Estuary at sites E-10 and E-14. Regression lines fitted to pooled data sets for all depths from both sites.

CONCLUSION AND RECOMENDATIONS

This research provides information on the concentration and distribution of various sedimentary P fractions in the Togcha River, estuary, and bay, and is the first of its kind to be conducted on Guam. Unlike most other studies, the fractionation scheme utilized here separates total inorganic P into apatitic and non-apatitic forms, thus identifying P fractions that are readily available to the biota. It also differentiates between apatitic P formed *in situ* and that derived from continental rocks. The findings, though preliminary in nature, provide a useful database with which future findings may be compared and evaluated. The study should therefore be of interest to water quality managers and regulatory agencies concerned with monitoring long-term changes in the nutrient status of these waters.

The question remains, however, as to whether Togcha River and its adjacent bay are overly enriched with P or not. This is difficult to establish in the absence of sedimentary P data for the area before the BGSTP was constructed. Nevertheless, limited information does exist for other coastal areas on Guam and there are a number of key references from other regions of the world. These works are summarized in Tables 7 and 8 for sediments and surface waters respectively. The tables provide the basis for the preliminary assessment outlined below for each compartment monitored during the current investigation.

SEDIMENT ASSESSMENT

From the sediment data presented in Table 7, it is apparent that total P is most commonly reported, followed by total inorganic P, and organic P. For convenience, the following assessment is therefore organized under these three broad categories. Where possible, reported data has been subdivided into apatitic and non-apatitic P and is discussed accordingly in the text. These are further broken down to their appropriate fractions for those authors who used sequential extraction techniques similar to Ruttenberg's SEDEX scheme.

Total P (TP) in River Sediments

Much of the reported P data for rivers are for polluted waters in temperate regions of the world. That presented by Berner and Rao (1994) for the Amazon River is a notable exception to this. These authors claim that the Amazon is the largest unpolluted river in the world and reported an average TP concentration of 474 μg/g for bottom sediments. This concentration is near the average TP level recorded for reference sites R-1 and R-5 in the Togcha River (503 μg/g), during the current study, suggesting that the watershed above BGSTP is relatively clean by world standards. It is also close to the October average for the entire river (518 μg/g), which indicates that TP concentrations return to baseline levels during wet season conditions despite the river receiving effluent from the treatment plant year round.

Huanxin et al. (1997) looked at sediments of impacted rivers in and around Washington, D.C. and reported TP concentrations of 1516-1730 μg/g near stormwater discharges and sewer outfalls. Their overall average value of 1121 μg/g is very similar to that estimated for the Togcha River in May (1030 μg/g).

Grossly polluted rivers have TP concentrations close to an order of magnitude higher, as evidenced by the works of Salomons and Gerritse (1981) for several rivers in Western Europe. The highest level reported for the Ems River, for example, approached 9000 μg/g, a value very

close to that measured here for the BGSTP outfall site during the dry season. Salomons and Gerritse concluded that TP concentrations in the Rhine River sediments had increased nearly 8-fold since 1920, while levels in the Ems and Meuse Rivers had nearly doubled over 6 and 14 year periods respectively.

Not all rivers receiving sewage effluent accumulate P in bottom sediments. For example, the Great Ouse River in England showed very little difference between sites upstream and downstream of a sewer outfall because stream flow rates were evidently sufficient to maintain P enriched particulates in suspension (House and Denison 1997). There are obvious parallels here with events occurring in the Togcha River during the wet season. In the case of the Great Ouse, however, flow rates were always high and especially so during the stormy months of winter and early spring when sedimentary P levels dropped appreciably as a result of scouring (Table 7). The recoveries noted during the drier, summer months were attributed to the co-precipitation of soluble P with calcium carbonate and had nothing to do with the discharge of sewage effluent. Therefore, while TP concentrations in the Great Ouse River were generally in line with those observed in the Togcha River, the predominant form of this nutrient was inorganic rather than organic.

Total P (TP) in Estuarine Sediments

Estuaries are transition zones between marine and freshwater environments and serve as repositories for river-borne contaminants. Many effectively retain P by a combination of biological assimilation and the deposition of particulates and biota to bottom sediments (Correll 1998). TP levels in the estuaries of such rivers are often appreciably higher than those found in the river itself. For many other rivers, including the Togcha, the difference between the two regions is negligible and independent of whether they are nutrient enriched or not. The Amazon, for example, revealed average TP concentrations of 474 µg/g and 502 µg/g in river and estuarine sediments respectively (Berner and Rao 1994), while maximum concentrations determined in both regions of the highly impacted Ems River were identical at 8910 µg/g (Salmons and Gerritse 1981). Presumably, physical parameters such as stream flow rates, winds, tides and coastal currents are important in determining whether river-borne P is dumped in the estuary or exported out to sea.

It must also be remembered here that estuaries are zones of rapid biogeochemical transformations and high biological productivity that can radically change the make up of the TP pool (Schlesinger 1997). Thus, while TP levels may be similar between a particular river and its estuary, there may be major differences in the relative abundance of each P fraction present. This was certainly found to be the case with Amazon sediments (Berner and Rao 1994) and was also demonstrated for the Togcha during the present study. Characterizing the nutrient status of a waterway based on sedimentary levels of biologically available P rather than TP would therefore seem to be a more appropriate means of assessment.

This point is reinforced when one attempts to compare TP levels found in the Togcha estuary with levels found in clean and polluted sediments from elsewhere in the world. Mean levels in the Amazon, for example, were only 20-30% lower than those reported here suggesting that the Togcha is only mildly enriched. In contrast, maximum values reported for the highly impacted estuarine sediments of Macao, in the South China Sea (Ferreira et al. 1996), and those of the eutrophic Peel-Harvey estuarine system, in W. Australia (McComb et al. 1998), were about the same as those found in the Togcha, which implies the latter is substantially enriched. Clearly then, nutrient status assessments based on TP alone are not particularly useful.

Table 7: Selected data for phosphorus fractions in aquatic sediments from Guam and elsewhere in the world (all data as µg/g dry wt.).

Location			Number of samples	Total P	Total Inorganic P	Non-apatitic P	Apatite	Organic P	Reference
RIVER SEDIMENTS	Togcha River, Guam	Reference sites	May = 2 Oct = 2	566 (503 - 637) 435 (409 - 463)	260 (244 - 276) 228 (225 - 231)	79 (76 - 83) 84 (84 - 84)	179 (168 - 190) 144 (141 - 147)	307 (259 - 364) 206 (178 - 238)	This Study
		Outfall	May = 1 Oct = 1	9195 401	5130 221	2800 103	2330 118	4065 180	
		Downstream of outfall	May = 6 Oct = 6	952 (750 - 1174) 573 (463 - 818)	645 (477 - 865) 366 (273 - 624)	363 (240 - 557) 159 (76 - 372)	273 (226 - 308) 194 (158 - 252)	305 (271 - 340) 201 (190 - 218)	
	Amazon River, Brazil		14	474 ± 105	Approx. 384	130 ± 53	AAP+ = 140 ± 71 DAP = 117 ± 74	90 ± 40	Berner & Rao, 1994
	Great Ouse River, England	Close to outfall	1 per season	Winter: 432	-	Winter: 29	-	-	House & Denison, 1997
				Spring: 88	-	Spring: 46	-	-	
				Summer: 1349	-	Summer: 20	-	-	
				Autumn: 476	-	Autumn: 24	-	-	
				Spring: 602	-	Spring: 19	-	-	
		Outfall	3 per season	Winter: 420 (283 - 545)	-	Winter: 46 (34 - 57)	-	-	
				Spring: 136 (120 - 154)	-	Spring: 66 (51 - 78)	-	-	
				Summer: 777 (696 - 834)	-	Summer: 43 (34 - 57)	-	-	
				Fall: 1161 (907 - 1529)	-	Fall: 43 (36 - 57)	-	-	
				Spring: 827 (529 - 1221)	-	Spring: 39 (35 - 44)	-	-	
	Potomac and Anacostia Rivers, Tidal Basin, Washington Channel, and Kingman Lake; Washington, D.C., USA	Close to outfall	TP = 27 P fractions = 8	1121 (738 - 1457)	857 (412 - 1342)	685 (260 - 1172)	171 (143 - 214)	245 (nd - 580)	Huanxin et al., 1997
		Outfall	TP = 5 P fractions = 4	1604 (1516 - 1730)	1256 (880 - 1404)	1079 (698 - 1221)	177 (152 - 192)	208 (174 - 233)	

LP only

Data are listed as geometric mean (range), average ± 1 standard deviation, or average only depending on reference cited; LP = loosely-sorbed P, FeP = ferric iron-bound P, AAP+ = authigenic apatitic P plus biogenic apatitic P plus $CaCO_3$ associated P, DAP = detrital apatitic P, OP = organic P, TP = total P, nd = not detected, dashes indicate no data.

Table 7 (cont.): Selected data for P fractions in aquatic sediments from Guam and elsewhere in the world (all data as µg/g dry wt.).

	Location		Number of samples	Total P	Total Inorganic P	Non-apatitic P	Apatite	Organic P	Reference
RIVER SEDS	Rhine River, Western Europe, 1922		15	600 - 950	80% of TP	-	-	20% of TP	Salomons & Gerritse, 1981
	Rhine River, Western Europe, 1973		10	3230 - 6360	80 - 99% of TP	> 75% of TP	-	1 - 20% of TP	
	Meuse River, Western Europe		30	1760 - 6500	77.6 - 99% of TP	-	-	1 - 22.4% of TP	
	Ems River, Western Europe		9	3820 - 8910	82.3 - 89% of TP	-	-	11 - 17.7% of TP	
	Scheldt River, Western Europe		18	1700 - 5550	88.2% of TP	-	-	11.8% of TP	
	World average for suspended river sediments		-	1147	-	-	-	-	Martin & Whitfield, 1983
ESTUARINE SEDIMENTS	Togcha River Estuary, Guam	Upper estuary E-1 to E-8	May = 8 Oct = 8	798 (681 - 881) 639 (582 - 680)	440 (372 - 497) 433 (378 - 485)	201 (167 - 243) 203 (185 - 384)	238 (179 - 297) 230 (193 - 263)	348 (311 - 443) 204 (172 - 240)	This Study
		Lower estuary E-9 to E-14	May = 6 Oct = 6	615 (428 - 807) 585 (407 - 689)	468 (411 - 569) 388 (235 - 465)	326 (259 - 384) 173 (104 - 222)	136 (77 - 199) 214 (131 - 283)	144 (84 - 238) 194 (167 - 224)	
	Amazon River, Brazil		12	502 ± 53	Approx. 376	233 ± 50	AAP+ = 112 ± 9.3 DAP = 31 ± 47	133 ± 47	Berner & Rao, 1994
	Weser River, Germany		8	1756 - 4462	-	>75% of TP	-	122 - 591	Calmano, 1981
	Macao, Macao Territory		13	300 - 800	-	-	-	-	Ferreira et al., 1996
	Ems Estuary, Western Europe		32	1770 - 8910	82.3 - 92.6% of TP	70%	-	7.4 - 17.7% of TP	Salomons & Gerritse, 1981
	Moresby River, Australia (suspended sediments)	Dry season	Total P = 6 LP fract. =	462 ± 203	-	LP = 28 ± 11	-	-	Eyre, 1994
		Wet season	Total P = 5 LP fract. =	2454 ± 1285	-	LP = 205 ± 242	-	-	
	Peel-Harvey Estuary, Australia		78	75 - 711	-	6 - 52% of TP	22 - 85% of TP	22 - 35% of TP	McComb et al. 1998

Data are listed as geometric mean (range), average ± 1 standard deviation, or average only depending on reference cited; LP = loosely-sorbed P, FeP = ferric iron-bound P, AAP+ = authigenic apatitic P plus biogenic apatitic P plus $CaCO_3$ associated P, DAP = detrital apatitic P, OP = organic P, TP = total P, nd = not detected, dashes indicate no data.

