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Tracking the dynamic ecological history of a tropical urban estuary as it responds to human pressures

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Abstract

Coastal cities in tropical areas are often low-lying and vulnerable to the effects of flooding and storms. San Juan, Puerto Rico is a good example of this. It is built around a lagoon-channel complex called the San Juan Bay Estuary (SJBE). A critical channel in the estuary, the Caño Martín Peña, has filled in and now frequently floods the surrounding communities with sewage-enriched waters, causing a series of human health and ecological problems. Sediment core analyses indicate that portions of the SJBE now function as settling basins. High urban and sewage runoff to the Caño contributes nitrogen (N), but stable isotope and sediment nutrient analyses indicate that this runoff may also enhance conditions for coupled sulfate reduction-nitrogen fixation. The amount of 'new' bioavailable N created from inert atmospheric N_2 gas may meet or exceed that from the runoff into the Caño Martín Peña. The ecological consequences of this appear to extend beyond the ponded channel, potentially contributing to the poor water quality of the SJBE, greater than contaminated runoff alone.

Resumen

Ciudades costeras en los trópicos generalmente se encuentran localizadas en lugares de baja elevación y vulnerables a los efectos de tormentas e inundaciones. San Juan, Puerto Rico es un

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buen ejemplo de esto. Esta ciudad fue construida alrededor de un sistema de lagunas y canales que se conoce como el Estuario de la Bahía de San Juan. Un canal crítico en este sistema es el Caño Martín Peña que en el pasado fue rellenado con sedimentos causando inundaciones en las comunidades vecinas. Estas aguas de escorrentía incluyen aguas residuales y aumentado el riesgo a problemas de salud pública y del ambiente. Análisis de los sedimentos indican que porciones de este sistema funcionan como lagunas de sedimentación. Gran flujo de aguas residuales y escorrentía urbana hacia el Caño aportan nitrógeno (N), pero el análisis de sedimentos y nutrientes por isótopos estables indica que esta escorrentía también aumenta las condiciones por procesos acoplados de reducción de sulfato y fijación de nitrógeno. La cantidad de ‘nuevo’ N biodisponible creado del gas nitrógeno inerte atmosférico podría lograr o exceder esa fijación del nitrógeno derivado de la escorrentía hacia el Caño. Las consecuencias ecológicas de esto parecen extenderse más allá de este canal estancado afectando así la calidad del agua en el Estuario, mayor aún que los contaminantes encontrados en la escorrentía pluvial por sí sola.

Keywords

dredging; stable isotope; nitrogen; carbon; sulfur; deposition

Introduction

Tropical urban estuaries are understudied. These often low-lying city-estuarine ecosystems are particularly vulnerable to hurricanes and storm surges and are at the frontline of rising sea levels (e.g., Mendelsohn and others 2012; Woodruff and others 2013). The San Juan Bay Estuary (SJBE) in Puerto Rico is an example of such a system, where the population density of the neighborhoods surrounding the most urban portion of the estuary, the Caño Martín Peña (CMP), is 8,775 people km^{-2} (Army Corps 2016). The bulk of the estuary is densely urban although the easternmost portion is encompassed by mangrove forest (Fig. 1). We present the environmental history of this complex ecosystem, explored via sediment cores and framed in the context of some of the social and environmental challenges of the people who live there.

The SJBE has been heavily altered by dredging, filling, and extensive shoreline modifications for more than two centuries. For example, a map of San Juan drafted in 1776 showed the CMP, an important channel in the estuary (Fig. 1), as being 3–4.3 m deep in the western half and 1.5–3 m deep in the east (O’Daly 1776 from ArmyCorps 2016). Today the western half of the CMP is maintained by periodic dredging while the eastern half is essentially infilled. Dredging and straightening of the western CMP was documented as early as the late 1910s to early 1920s. In 1927, the Puerto Rican Government authorized the sale of mangrove forest, implicitly encouraging the deforestation and infilling of forest for urban development, with the intended co-benefit of reducing mosquito habitat. This legislative action in conjunction with a series of devastating hurricanes, the decline of the rural sugarcane industry, and an increase in industrial jobs in the San Juan urban areas starting in the 1940s, led to rapid destruction of mangrove forest surrounding the CMP in the first half of the 20th century (Army Corps 2016). Deforested peat was filled with garbage and debris until it was firm enough to build homes upon. Surveys of the canal and its banks

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have found trash and other debris up to 2.75 m below the surface (Army Corps 2004). The resultant unplanned communities have neither basic sewerage infrastructure nor other features of more deliberate development, including connections to utility companies. For example, many streets are too narrow to allow access by garbage trucks. While adjacent communities were ejected from the western CMP when the canal was dredged and bulkheaded into a 3m deep, 61m wide channel in the mid-1980s (Army Corps 2016), the eastern half of the Caño wasn't dredged and its residents are exposed to flood waters contaminated with high levels of fecal coliform bacteria after even small rainfalls. The primary social-ecological concern in the SJBE, as a whole, is how the closure of the eastern CMP effects the estuary and the provision of services (including human health and well-being) to the adjacent communities.