Table 7 (cont.): Selected data for P fractions in aquatic sediments from Guam and elsewhere in the world (all data as µg/g dry wt.).

	Location		Number of samples	Total P	Total Inorganic P	Non-apatitic P	Apatite	Organic P	Reference
MARINE SEDIMENTS	Togcha Bay, Guam	<100m from mouth	May = 2 Oct = 2	332 (292 - 378) 386 (336 - 443)	252 (241 - 264) 272 (232 - 319)	160 (151 - 170) 179 (172 - 187)	90 (71 - 113) 90 (60 - 132)	76 (51 - 113) 114 (104 - 125)	This Study
		>100m from mouth	May = 13 Oct = 13	234 (200 - 291) 254 (156 - 351)	201 (163 - 246) 225 (143 - 301)	166 (126 - 214) 197 (118 - 273)	35 (31 - 41) 27 (23 - 36)	32 (20 - 48) 28 (12 - 50)	
	Florida Bay, USA		40	31 - 434	7 - 100	27% of TP	50% of TP	24% of TP	Zhang, 2002
	Bailey's Bay, Bermuda		24	78 - 217	-	LP = nd - 9 FeP = 9 - 37	AAP+ = 47 - 140	6 - 68	Jensen et al., 1998
	Tumon Bay, Guam		-	-	186 ± 28	-	-	-	Matson, 1989
	Cocos Island, Guam		-	-	303 ± 47	-	-	-	
	Ipan Lagoon, Guam (Site 1)		-	-	232 ± 25	-	-	-	
	Ipan Lagoon, Guam (Site 2)		-	-	260 ± 34	-	-	-	
	Ipan Offshore		-	-	247 ± 31	-	-	-	
	Malesso Channel, Guam		-	-	253 ± 25	-	-	-	
	Ylig Bay, Guam		-	-	155 ± 149	-	-	-	
	Rio de Janeiro, Brazil		16	1075 (370 - 2300)	659 (243 - 1814)	543 (nd - 1605)	-	411 (127 - 839)	Carreira & Wagener, 1988
	Oropouche Bank, Trinidad		84	150 -1550	6 - 1164	-	-	6 - 642	Kumarsingh et al., 1998
	Long Island Sound, USA		1	436	340	LP = 35 FeP = nd	AAP+ = 126 DAP = 179	96	Ruttenberg & Berner, 1993
	Mississippi River, USA		1	605	436	LP = 48 FeP = 182	AAP+ = 139 DAP = 67	169	
	Gulf of St. Lawrence, Canada		5	1628 ± 93	1522 (approx.)	LP = 34 ± 19 FeP = 694 ± 105	794 ± 28	105 ± 16	Sundby et al., 1992

Data are listed as geometric mean (range), average ± 1 standard deviation, or average only depending on reference cited; LP = loosely-sorbed P, FeP = ferric iron-bound P, AAP+ = authigenic apatitic P plus biogenic apatitic P plus $CaCO_3$ associated P, DAP = detrital apatitic P, OP = organic P, TP = total P, nd = not detected, dashes indicate no data.

Total P (TP) in Coastal Sediments

TP levels in unimpacted marine sediments reflect their organic and inorganic composition. In nearshore tropical regions unaffected by rivers, carbonate sands tend to dominate the sediments (Howarth et al. 1995). Such sediments are typically low in P. Parts of Florida Bay, for example, have unproductive sediments composed of ~90% calcium carbonate with TP concentrations ranging from 31-62 µg/g (Zhang 2002). These values are among the lowest ever recorded for marine sediments and probably represent true baseline values for unimpacted coral reef environments.

Such low levels make it relatively easy to identify nutrient enrichment associated with domestic waste discharges, as in the case of Bailey's Bay, in Bermuda. Here, leachate from residential septic tanks raised TP levels in hitherto clean coral sands to around 200 µg/g and transformed the bay into an eutrophic environment (Jensen et al. 1998).

Identifying changes in the nutrient status in tropical coastal areas that are influenced by rivers, like Togcha Bay, is a little more difficult because sediments are composed of a variable mix of marine carbonates, terrigenous clays, iron and organic material. Thus, TP levels are frequently much higher than those encountered in clean coral sands (Howarth et al. 1995).

Productive sediments in Florida Bay, for example, were found to contain TP concentrations of 341-434 µg/g, not too different from the range of values (155-443 µg/g) encountered in Togcha Bay over the study period. Since Florida Bay is not regarded as overly enriched with P (Boyer and Jones 1999), the same might be said for Togcha Bay. In any event, levels encountered in sediments from both environments were generally much lower than those recorded from the tropical waters of Oropouche Bank in Trinidad (150-1500 µg/g), an area that receives substantial quantities of domestic and commercial effluent (Kumarsingh et al. 1998). They were also well below the average value (1075 µg/g) reported for the sewage-impacted coastline of Rio de Janeiro in Brazil (Carreira and Wagener 1998).

In closing this subsection, attention is once again drawn to the significance of using the biologically available forms of sedimentary P for nutrient assessment purposes rather than TP. Data for temperate waters included in Table 7 clearly show that the rather high TP levels recorded in sediments from the Gulf of St. Lawrence, in Canada (Sundby et al. 1992), and Long Island Sound and the Mississippi delta, in the USA (Ruttenberg and Berner 1993), reflect a predominance of apatitic P in the samples. As this form of P is non-biologically available, it is of little environmental concern. Had the authors of these reports not determined this fraction they may well have overestimated the degree of enrichment for the environments investigated.

Total Inorganic P (TIP) in River Sediments

TIP constitutes the residual P fraction after OP has been deducted from the TP pool. Based on the findings of Berner and Rao (1994) for the Amazon River, and those encountered here for the Togcha River reference sites, TIP levels in non-polluted waters are probably in the 200 to 400 µg/g range (Table 7). Closer to obvious point sources of P, values increase substantially. This was shown for the moderately impacted rivers around Washington, D.C. where the maximum sedimentary TIP level was about 1400 µg/g (Haunxin et al. 1994), and in several grossly polluted rivers from W. Europe where concentrations in some samples exceeded 5000 µg/g (Salomon and Gerritse 1981). From these data, we conclude that the BGSTP outfall site qualifies as a highly P-enriched section of the Togcha River during low stream flow

conditions, whereas levels downstream generally fall into the mild to moderate enrichment category during wet and dry seasons respectively.

TIP can be conveniently subdivided into two major sub-fractions, apatitic P (AP) and non-apatitic P (NAP). It will be recalled that AP includes both authigenic and detrital apatites, in addition to P associated with carbonates and clays. NAP, on the other hand, essentially covers all other inorganic forms of P but is dominated by those associated with iron. For nutrient assessment purposes it is necessary to differentiate between both sub-fractions because only NAP is considered to be of importance from a biological availability standpoint (Ruiz et al. 1997, Lucotte and d'Anglejan 1984, Calmano 1981). Further refinement is possible if TP levels are also known because the proportion of the TP pool represented by NAP increases as the degree of nutrient enrichment increases.

The relationship between NAP and TP was first recognized by Calmano (1981) who showed that the NAP fraction accounted for ~80% of the TP pool in sediments from the four heavily polluted rivers studied by Salomons and Gerritse (1981) in W. Europe. Unimpacted waters normally yield ratios that are considerably lower than this. For example, NAP represented only 27% of the TP pool in sediments from the Amazon River (Berner and Rao 1994) compared with ~70% for relatively polluted rivers from the Washington, D.C. area (Huanxin et al. 1997).

Background levels of available iron and organic matter are influential in determining the NAP:TP ratios in clean sediments, as are factors related to resident biota, local geology, and climatic conditions. Therefore, the lower limit of the NAP:TP ratio for unimpacted sediments will vary somewhat from one water body to another. The data obtained from the reference sites in the Togcha River during the present investigation suggests that NAP normally constitutes 13-15% of TP in the dry season and 18-20% during the wetter months. Values determined at all other sites in the river ranged from 31-48% in May with an overall average of 37%. The October samples yielded somewhat lower values of 20-45% with a mean of 28%. These figures indicate that, while the river is to some extent purged of its elevated nutrient load during high stream flow conditions, it does not return to baseline conditions as we are led to believe from TP evaluations alone.

Based on the criterion established by Calmano (1981), whereby highly polluted sediments have NAP:TP ratios of ~0.8, we again conclude that the Togcha River falls somewhere between the mild to moderate nutrient enrichment category depending on the time of year.

Total Inorganic P (TIP) in Estuarine Sediments

Comparatively few studies report TIP levels in estuarine sediments. From the two examples listed in Table 7, it can be seen that concentrations range from a little under 400 µg/g in unimpacted estuaries (Berner and Rao 1994) to well over 5000 µg/g in heavily polluted waters (Salomons and Gerritse 1981). During the present work, average values for TIP in the Togcha estuary ranged from 413 µg/g to 435 µg/g in October and May, respectively. This would suggest that the area is only lightly enriched with P by world standards. The TIP data sets also suggest that P levels were relatively uniform between the upper and lower portions of the estuary on both sampling occasions. Moreover, the fact that the May average for the entire estuary was 30% lower than that calculated for all river sites downstream of the BGSTP (452 µg/g vs. 645 µg/g) suggested a gradual improvement in nutrient status towards the mouth.

Examination of the NAP:TP ratios within the estuary portray a very different picture, however, and highlight the inadequacy of nutrient assessments based on TIP evaluations alone. In May, for example, the average NAP concentrations in the lower estuary (sites E-9 to E-14) accounted for 54% of the TP pool compared with only 25% further upstream (sites E-1 to E-8). This doubling of the potential biologically available P fraction in the lower reaches during the dry season was caused by the gradual build up of FeP in the surface sediment as result of benthic regeneration processes in the anoxic mud. As mentioned earlier, the relatively high organic matter loading in the lower estuary was considered to be the driving force behind such transformations.

The natural accumulation of oxidizable organic matter in estuarine sediments tends to increase the relative abundance of NAP in river mouths. Data presented for the Amazon in Table 7 clearly demonstrates this with NAP accounting for 46% of the TP pool in the estuary as opposed to just 27% in the river itself (Berner and Rao 1994). This differential between estuary and river was appreciably larger for the Togcha as NAP levels accounted for as much as 65% of the TP pool in the lower estuary compared with a high of only 15% in sediments from the upper river reference sites. Undoubtedly, this greater disparity in relative abundance is inexorably linked to discharges emanating from the BGSTP.

The relatively high proportions of sedimentary NAP encountered in May sediments from the lower estuary (43-65%) generally fall between those reported for eutrophic estuarine waters from elsewhere in the world (Calmano 1981, Salomons and Gerritse 1981, McComb et al. 1998). It is therefore concluded that the P status of this region lies somewhere between the moderate to high enrichment category during the dryer months. However, this situation changes dramatically following periods of prolonged, heavy rain when much of the accumulated FeP is buried under fresh deposits of silt and soil washed down the river from further upstream. Under these conditions, NAP:TP ratios throughout the entire estuary revert to near normal conditions.

Total Inorganic P (TIP) in Coastal Sediments

World values for TIP in coastal sediments (Table 7) range from less than 10 µg/g in clean, coral sands (Kumarsingh et al. 1998, Zhang 2002) to ~1200 µg/g in polluted waters (Carreira and Wagener (1988). One earlier study in Guam revealed TIP levels averaging 155-303 µg/g from several coastal sites around the island (Matson 1989). The lowest mean value was reported for Ylig Bay, a small inlet, just north of the current study location. Although Ylig Bay does not receive any significant nutrient load from domestic wastewater, the river that drains into it transports substantial quantities of soil and other terrestrial material into the ocean during major storm events. Data from this bay therefore serves as a useful comparison with that obtained from Togcha Bay during the present study. It is noteworthy, then, that the mean TIP level reported for Ylig Bay was 25-33% lower then the seasonal means calculated here for Togcha Bay despite evidence of appreciable data variability at the former location (Table 7).

While sediments from nutrient enriched waters tend to yield higher TIP concentrations than those from unimpacted environments, background levels of apatitic P can obscure the relationship, particularly in areas receiving river drainage. For this reason, NAP:TP ratios are once again recommended as the more reliable assessment tool for determining biological impact. These were estimated, where possible, from the data presented in Table 7. The results suggest that NAP represents less than 30% of the TP pool in comparatively clean coastal sediments (Ruttenberg and Berner 1993, Zhang 2002), and more than 50% in significantly enriched waters

(Carreira and Wagener 1988). With NAP representing up to 83% of TP in sediments from Togcha Bay, this area clearly falls into the latter category.

Organic P (OP) in Sediments

Sedimentary OP includes all forms of P associated with organic molecules of plant and animal origin. For convenience, such forms can be grouped into labile and non-labile compounds, depending upon whether they are immediately available to biota or not. Labile forms of P are generally small, relatively soluble compounds (Newman and Robinson 1999) derived from the initial, rapid degradation of larger biomolecules, e.g., nucleic acids and phospholipids. They are readily assimilated by aquatic organisms, and consequently, have extremely short residence times in the abiotic environment (Wetzel 1999). Non-labile forms, in contrast, are relatively recalcitrant, high molecular weight components of limited water solubility, e.g., inositol phosphates, phosphomonoesters, and humic acids (Sharpley 1999). Such compounds tend to resist further degradation, and hence, undergo mineralization to biologically available forms only very slowly (Wetzel 1999).

Needless to say, labile forms of OP are extremely difficult to measure due to their high reactivity. For this reason, almost all OP data reported in the literature are for the non-labile fraction alone. Although the SEDEX procedure used during the current work separates labile from non-labile forms of OP, the former are co-extracted with LP and thus become part of the NAP fraction (Ruttenburg 1990). Though analytically challenging, this is perfectly acceptable from a monitoring standpoint because NAP is considered to represent the major forms of potential biologically available P in aquatic sediments, as discussed earlier.

As an assessment tool, non-labile forms of OP (hereafter simply referred to as OP) are not particularly useful in determining the nutrient status of a water body. Granted, OP concentrations in sediments from P enriched waters tend to be higher than those from cleaner surroundings (Table 7). However, background levels in the latter are highly dependent on the productivity characteristics of the environment. As a consequence, baseline values for OP can vary considerably within and between locations, obscuring subtle trends in distribution and abundance. More importantly, though, OP has little bearing on sedimentary levels of biologically available P.

Assessments based on the relative abundance of OP are also of little practical use as no obvious relationship exists between P enrichment and proportionate amounts of OP in the TP pool. According to Wetzel (1999) OP usually accounts for around 30% of the TP pool in clean, aquatic environments. However, the literature indicates considerable variation in relative abundance of this fraction with values ranging from <10% to >50% in oligotrophic and mesotrophic waters respectively (Jensen et al. 1998, Kumarsingh et al. 1998, Reddy et al. 1998, Newman and Robinson 1999). Moreover, in eutrophic waters the relative abundance of OP actually decreases, in line with proportionate increases in NAP, and can account for as little as 1% of the TP pool in grossly polluted waters (Salomons and Gerritse 1981).

To further complicate matters, it is evident from the current work that OP levels in sediments from sewage outfall sites can account for close to 50% of the TP pool, presumably as a result of moderately labile OP components co-extracting with the non-labile fraction (Table 7). Admittedly, this reflects an analytical inadequacy rather than an environmental anomaly. Nevertheless, it adds additional uncertainty to the data from an interpretive standpoint.

In light of the above, it is clear that OP measurements are of limited value from a monitoring perspective. Further discussions and comparative evaluations of this fraction with the work of others were, therefore, considered unnecessary.

ESTUARINE WATER ASSESSMENT

A selection of published works focusing on reactive P (RP) levels in surface waters is presented in Table 8 for freshwater, estuarine and marine environments. Data for all three water types were considered necessary for evaluative purposes because of the marked salinity stratifications encountered in the Togcha Estuary during the current work.

To recap, RP concentrations in waters of the Togcha Estuary at the time of sampling ranged from <0.3-21.7 μg/L and were strongly salinity dependent. The relatively high levels measured in the low salinity, surface waters reflected groundwater intrusion, an assumption subsequently confirmed by the analysis of seeps entering the bay around the river mouth at low tide. RP levels in these seep samples (13.7-18.7 μg/L) were similar to those reported by other researchers for beach seeps and springs on the other side of the island (Matson 1991a and b, Matson 1993, Denton et al. 2005). They were also within the range of RP concentrations found in groundwater from the island's drinking water production wells (Denton et al. 2005). This infers that the BGSTP has little, if any, influence on groundwater levels of RP entering the estuary.

Maximum levels determined in the estuary, though higher than incoming bay water, ranked among the lower values reported for impacted estuaries from other parts of the world (Table 8). For example, Galope-Bacaltos et al. (1999) reported RP levels of up to 98 μg/L in the eutrophic waters of the Santa Rita estuary in the Philippines, while Braga et al. (2000) recorded an average value of 92 μg/L for the polluted Baixada Santista estuarine system in Brazil. These values are 5-10 times higher than the maximum values encountered here.

Minimum RP values recorded during the present work were confined to full-strength ocean water collected at the river mouth at high tide. Levels recorded here were consistently below the limits of analytical detection (0.34 μg/L) at all depths in the water column. Such low levels characterize the ocean water entering the bay as oligotrophic based on studies conducted on outer barrier reefs in Australia (Schaffelke et al. 1999) and the Caribbean (Lapointe et al. 1987, 1993). It would appear, then, that ocean waters around the island of Guam are indeed P limiting as previously suspected by Denton et al. (1998). Data from this investigation also suggests that they are nitrogen limited considering that levels of dissolved inorganic nitrogen (DIN = NH_4^+ + NO_3^- + NO_2^-) measured at the river mouth at high tide (<5 μg/L) were below threshold values (35-70 μg/L) necessary to promote algal growth (Lapointe 2004).

The identification of benthic regenerated influxes of RP into the water column of the Togcha estuary was an important finding because this mechanism provides a continuous source of biologically available P into the bay regardless of stream flow conditions. It also accounts for the build-up of sedimentary FeP in the lower estuary during the dry season and explains why this fraction was a dominant component of TP in bay sediments sampled.

Table 8: Selected data for reactive P in waters from Guam and elsewhere in the world

	Location		Number of samples	Salinity (ppt)	RP[a] Concentration (µg/L)	Reference
FRESH WATER	Guam aquifer (water wells)		97	< 0.1 - 1.6	12.7 (6.70 - 38.5)[a]	Denton et al., 2005
ESTUARINE WATERS	Togcha River Estuary, Guam	Surface water	14	10.0 - 34.4	15.3 (0.34 - 21.7)	This Study
		Middle water	14	26.5 - 34.4	7.61 (0.34 - 10.4	
		Bottom water	14	29.2 - 35.9	11.1 (0.34 - 18)	
	Togcha Bay (seeps), Guam		2	1.7 - 8.1	16.2 (13.7 - 18.7)	
	Tumon Bay (major springs), Guam		24	0.5 - 7.8	16.8 (14.0 - 22.8)[a]	Denton et al., 2005
	Tumon Bay (seeps), Guam		198	0.7 - 28.8	14.1 (1.30 - 31.9)[a]	
	Agana Bay (seeps), Guam		9	0.1 - 3.5	19.0 (12.6 - 30.8)[a]	
	Haputo Point (seeps), Guam		16	0.3 - 4..7	22.7 (19.3 - 27.2)[a]	
	Gun Beach (seeps), Guam		6	3.1 - 6.8	20.0 (17.4 - 22.3)[a]	
	Tarague Beach (seeps), Guam		-	-	27 ± 9.0	Matson, 1993
	Northwest Coast (seeps), Guam		-	-	16 ± 9.9	
	Tumon Bay, Guam	5-10m offshore	2	14.2 - 22.2	25.6 - 28.3	Fitzgerald, 1976, 1978
	Tumon Bay (seeps), Guam		-	-	17.1 - 40.3	Matson, 1991 a, b
	Moresby River Estuary, NE Australia	Dry Season	17	11 - 35	12.1 ± 12.1	Eyre, 1994
		Wet Season	21		4.65 ± 4.34	
	Pearl River Estuary		240	-	7.0 - 36.0	Huang et al., 2003
	Baixada Santista Estuarine System, Brazil		30	19.4 - 32.8	92	Braga et al., 2000
	Macao, China		-	2 - 18.6	20 - 75	Ferreira et al., 1996
	Sta. Rita River Estuary, Philippines		24	2 - 33	40 - 198	Galope-Bacaltos et al.,
	New River Estuary, North Carolina		-	-	64	Mallin et al., 2000
	Neuse Estuary, North Carolina		-	-	46	
	Pamlico Estuary, North Carolina		-	-	28	
	Cape Fear, North Carolina		-	-	36	
MARINE WATERS	Tumon Bay, Guam		100	5.6 - 34.0	1.7 (<0.34 - 13.34)[a]	Denton et al., 2005
	Tumon Bay, Guam		170	32.4 - 34.3	3.4 - 8.7	Matson et al., 1996
	Tumon Bay, Guam	50-100m offshore	2	30.5	8.93 - 20.6	Fitzgerald, 1976, 1978
	Central Great Barrier Reef, Australia		168	-	Majority < 0.62	Schaffelke et al., 1999
	Florida Bay, USA		-	-	0.06 - 2.0	Zhang, 2002
	Curlew Cay, Belize		16	-	< 0.93	Lapointe et al., 1993
	Curlew Cay, Belize		12	-	< 0.93	Lapointe et al., 1987
	Tobacco Reef, Belize		8	-	2.48	Lapointe et al., 1993
	Glovers Reef, Belize		-	-	10.9 - 31.0	McClanahan et al., 2002
	Glovers Reef, Belize		2	-	1.55	Tomasko & Lapointe, 1991
	Negril Marine Park, Jamaica	Winter 1998	48	-	0.53 ± 0.31	Lapointe and Thacker, 2002
		Summer 1998	48	-	1.46 ± 0.90	
	Looe Key, Florida Keys		258	-	1.55 ± 2.17	Lapointe et al., 2002
			48	-	1.24 ± 2.17	Lapointe et al., 2002
			90	-	1.24 ± 0.93	Lapointe et al., 2002
			52	-	2.79 ± 0.62	Lapointe et al., 2002
	Golden Horn Bay, Vladivostok, Russia		-	-	Max. = 100	Tkalin et al., 1993
	Rio de Janeiro, Brazil	Surface water	-	-	nd - 93	De Luca et al., 1992
		Middle water	-	-	1.55 - 102	
		Bottom water	-	-	3.72 - 74.4	