The CMP is arguably the most heavily modified portion of the SJBE, but the Lagunas San José and La Torrecilla have also been dredged and had their shorelines modified. About 17% of the Laguna San José was dredged between the 1950s and early 1970s, largely along the east and southeast coasts (Fig. 1, Ellis 1976). Most of the dredging was associated with the construction of the airport adjacent to the lagoon. Also, the 4 km long Caño Suarez, which connects Laguna San José with Laguna La Torrecilla, was widened and deepened sometime between 1962 and 1967 (Fig. 1, Ellis 1976). Caño Suarez now ranges in width and depth from 5×1 m at the narrowest point to approximately 30×10m in its middle reach (Bunch and others 2000). In Laguna La Torrecilla, the inlet channel to the Atlantic Ocean was widened and deepened in 1962 and there have been a variety of shoreline modifications along the southern shore (Ellis 1976). In contrast to the rest of the SJBE system, Laguna Piñones is surrounded by the largest remaining mangrove forest in Puerto Rico, the Bosque Estatal de Piñones, and is connected to La Torrecilla via a poorly maintained channel and flow through the mangroves (Webb and Gomez 1998). The SJBE system is a gradient of extremes: from the urban, industrialized San Juan Bay with its full open exchange with the sea, to the forested Laguna Piñones with no direct connection to offshore waters (Fig. 1).

While most of San Juan's treated wastewater has been discharged offshore since 1985, pollutants still enter the SJBE via combined sewer overflows, runoff, faulty sewage lines, tributaries, and unsewered areas adjacent to the eastern CMP (Bunch and others 2000). Household wastewater from the communities surrounding the eastern CMP drains to cesspools, storm drains, or directly to the channel; all of which are often full of standing water. Small amounts of rainfall in the watershed leads to widespread flooding of this area, filling low-lying homes, schools, and businesses with stormwater containing fecal coliform concentrations of up to 2×10^6 cfu 100 ml^{-1} (health limits are 200 cfu 100 ml^{-1}, Army Corps 2016). The floodwaters have been linked to higher prevalence of gastrointestinal illness and asthma for the exposed communities when compared to neighborhoods elsewhere in San Juan (Sheffield and others 2014).

Organizing with the Corporación Proyecto ENLACE del Caño Martin Peña, the eight communities along the Caño have been working collectively, collaboratively, and systematically on issues of social justice and human health associated with the clogging of the eastern Caño for more than a decade (http://cano3punto7.org/nuevo/index.html). Their efforts have been internationally recognized and featured in a variety of popular press articles (e.g., Franco 2016, Stanchich 2017, Hartz 2018, Zaitchik 2017) which highlight the role of community action in the social-ecological coupling of intensely urban coastal systems. Here we seek to assess how the SJBE system, including the CMP, has responded to the urban influences modifying it over the past century and hypothesize that changes in hydrodynamics associated with the infilling of the CMP have affected the sediment and nutrient dynamics in the adjacent Laguna San José and Laguna La Torrecilla. We provide geochemical insight into the ecological effect of urbanization on these dynamics, as recorded in the sediment history of the San Juan Bay estuarine ecosystem east of San Juan Bay proper.

Methods

Subtidal cores were collected from 3–5 March 2016 in areas that had not been dredged in the last 30 years. Cores were collected in duplicate from lagoon sites and triplicate from the CMP using 5.7 cm inner diameter PVC cores fixed to a core handle (Fig. 1). Cores were split and sectioned in 1 cm slices from 0–3 cm and then 2 cm slices to a maximum depth of 60 cm.

Chronological models were developed for one core from each site based on down-core abundances of excess Pb-210 (Pb-210_{ex}) (Fig. 2, Table 1). Bulk density was measured in subsamples that were then sieved (2 mm) and 3.4cc of the fine fraction was loaded into plastic vials, triple sealed (rubber septa, epoxy, vial cap), and held for ≥ 21 days to develop secular equilibrium between Ra-226 and Rn-222. Gamma spectra were then counted on a Canberra GSW120 SAGe well detector for a minimum of 80,000 s and converted to estimations of radionuclide abundance using Canberra Genie 2000 software calibrated with multi-radionuclide geometric standards from Eckert and Ziegler. The activity of Pb-210_{ex} was determined by subtracting Pb-214 activity from total Pb-210 activity. Horizon dates were derived from Pb-210_{ex} profiles using the constant rate of supply model (Appleby and Oldfield 1978). Accretion rates (g cm^{-2} yr^{-1}) were calculated from depth intervals between dated horizons, which were aggregated in some cases to avoid overlapping 1 sigma error ranges, and multiplied by interval weighted dry bulk density to avoid potential biases introduced by sediment compaction.