[a]Reactive P; [b]geometric mean (range); all other data listed as average (range), average ± 1 standard deviation, or mean only depending on reference cited, nd = not detected, dashes indicate no data.

While much of the benthic regenerated RP appears to be recycled within the estuary during the dry season, concentrations exported into the bay at all depths are significantly higher than those imported into the estuary from the ocean. This is important because threshold levels of RP that promote macroalgae blooms in tropical reef waters lie somewhere between 1.5-3.0 μg/l (Lapointe et al. 2002, Lapointe and Thacker 2002), which is right around the range of values recorded during the present study in bottom and mid-depth waters leaving the estuary at low tide (1.8-3.8 μg/l).

The impact of this enrichment is evidenced by the prolific growth of the filamentous green alga, *Enteromorpha clathrata*, on stable substrates of the cross-mouth bar (small boulders and coral rubble) and adjacent shoreline. Members of this genus are well known indicators of nutrient enriched waters (Lapointe 2004) and are commonly encountered on Guam beaches affected by groundwater intrusion (Denton et al. 2005).

Effects on biotic communities further afield from the cross-mouth bar are far less obvious and have yet to be described. Casual observations indicate an over abundance of cyanobacteria (*Ocsillatoria* spp.) on surface sediments between the bar and old river channel. Members of this group are also common invaders of nutrient enriched waters (McClanahan et al. 2004). The moat area is also extensively colonized by seagrass (*Enhalus uninervis*) that may possibly be capitalizing on the relatively high proportions of NAP in the total P pool that exist there.

The question remains, however, as to whether there is a connection between wastewater discharges from the BGSTP and the blooms of macroalgae that periodically wash ashore and decompose on the beach. Anecdotal evidence, based on the testimony of local residence, suggests there is. In fact, one witness who grew up in the area and fished the bay regularly as a boy adamantly claimed there were no foul-smelling blooms prior to 1977 when the BGSTP first came on line.

Although the current work does not specifically address this issue, it does provide convincing evidence of elevated nutrient enrichment in the Togcha Bay area. And while a component of this enrichment is attributed to benthic regeneration processes in the river estuary, the subterranean flow of wastewater into the bay from the point of insurgence, further upstream, is considered to have a far greater impact on algal blooms in the outer bay area. Given the geological nature of the hinterland, it is very probable that wastewater, captured in this way, moves down gradient along preexisting fractures and fault lines into the old river channel. Submarine springs are certainly known to occur in the area although they have yet to be mapped and chemically characterized.

FUTURE RESEARCH RECOMMENDATIONS

Areas of further investigation that emerge from this research are listed below:

- A dye trace study is urgently needed to locate entry points into the bay of wastewater captured by insurgence at river site R-7.
- Additional sediment sampling is required to delineate NAP:TP ratios throughout the entire bay and highlight areas of enrichment. Only then can the full impact of nutrient contributions from the BGSTP be properly evaluated.

- The seasonal distribution and abundance of dominant macrophytes within the bay need to be established and carefully monitored, especially in areas adjacent to identified points of wastewater emergence.
- N:P and C:N ratios in plants provide useful clues on nutrient abundance and should be determined in dominant flora within the bay. Normal mean ratios for marine plants are around 16:1 and 22:1 for N:P and C:N respectively (Redfield 1958, Atkinson and Smith 1983).
- The nutrient status of seawater in the bay has yet to be addressed and should take into account variable effects associated with wind, tides and season.
- Ocean water intruding into the bay also requires further analysis to substantiate suspected N and P limitations outside the reef.
- Carbon isotope ratios can distinguish between organic matter of animal and plant origin and would be a useful means of determining dominant sources of organic matter (i.e., algae, sewage) throughout the study area.
- Further work is necessary to establish NAP:TP ratios in sediments from other rivers and bays on Guam. Data of this nature is vital for the successful implementation of any coastal zone management plan designed for the island.

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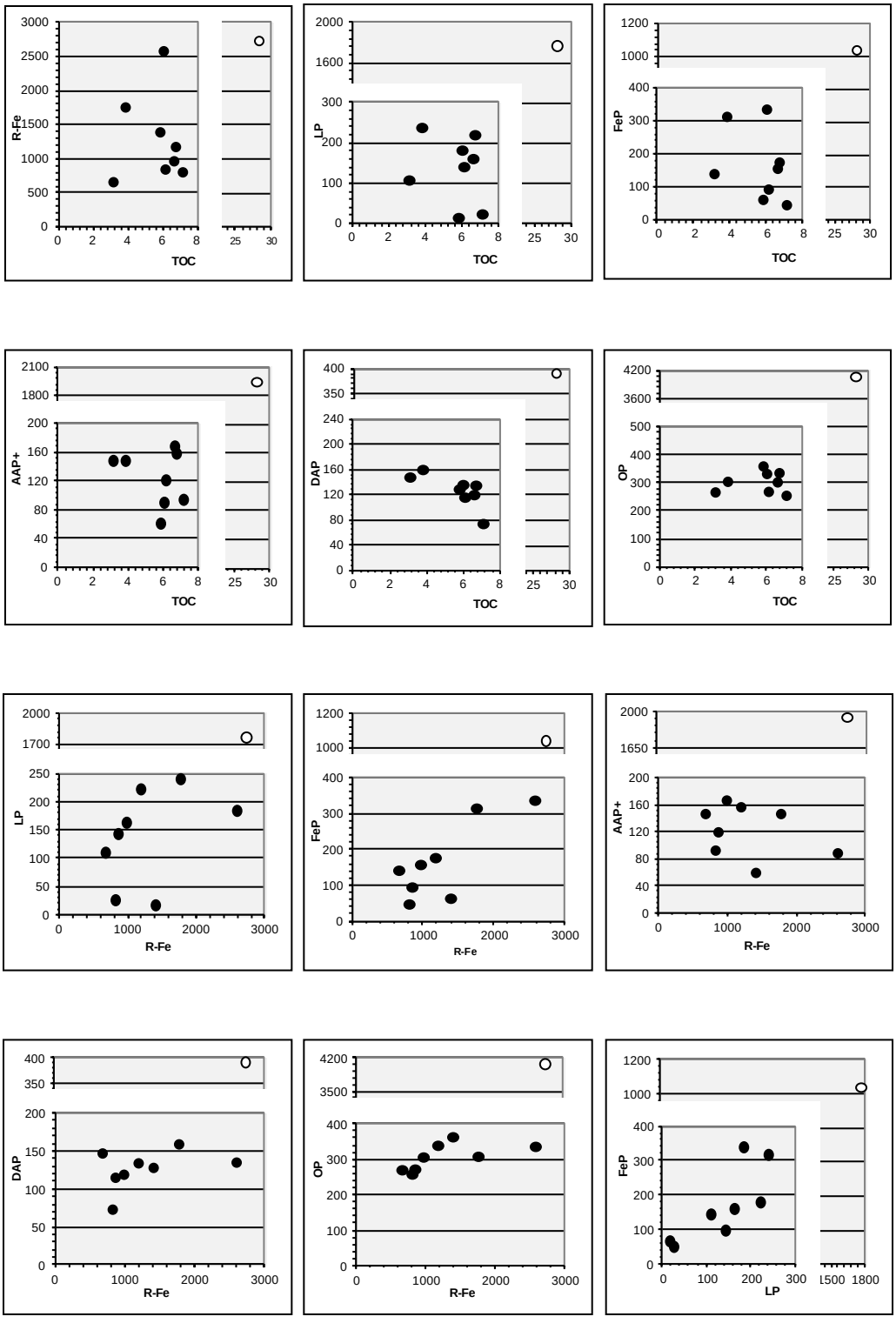
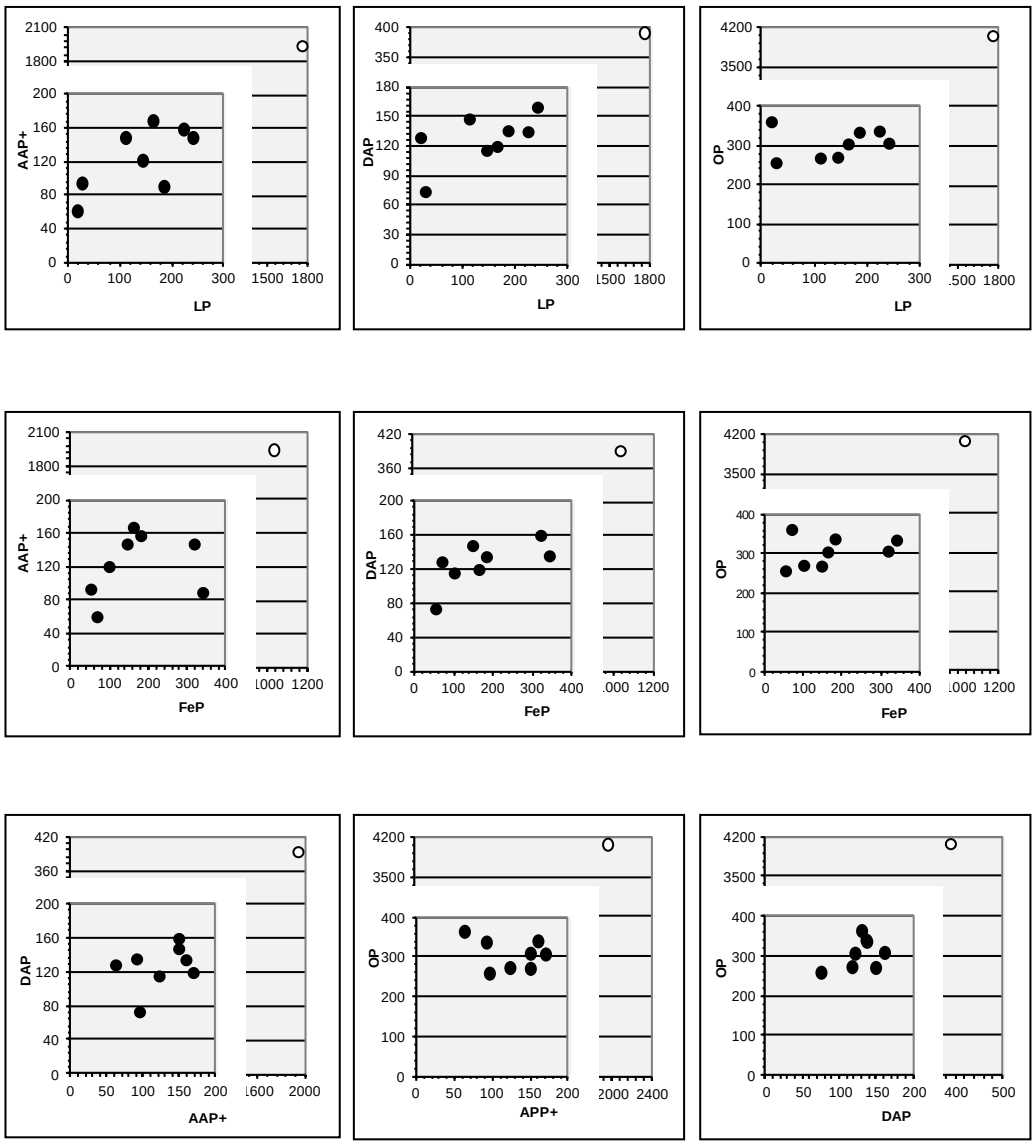
APPENDICES