For loss on ignition, sediment subsamples were dried, ground, heated to 550°C for four hours, cooled to ambient temperature, and reweighed. Percent organic matter (%OM) was calculated as 100*(1-weight after 550°C/initial weight). Subsamples were then heated to 950°C for two hours, cooled and reweighed to determine percent carbonate content which was calculated as 100*(1-(550°C-950°C weights)/initial weight) (Heiri and others 2001). Additional subsamples were gently rinsed through a 2 mm sieve using deionized water, treated with H_2O_2 to remove organic material, and analyzed on a Malvern Hydro 2000S/ Mastersizer 2000 system (Gray and others 2010). Particle size distributions were analyzed for texture and statistically described using Gradistat.v8 software (Blott and Pye, 2001). Sediment textures were defined as per Friedman and Sanders (1978). Particle sizes (i.e., diameters, d) were converted to phi (φ) units using the formula $\varphi = -\log_2 d$, and the full logarithmic method of moments was used to calculate mean particle size and sorting as follows:

$$Mean_{\varphi} = \frac{\sum f m_{\varphi}}{100} \quad (1)$$

$$Sorting_{\varphi} = \sqrt{\frac{\sum f(m_{\varphi} - Mean_{\varphi})^2}{100}} \quad (2)$$

where f is the frequency in percent and m is the midpoint of each size class interval. Graphical analysis of $Mean_{\varphi}$ vs. $Sorting_{\varphi}$ space was conducted to discriminate between high energy ‘storm/channel’ and low energy ‘settling’ depositional domains defined by Tanner (1995) and Lario and others (2002) (Fig. 3).

Total phosphorous (P) concentrations of sediment subsamples were determined using and HCl acid digestion and spectrophotometry (Aspila and others 1976). Subsamples for organic carbon (C) analysis only were fumigated with 10 M HCl (Harris and others 2001) and C and N isotope compositions ($\delta^{13}C$ and $\delta^{15}N$) were determined on an Elementar Vario Micro elemental analyzer connected to a continuous flow Isoprime 100 isotope ratio mass spectrometer (Elementar Americas, Mt. Laurel, NJ). Standard reference materials USGS 40 and USGS 41 were used to normalize samples to the air ($\delta^{15}N$) and Vienna Pee Dee Belemnite ($\delta^{13}C$); precision was better than ±0.3‰ for both. The %C and %N were calculated by comparing the sample peak area to those of standards. Sulfur analyses for $\delta^{34}S$ and %S was conducted at the Center for Stable Isotope Biogeochemistry at the University of California at Berkeley where analyses followed the SO_2 EA-combustion-IRMS method. Precision of $\delta^{34}S$ values is better than ±0.2 ‰.

We used ANOVA to determine whether material deposited prior to the dredging and urbanization (1900–1950) was significantly different from that deposited more recently (1995–2016). Separate models were fit for %N, %C, %S, %P, %OM, $\delta^{15}N$, $\delta^{13}C$, $\delta^{34}S$ values and log-transformed molar OM:N, and C:N ratios using SAS Version 9.4. Models were first fit using just the dated cores and again for all available cores. For dated cores, two-factor ANOVA models were fit with time period and site as fixed factors. Differences among cores (at the 95% confidence level) were evaluated for each time period and differences between time periods were assessed within each core. Pairwise comparisons were performed with CMP east as a reference site using Dunnett’s test (site comparisons, no interactions) or Bonferroni (all others). Age models from dated cores were applied to undated cores to estimate time periods. For the undated core models, replicate cores were treated as a random nested effect within the fixed location variable and F-tests were adjusted so that the core random effect term was used in the denominator. Pairwise comparisons for undated core data were performed the same as with the dated cores.

Results

Sediment dating and composition

Accretion rates generally ranged from 0.03–0.3 g cm^{-2} yr^{-1} (Figs. 2, 4, Table 1). All dated locations experienced increases in accretion rates beginning around 1960’s to 1970’s with the exception of the Laguna San José dated core, which stepped down to lower accretion rates around 1960, and then increasing from the end of the 20th century to the present. The CMP west accretion rates increased by an order of magnitude between 1960 and the 1990s, and then decreased to a latest accretion rate 5 times that of pre-1960s conditions. At CMP east accretion rates increased (+ 60%) from 1960 to 1990, and then declined to 40% less than pre-1960 rates. Accretion rates at La Torrecilla and Piñones increased for a few decades starting around 1960 or in the 1970's by 4 and 7-fold, respectively, before stabilizing at higher rates (4–6 times greater than pre-1960) over the last 2 to 3 decades.

Textures ranged from mud (silt and clay, < 10% sand) to sand (> 90% sand), with most horizons composed of sandy mud (10–49% sand) to muddy sand (50–89% sand). The CMP west displayed distinct coarsening after the period of dredging. The CMP east bore relatively stable particle size distributions throughout, with occasional coarse horizons. San José, La Torrecilla, and Piñones all displayed high variability in particle size distributions among horizons. Rhythmic oscillations between fine and coarse horizons were found at Piñones, perhaps reflecting periodic tropical storms. Particle size based settling domains were relatively stable at CMP east (low energy settling regime) and Lagunas San José and La Torrecilla (storm/channel regime) (Figs. 3, 5). The CMP west transitioned from a settling dominated system during the 1900–1950 period to a storm/channel regime from 1990–2016. Piñones transitioned from a storm/channel to a settling dominated system over the same periods.

The %OM in the cores ranged from 7% to 45% across all sites (Fig. 4), with significantly more %OM in the recently deposited sediments (1990–2016 vs 1900–1950). Sediment carbonate content ranged from 1–17% in all cores, except for Piñones, where, with the exception of the top 3 cm of a single core (where carbonate =9%), all cores were carbonate free.