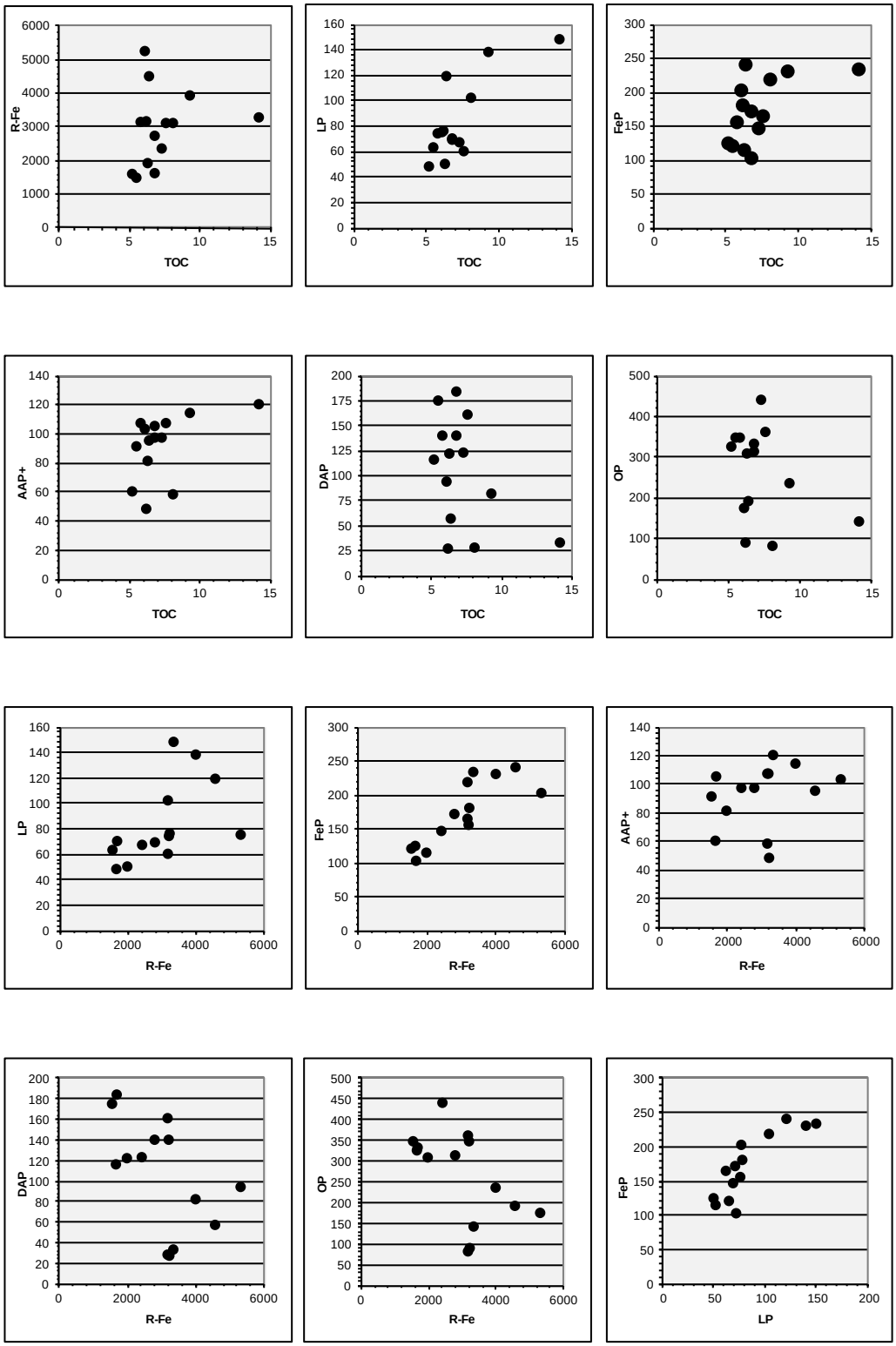
Appendix 1: Scatterplots of all variable pair data sets for Togcha River sediments (May 1999). Axes abbreviations are included at the bottom of the table.



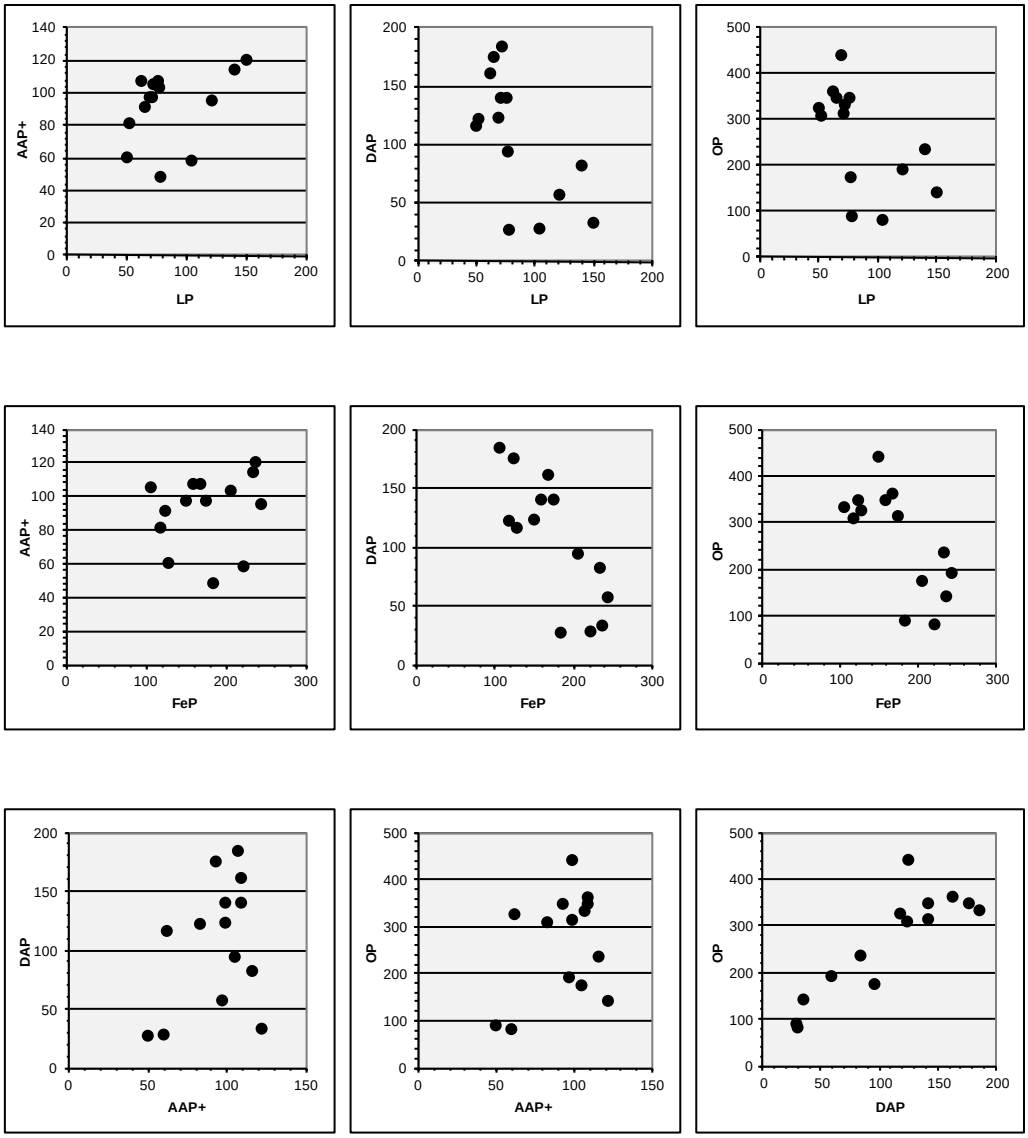
Appendix 1 (cont.): Scatterplots of all variable pair data sets for Togcha River sediments (May 1999).