Sediment nutrients (N, P, C, S)

Recently deposited sediment (1990 to 2016) contained more N than that deposited between 1900 and 1950 (Fig. 5, Tables 2, 3). When considering all cores collected, %P and %C were significantly higher in more recent sediments (1990–2016) than in those deposited earlier (1900–1950). In the dated cores, CMP east had significantly higher %P than CMP west, Piñones, and La Torrecilla and %C increased in CMP east and Laguna San José (1990–2016 vs. 1900–1950). The carbon to nitrogen ratios (C:N) decreased significantly through time in Lagunas San José (all cores), La Torrecilla (all and dated cores), and Piñones (just dated core). The CMP east has had higher C:N than Piñones for the entire period of record, and in the recently deposited sediments, C:N ratios in CMP east were significantly greater than those from Laguna San José.

At CMP west, $\delta^{34}S$ declined from 4‰ in 1960 to −12‰ since approximately 2009 (early vs. recent significant for dated and all cores, Fig. 6). The $\delta^{15}N$ and $\delta^{13}C$ values at CMP west also declined since the dredging was completed. Similarly, $\delta^{15}N$ and $\delta^{13}C$ values in the CMP east have been declining since the 1980s and, in the dated cores, there were significant decreases between earlier (1900–1950) and more recent (1990–2016) values (Table 2). In contrast, $\delta^{34}S$ values at CMP east increased (older vs. recent, dated cores) with positive values since the 1960s, increasing by roughly 10‰ from 1987 to 2000. In Lagunas San José and La Torrecilla, $\delta^{15}N$ values measured in the dated cores have shown a significant increase between earlier and more recent time periods.

As with %P, CMP east had higher $\delta^{34}S$ values than CMP west, Piñones, and La Torrecilla (all cores), particularly in the most recent sediments (1990–2016, dated cores).

Discussion

Aggradation of the eastern portion of the Caño Martín Peña caused it to transition from a through-flow to settling environment and this occurred over the course of one human lifetime in an intensely urban area. The infilling of the mangroves along the Caño with sediment and debris intensified during the development of the adjacent communities in the 1940s and 1950s. The eastern CMP then began to narrow as development continued to encroach and portions of it were reported as completely blocked as early as the year 2000. Accordingly, as the eastern half of the Caño Martín Peña became increasingly filled in, accretion rates declined (Figure 2). Both the timeline of this depositional history and the subsequent frequent flooding by sewage-enriched waters that now occurs in the residents' homes, streets, and schools are well-documented (e.g., ArmyCorps 2016). Our contribution to understanding this environmental problem is to describe the ecological effects of the modern CMP on the San Juan Bay Estuary system in the context of the historical human-induced hydrodynamic and sedimentological changes. We used geochemistry to document some of the effects that people cannot directly see.

In the SJBE, it can be unclear where the land ends and the estuary begins. This is true of both the mangrove fringed portions of the basin (La Torrecilla, Piñones) and the intensely urban areas (CMP). Human modification of these boundaries has had a profound influence on the estuarine environment and hydrodynamics (e.g., Cerco and others 2003, ArmyCorps 2016, Branoff 2019). Flow through CMP east decreased by roughly half between 1974 and 1995 (from 4–6 $m^3 s^{-1}$ to ~2 $m^3 s^{-1}$, Bunch and others 2000) and declines have continued since. Sediment from CMP east is characterized by fine-grained particles typical of settling basins and has been for more than a century. An 1899 survey of the region, conducted prior to any major deforestation and infilling of the adjacent mangroves, described the bottom as black mud (Evermann 1900, Army Corps 2016). While the Caño used to serve as the primary outlet for Laguna San José, it also had a benthic environment characteristic of mangrove dominated inner estuaries (e.g., Pait and others 2012, Army Corps 2016). Sediments meeting the settling classification have increased in Laguna San José, illustrating the changing hydrodynamics of the lagoon, where the residence time is 17+ days when it should be <4 (Army Corps 2016, Pérez-Villalona and others 2015). The recent fine-grained material deposited in San José is high in organic matter, with a higher proportion of N and lower C:N; consistent with a more N enriched system. Overall the accretion rates in the Lagunas San José and La Torrecilla do not appear to reflect the dredging projects that occurred from the 1950s to 1970, which is not entirely unexpected as the core locations were far from reported dredge locations (Ellis 1976). In contrast, accretion rates have increased since ~1960 in Piñones (Fig. 2) and it is possible that this shift could be associated with the damming of the Río Loíza in 1953 (Quiñones and others 1989), a large river flowing some 6 km east of the lagoon, possibly reducing freshwater flows and fluvial sediment flux to the lagoon.

Total P content of recently deposited sediment (1995–2016) is slightly higher than that deposited pre-dredging (1900–1950). The higher N content of the recently deposited sediment could indicate that the SJBE is now filling with organic matter of a higher nutritional quality, or it could be highlighting the effect of diagenesis of the older sediments. However, the elevated N in the recent sediments from LSJ, relative to the other core locations, support our hypothesis that this lagoon is now functioning as a settling basin. While changes in bulk N content can be difficult to interpret, the stable isotope data give some indication of the organic matter sources. While $\delta^{13}C$ values can distinguish C sources (Fry 2006) as well as net ecosystem productivity (Oczkowski and others 2018), they were fairly homogenous (~−26‰) throughout most of the cores. The CMP was the exception. After the dredging of the western CMP was completed in the late 1980s, $\delta^{13}C$ values in the dated CMP cores (Fig. 6) declined from roughly −26‰ to ≤−28‰, consistent with more terrestrial carbon sources (Fry 2006).