Key to Axes Labels:

TOC:	Total organic carbon (%)
R-Fe:	Reactive iron (µg/g dry weight)
LP:	Loosely-sorbed P (µg/g dry weight)
FeP:	Ferric iron-bound P (µg/g dry weight)
AAP+:	Authigenic apatitic P + biogenic apatitic P + $CaCO_3$ associated P (µg/g dry weight)
DAP:	Detrital apatitic P (µg/g dry weight)
OP:	Organic P (µg/g dry weight)
◯	R-2 river site (outfall)



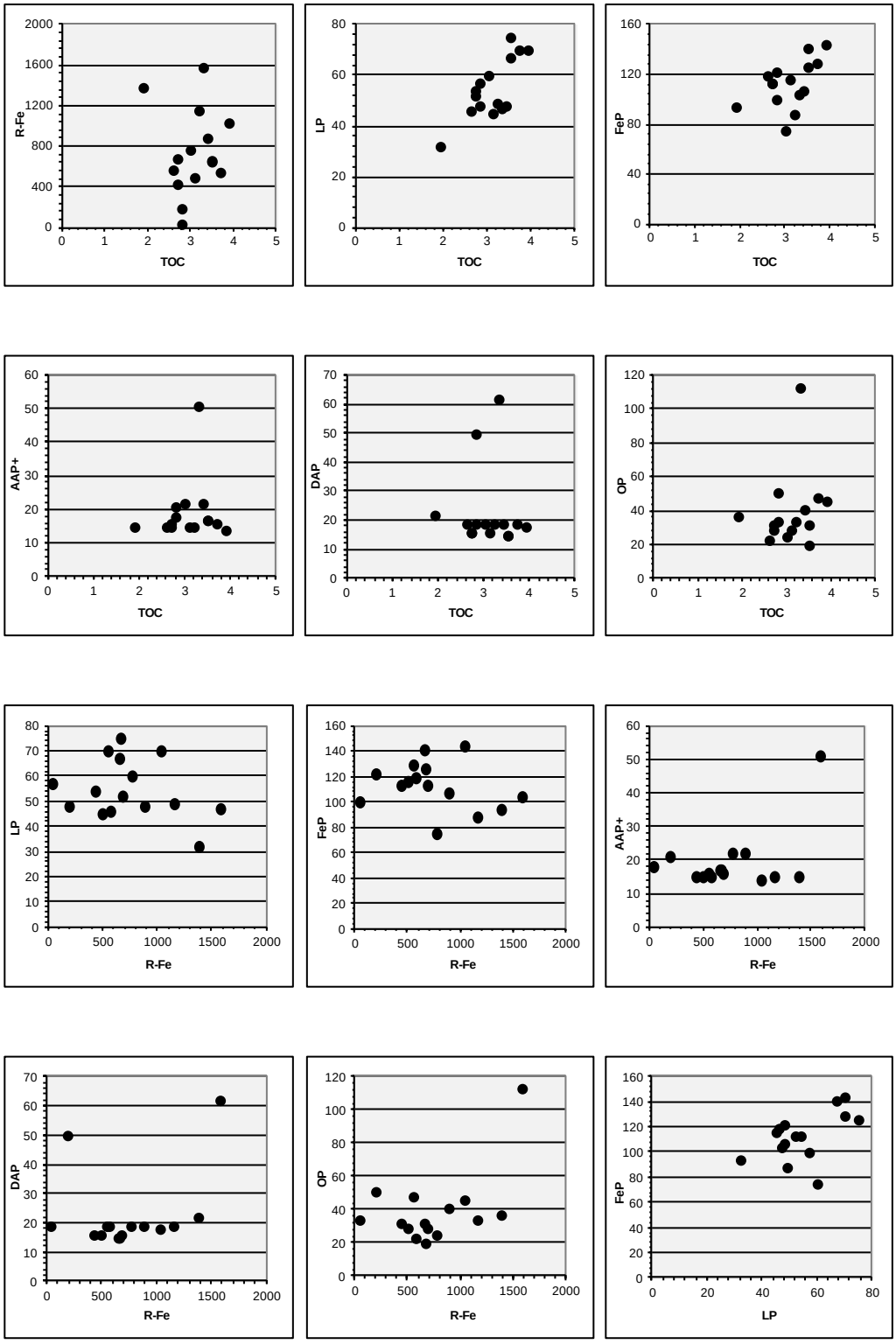
Appendix 2: Scatterplots of all variable pair data sets for Togcha Estuary sediments (May 1999). Axes abbreviations are included at the bottom of the table.



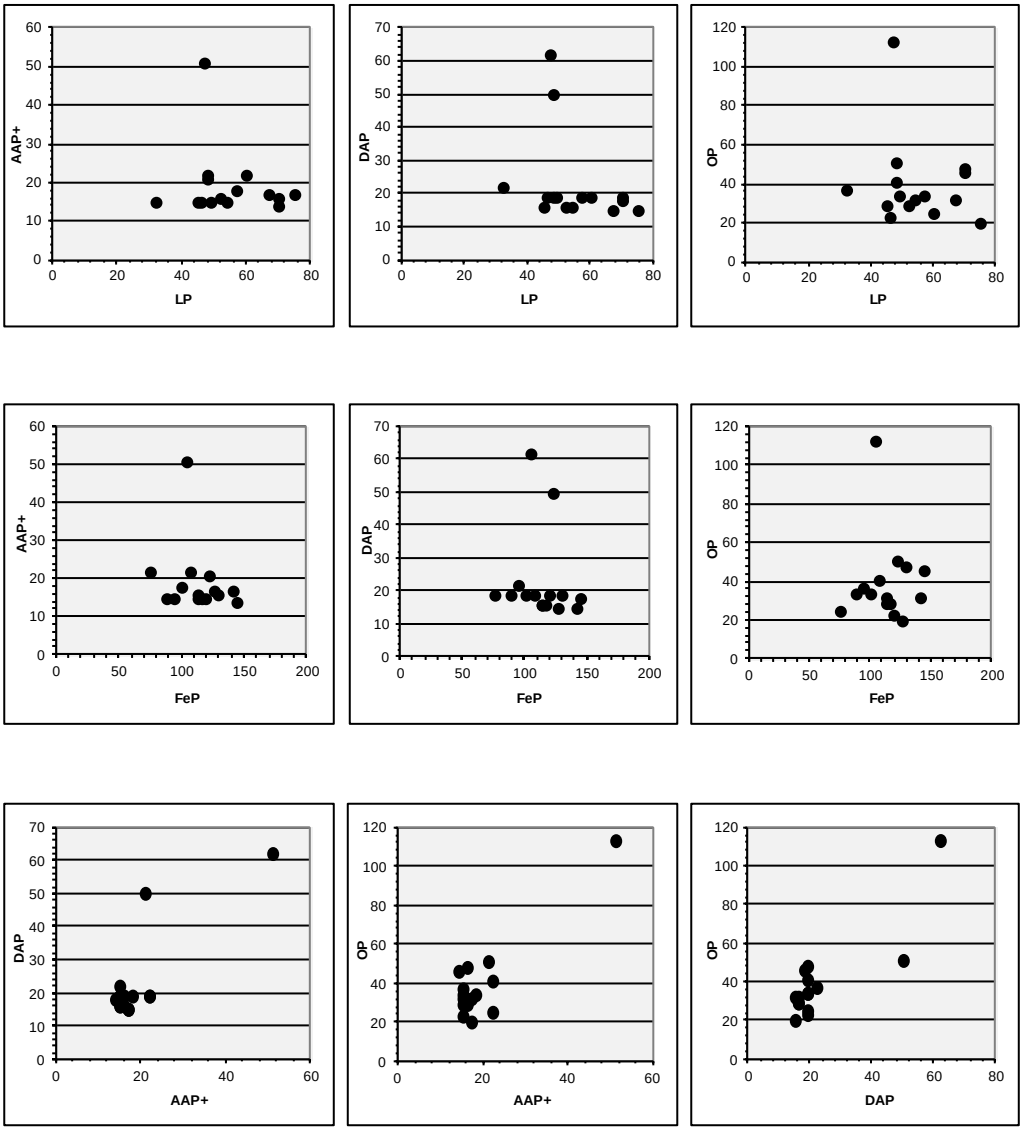
Appendix 2 (cont.): Scatterplots of all variable pair data sets for Togcha Estuary sediments (May 1999).

<u>Key to Axes Labels</u>:

TOC:	Total organic carbon (%)
R-Fe:	Reactive iron (µg/g dry weight)
LP:	Loosely-sorbed P (µg/g dry weight)
FeP:	Ferric iron-bound P (µg/g dry weight)
AAP+:	Authigenic apatitic P + biogenic apatitic P + $CaCO_3$ associated P (µg/g dry weight)
DAP:	Detrital apatitic P (µg/g dry weight)
OP:	Organic P (µg/g dry weight)



Appendix 3: Scatterplots of all variable pair data sets for Togcha Bay sediments (May 1999). Axes abbreviations are included at the bottom of the table.



Appendix 3 (cont.): Scatterplots of all variable pair data sets for Togcha Bay sediments (May 1999).

Key to Axes Labels:

TOC:	Total organic carbon (%)
R-Fe:	Reactive iron (µg/g dry weight)
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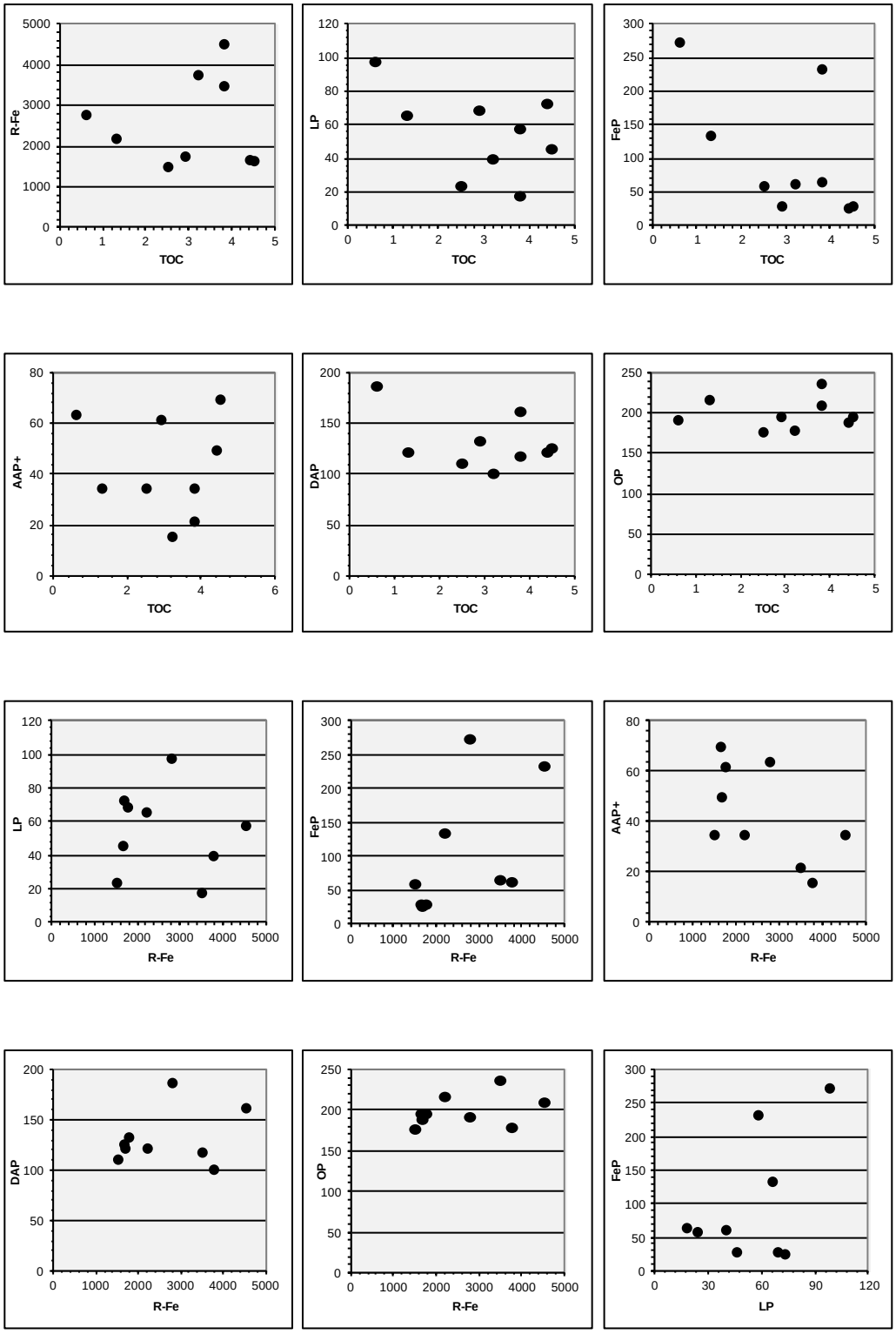
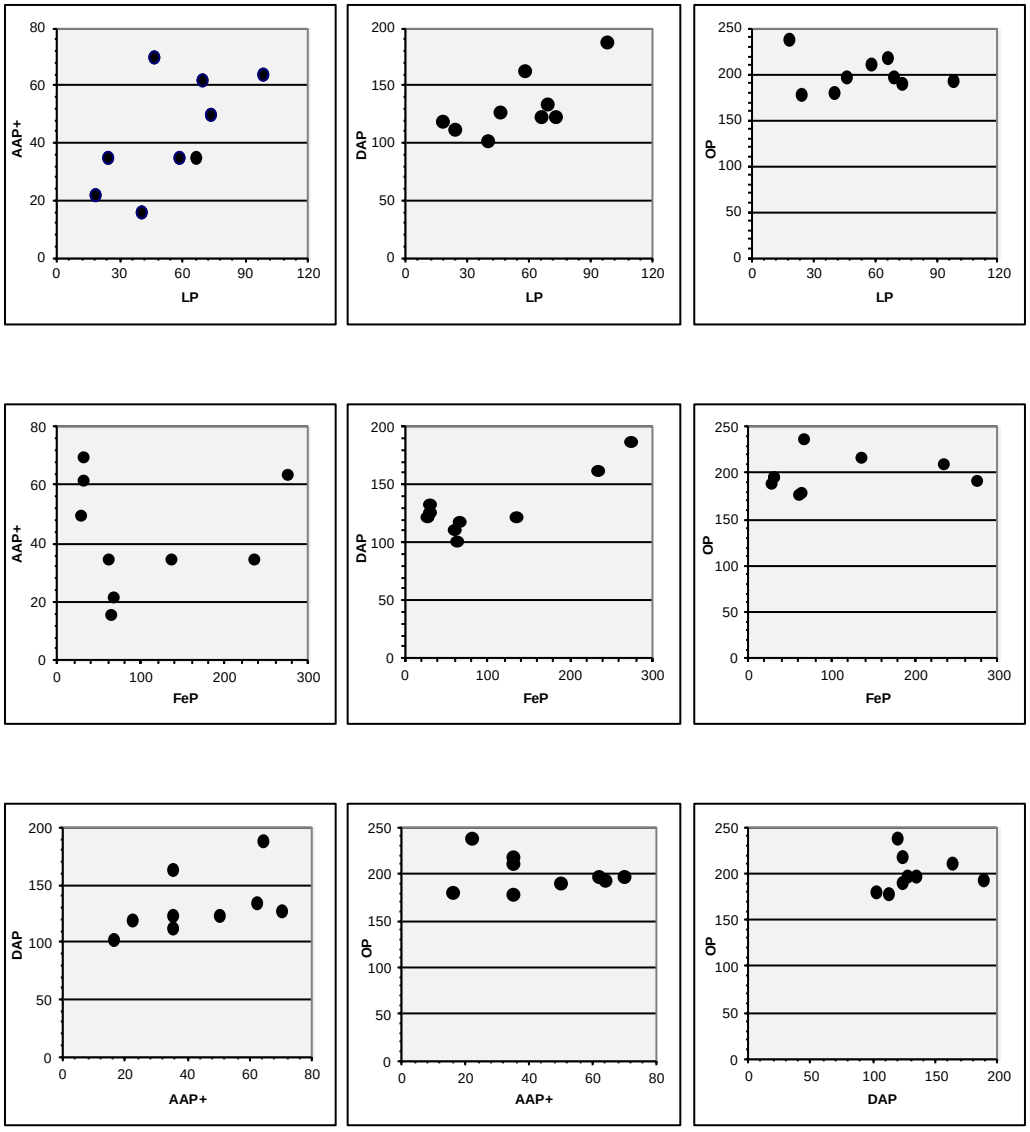


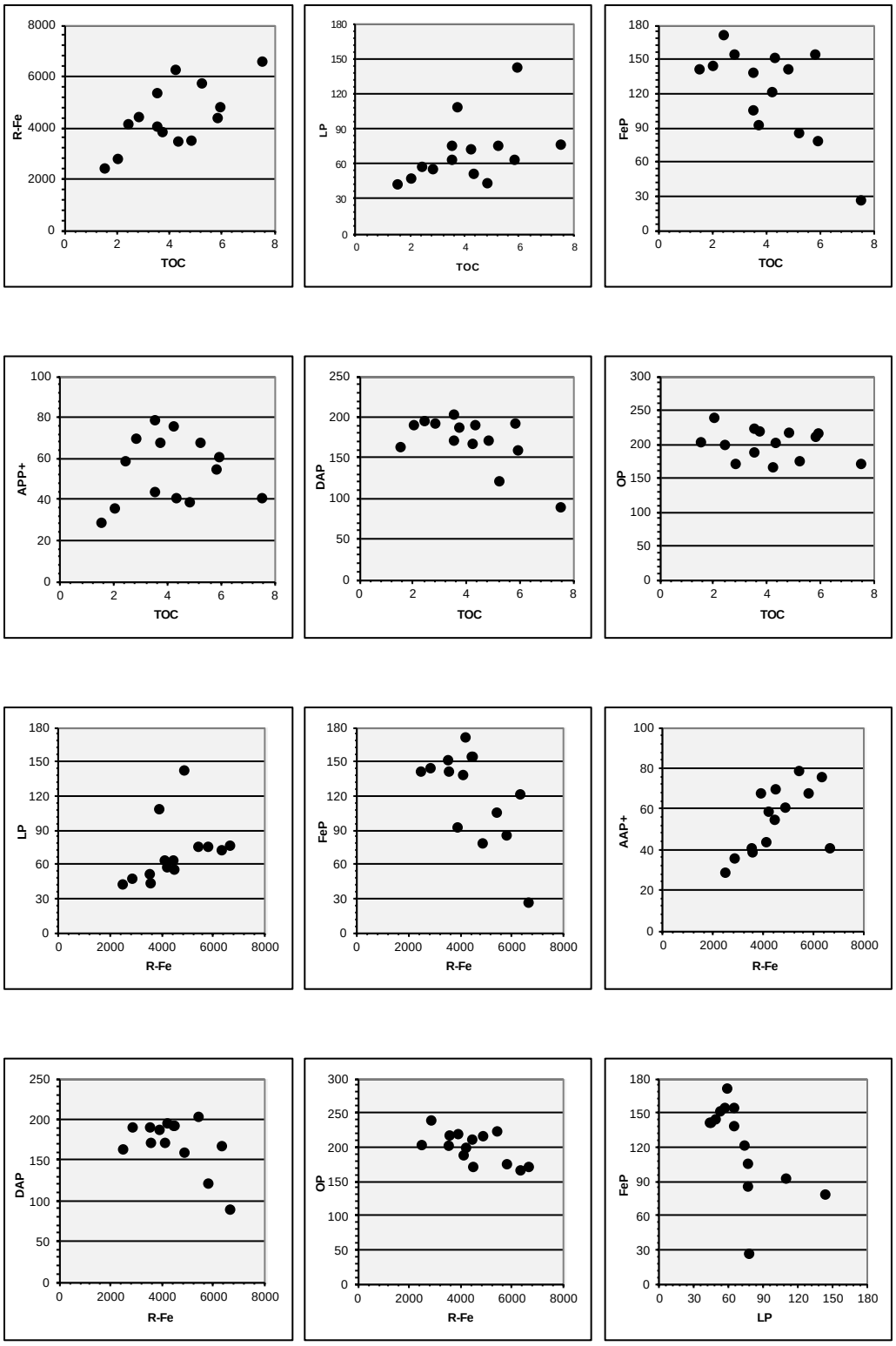
Appendix 4: Scatterplots of all variable pair data sets for Togcha River sediments (Oct 1999). Axes abbreviations are included at the bottom of the table.



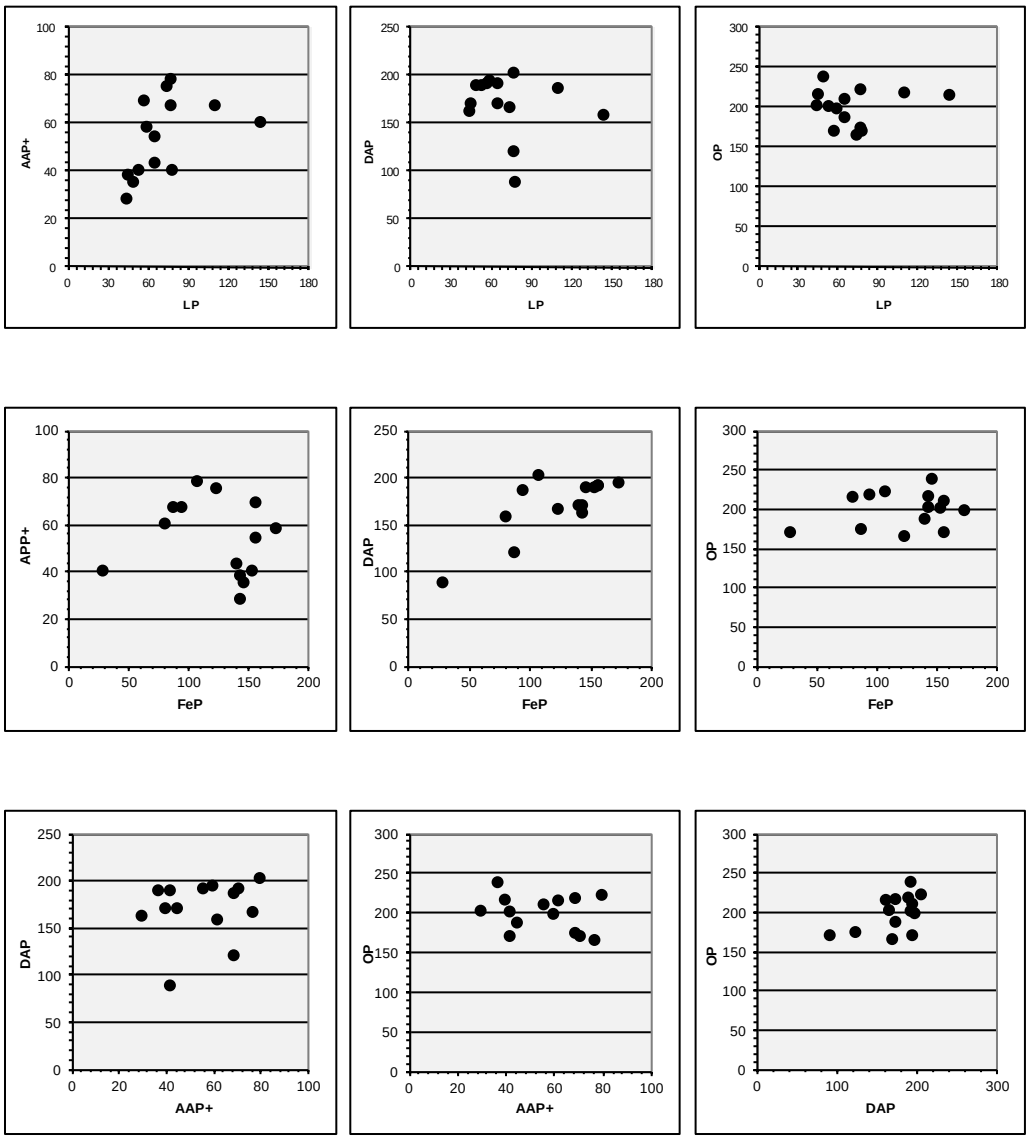
Appendix 4 (cont.): Scatterplots of all variable pair data sets for Togcha River sediments (Oct 1999).

Key to Axes Labels:

TOC:	Total organic carbon (%)
R-Fe:	Reactive iron (µg/g dry weight)
LP:	Loosely-sorbed P (µg/g dry weight)
FeP:	Ferric iron-bound P (µg/g dry weight)
AAP+:	Authigenic apatitic P + biogenic apatitic P + $CaCO_3$ associated P (µg/g dry weight)
DAP:	Detrital apatitic P (µg/g dry weight)
OP:	Organic P (µg/g dry weight)



Appendix 5: Scattergrams of all variable pair data sets for Togcha Estuary sediments (Oct 1999). Axes abbreviations are included at the bottom of this table.



Appendix 5 (cont.). Scattergrams of all variable pair data sets for Togcha Estuary sediments (Oct 1999).

Key to Axes Labels:

TOC:	Total organic carbon (%)
R-Fe:	Reactive iron (µg/g dry weight)
LP:	Loosely-sorbed P (µg/g dry weight)
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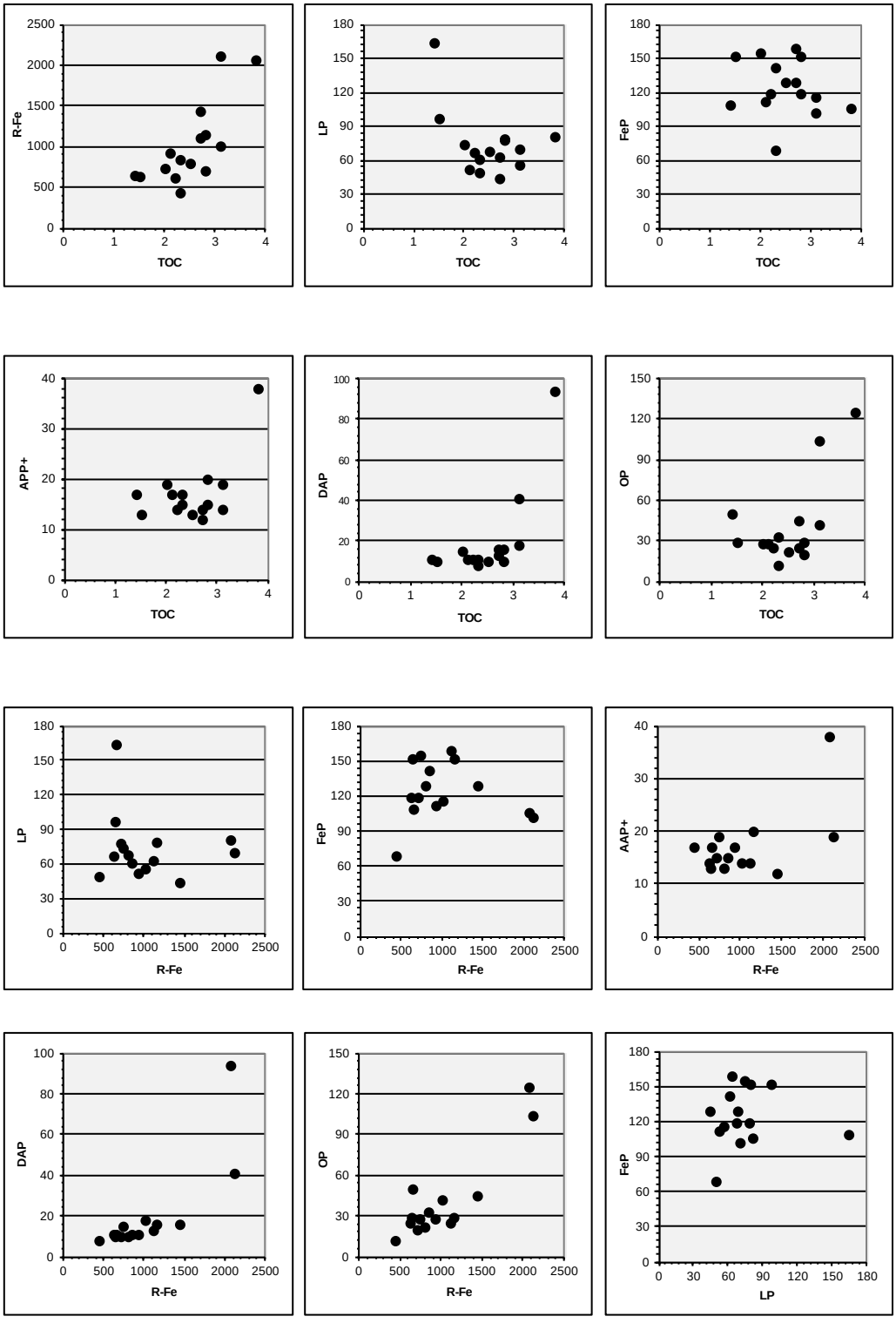
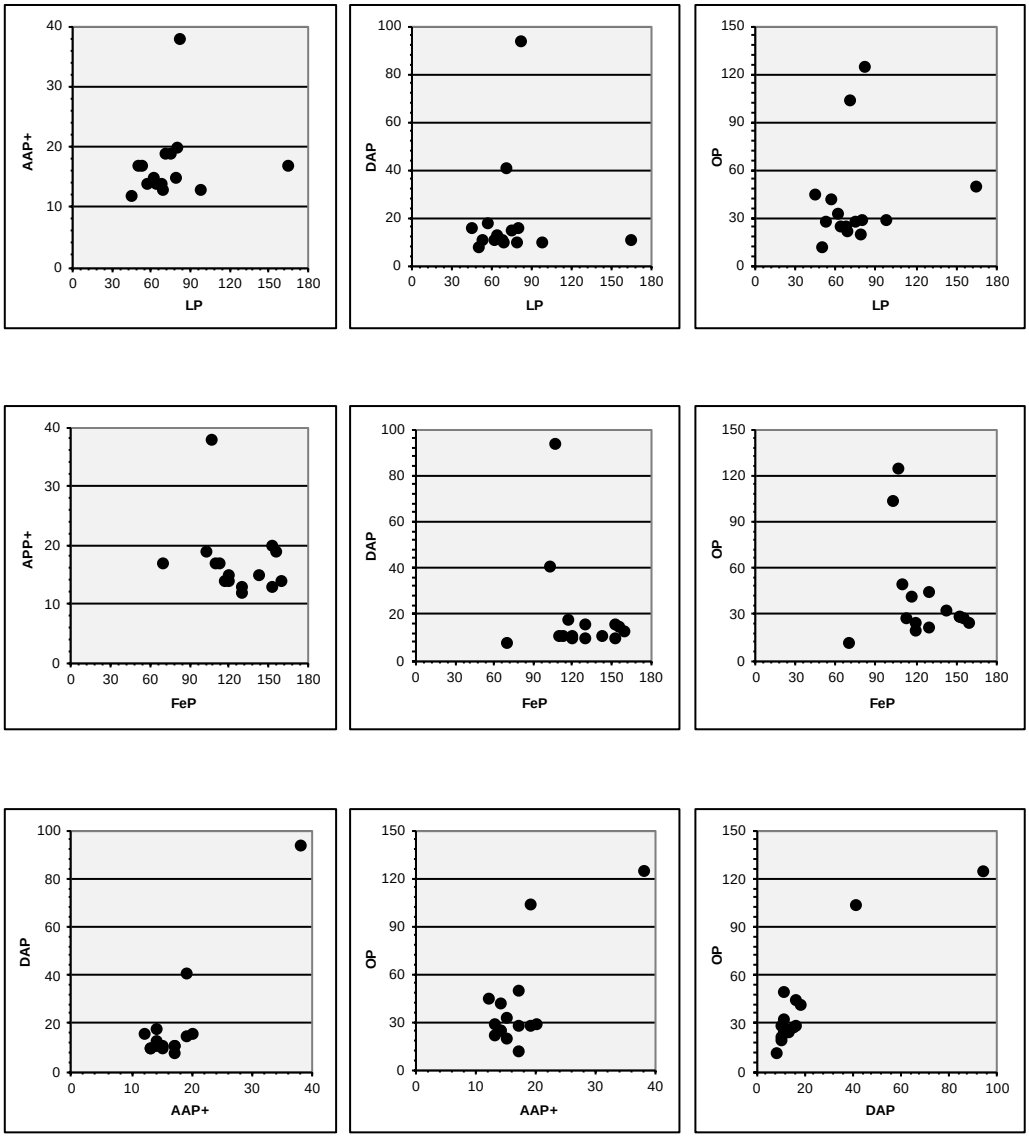


Appendix 6: Scattergrams of all variable pair data sets for Togcha Bay sediments (Oct 1999). Axes abbreviations are included at the bottom of the table.



Appendix 6 (cont.). Scattergrams of all variable pair data sets for Togcha Bay sediments (Oct 1999).

Key to Axes Labels:

TOC:	Total organic carbon (%)
R-Fe:	Reactive iron (µg/g dry weight)
LP:	Loosely-sorbed P (µg/g dry weight)
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DAP:	Detrital apatitic P (µg/g dry weight)
OP:	Organic P (µg/g dry weight)

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