Typically, enhanced human inputs, particularly from sewage, are associated with higher $\delta^{15}N$ values (generally >10‰), as are longer hydrologic residence times (Fry 2006). Processes that cycle or process nitrogen, like denitrification, preferentially remove the lighter ^{14}N isotope by converting it to N_2 gas, leaving the remaining N pool enriched in ^{15}N (e.g. Montoya 2007). Nitrogen isotope values in Lagunas San José and La Torrecilla rose over time, consistent with systems serving more and more as depositional basins for enhanced anthropogenic inputs, as the breakdown of organic matter and subsequent denitrification of nitrate to N_2 gas elevates remaining $\delta^{15}N$ values. The $\delta^{15}N$ data from Piñones, the lagoon surrounded by mangrove forest, showed no clear trends, suggesting no major changes in N sources or cycling. In contrast, the $\delta^{15}N$ values in the dated CMP east and west cores, which bracketed the most urbanized and filled-in stretch of the Caño, *decreased* significantly over time (1990–2016 vs. 1900–1950).

The eastern half of the CMP receives unchecked sewage and urban runoff which, given the ponded nature of the Caño and the reduced flushing, likely remains in the system for extended periods of time; all factors usually associated with higher $\delta^{15}N$ values. Anaerobic ammonium oxidation (anammox), which converts dissolved ammonium and nitrate to N_2 gas in a low oxygen environment could also be an important N-pathway in this environment. But, like denitrification, anammox preferentially removes ^{14}N, leaving the remaining ammonium pool enriched in ^{15}N and increasing stable isotope ratios in the pore water dissolved inorganic nitrogen (Brunner and others 2013), which is the opposite of what we measured in the cores taken at either end of the eastern half of the CMP (CMP west and CMP east cores, Fig. 1).

Nitrogen fixation, which is the transformation of inert N_2 gas into organic N, is the only process in the N-cycle that is associated with low $\delta^{15}N$ values (Montoya 2007). We suggest that the microbial fixation of N from inert atmospheric N_2 to bioavailable forms may be an important N source to the CMP, as fixed N has a $\delta^{15}N$ value of ~0‰ (Fry 2006). N-fixation in mangrove habitats can supply ≥40% of the bioavailable nitrogen to some mangrove forests (e.g., van der Valk and Attiwill 1984, Zuberer and Silver 1978). In their review of mangrove sediment microorganisms, Holguin and others (2001, p. 269) observed that "…N_2 fixation is a major bacterial activity in mangrove ecosystems, second only to carbon decomposition of detritus by sulfate-reducing bacteria." Many sulfate-reducing bacteria are also N-fixers in mangrove ecosystems (e.g., Romero and others 2015) and the fixation is not inhibited by high concentrations of dissolved bioavailable N, rather it appears to be positively correlated with the supply of organic matter (Bhavya and others 2016, O'Neil and Capone 1989). This fixation could be occurring in the soil itself as well as in the water column. In shallow stretches of the eastern, undredged Caño the substrate is often covered in filmy white mats similar in appearance to the *Beggiatoa* mats documented by Jean and others (2015). Beggiatoaceae are sulfur-oxidizing bacteria that often form distinctive mats in marine and freshwater environments and are also frequently N-fixers. We do not know if these bacterial mats fix N, or if they would fix N when bio-available N is plentiful (Nelson and others 1982, also see http://web.estuario.org/en/home-english/ for monitoring data). The *Beggiatoa* mats in mangrove forests in the Guadeloupe archipelago, to the east of Puerto Rico and also in the Caribbean Sea, were characterized by δ^{15}N values of ~3 ‰ and δ^{13}C values of ~−29‰. These isotope values are similar to the values measured in recent sediment deposits in the CMP and the δ^{15}N values are consistent with N-fixation (Pascal and others 2016).

In a recent study conducted in Laguna San José, large fluxes of N_2 into the sediments were measured during some core incubations that were exposed to light (>250 μM m^{-2} h^{-1}, Pérez-Villalona 2014, Pérez-Villalona and others 2015). In fact, N_2-N fluxes were negative (N_2 going into the sediment) in 17% of the light-exposed ambient cores (Pérez-Villalona 2014). While lagoon-wide denitrification rates were high, similar to the dissolved inorganic nitrogen loads to the lagoon, they were also three times lower than the ammonium effluxes from the sediment (Pérez-Villalona 2014, Pérez-Villalona and others 2015). Pérez-Villalona (2014) suggested that the high ammonium effluxes may be due to the breakdown of high loads of allochthonous organic matter and we wonder if N-fixation may also be contributing to this phenomenon, particularly given the N_2 fluxes into the soil. It is unclear how this unaccounted for additional N source could be contributing to the poor water quality in the Caño and adjacent Laguna San José (e.g., Pérez-Villalona and others 2015).

Although seawater sulfate has a δ^{34}S value of +20.6‰ (Bottcher et al. 2004), negative sediment sulfur isotope values are common in eutrophic and low-oxygen bottom waters (Yamanaka et al. 2003). This is because of the high kinetic fractionation associated with sulfate reduction (20–40‰) (Canfield 2001): ^{32}S is more quickly reduced than ^{34}S, resulting in lighter sulfides and enriched sulfates (Brownlow 1996). However, when the sulfate supply is restricted, closed system conditions exist, sulfate reducers turn to more enriched sulfate, and δ^{34}S values of sulfides become more positive (Emery and Robinson 1993). Across our core sites, we found that the δ^{34}S values were roughly correlated with flushing, at least in the recently deposited sediments. Better flushed portions of the system had lower values. La Torrecilla, arguably the most well-flushed site, had the lowest surface sediment δ^{34}S values (−21.3±3.1‰) while Piñones and San José, which have no open exchange with the sea, were closer to zero (−5.2±4.0‰ and −0.4±4.9‰).

In the dated cores, $\delta^{34}S$ values significantly declined over time in CMP west but increased in CMP east (1990–2016 vs. 1900–1950). The shifts could be related to both flushing and organic matter supply. In the decade prior to dredging, $\delta^{34}S$ values were approximately +5‰ at CMP east. After dredging, values rose to +10‰ in all of the (undredged) CMP east cores. High rates of sulfate reduction combined with the poor flushing may cause sulfate reducers to take up more of the energetically less favorable ^{34}S in this poorly flushed, anoxic system. Altered $\delta^{34}S$ values, depleted $\delta^{15}N$ values, and high soil OM and organic C all suggest substantial sulfate-reduction at the CMP east site. Sulfate-reduction produces H_2S and HS, which then react with P-containing iron compounds to release P into the bio-available pool (e.g., Holguin and others 2001). There was some evidence for sulfate-reduction as a P source in sediments from the adjacent San José (Pérez-Villalona and others 2015) and CMP east had higher %P than CMP west, Piñones, and La Torrecilla (dated cores). Further, H_2S concentrations in the air around the Caño are so high that they exceed minimum acceptable levels for chronic exposure for children (Army Corps 2016). Another possible source of higher $\delta^{34}S$ values could be the sewage particulate matter discharging into CMP east. Sewage sludge and particulate organic matter (POM), at least in temperate areas, range from ~0 to 6‰ (see Tucker and others 1999). Fecal coliform concentrations do indicate substantial sewage contamination (ArmyCorps 2016) and sewage effluent could be contributing to high $\delta^{34}S$ values both directly (the POM itself) or indirectly, as a source of organic matter to fuel sulfate reduction and nitrogen fixation (e.g. Holguin and others 2001, O'Neil and Capone 1989). In contrast to CMP east, $\delta^{34}S$ values significantly declined over time at CMP west. In the dated core, $\delta^{34}S$ declined from 4‰ in 1960 to −11‰ in the 1980s. While CMP west was dredged in the 1980s, the neighborhoods adjacent to this portion of the Caño started to be eliminated in the 1950s (Figure 1). Local population declines, and the associated decline in urban runoff and sewage, is consistent with the decline in $\delta^{34}S$ values that was observed in the CMP west core prior to the dredging.

Dredging and filling has led to changes in hydrodynamics which subsequently affected sediment deposition and nutrient cycling in the urban SJBE. Despite dredging in the western half of the CMP, the geochemical data in the Caño cores reflect worsening water quality. The effect of bioavailable N to the estuary may be augmented by microbial processes, such that reduced conditions in the eutrophic eastern half of the CMP encourage N-fixation moderated by sulfate reduction, thus exacerbating the environmental problems in the system. While the environmental effects described here are small compared to the challenges faced by the whole social-ecological system, we document how human alterations can affect coastal ecosystems in unexpected ways.

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Manuscript Highlights

- Urbanization of a tropical estuary has far reaching effects on ecosystem functioning
- N-fixation may be a major N source to a system already enriched with urban runoff
- Anthropogenic N inputs to urban tropical estuaries may be exacerbated by reduced flushing associated with human activities

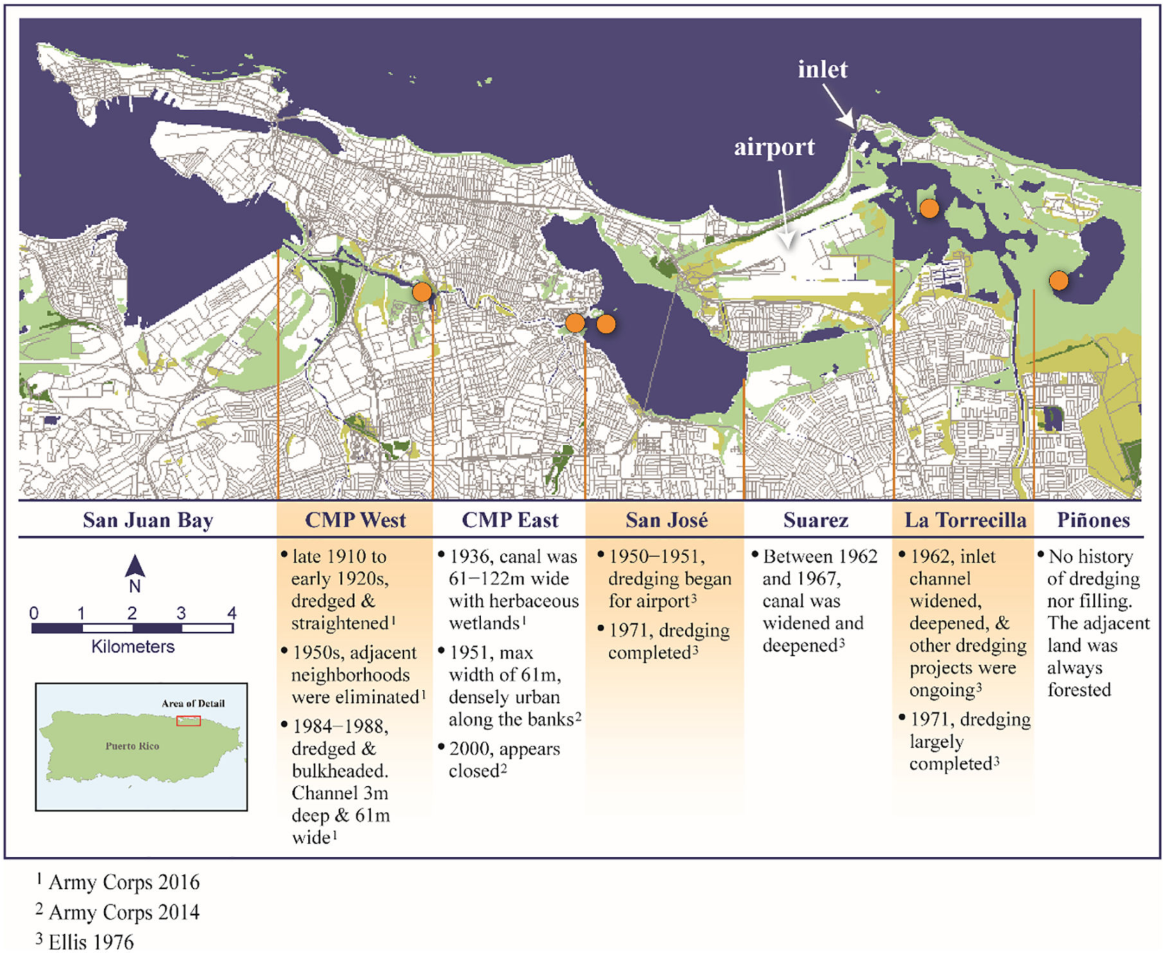

Fig. 1.

Map of the San Juan Bay Estuary. Core locations are denoted by the orange circles. Estuarine sub-areas are given below the map and brief dredging histories are outlined.

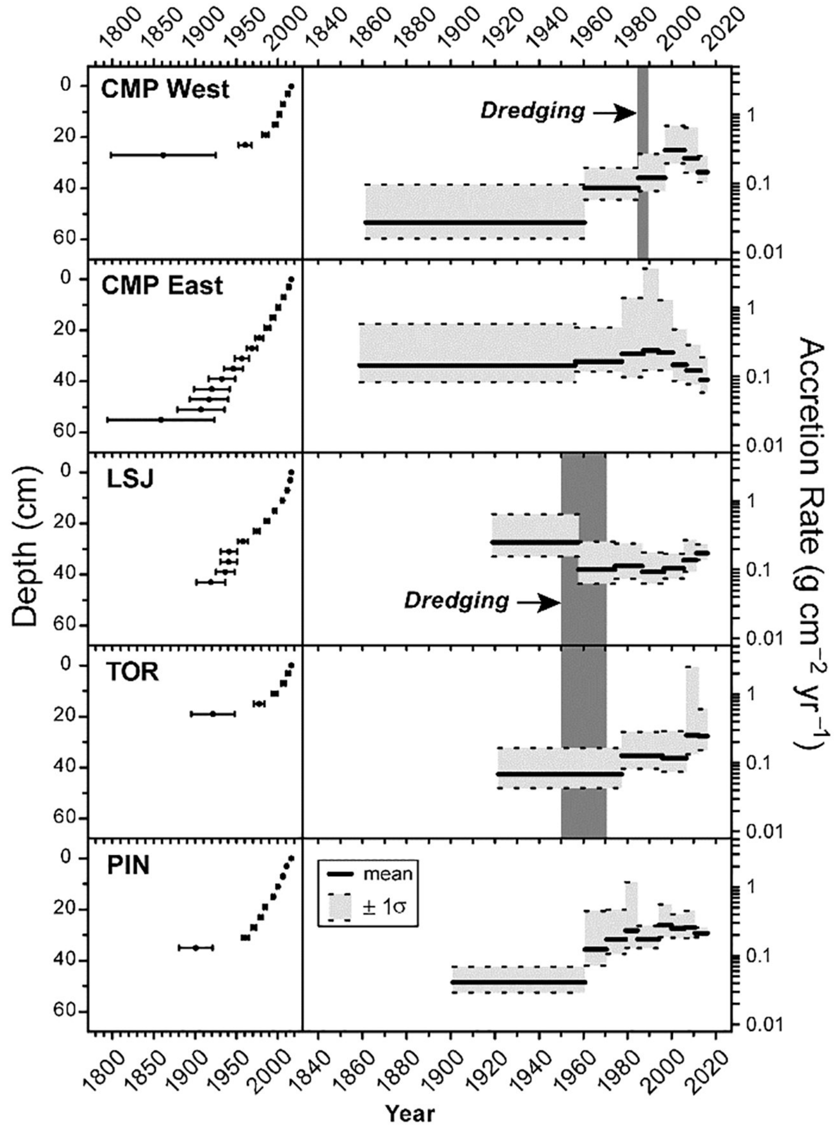

Fig. 2.

Age-depth (left column) and accretion rate time series (right column) plots for each core, with 1 sigma error bars or shaded regions, respectively. Age-depth plots obtained from the Pb-210_{ex} constant rate of supply modeling. Accretion rates computed between dated intervals were aggregated to eliminate overlapping of 1 sigma dating errors. Here, LSJ is Laguna San José, TOR is Laguna La Torrecilla (TOR), and PIN is Laguna Piñones.

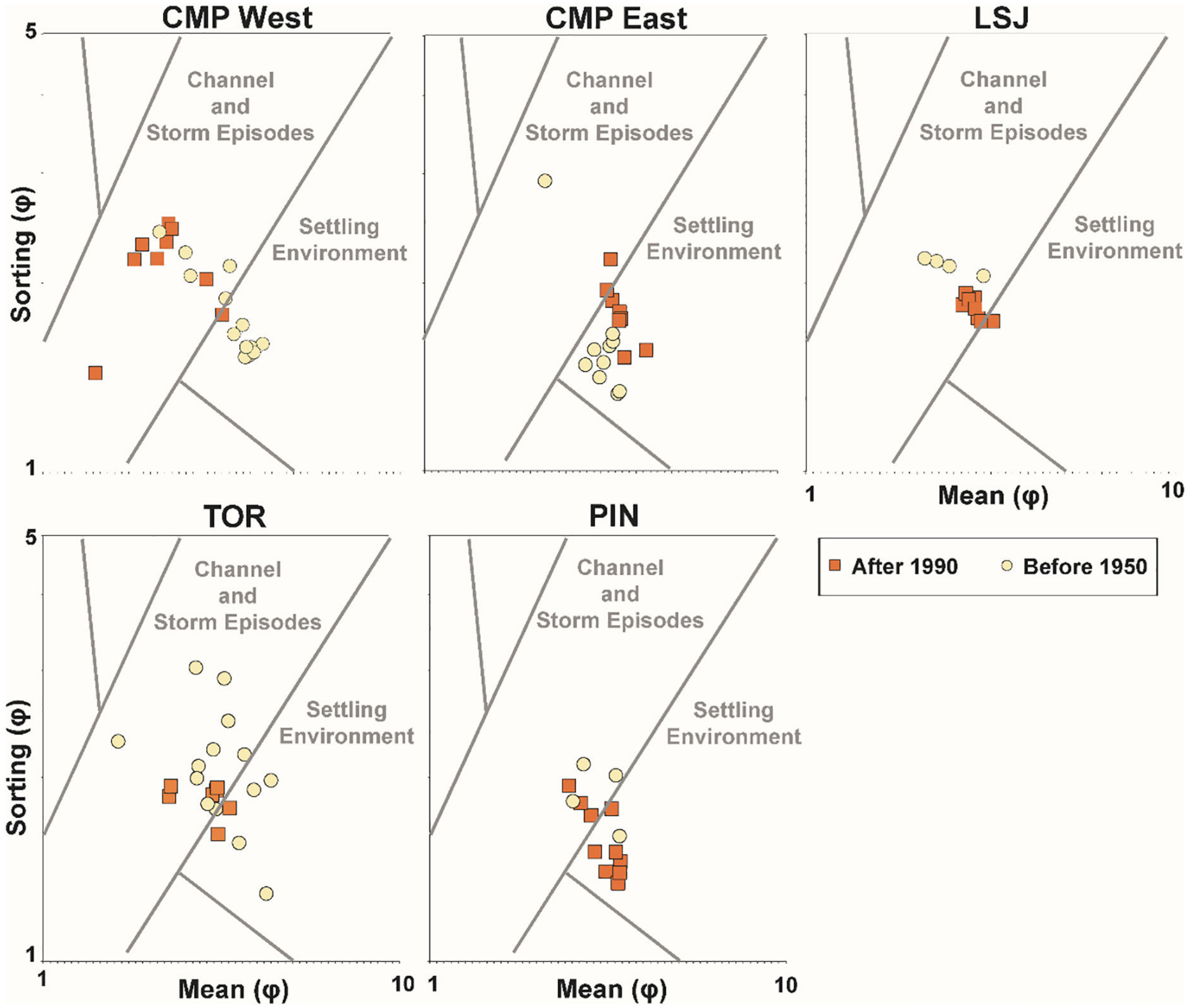

Fig. 3.

Depositional domain analysis results for each dated core where LSJ is Laguna San José, TOR is Laguna La Torrecilla (TOR), and PIN is Laguna Piñones. Sorting and mean values were estimated using the method of moments. Depositional domains based on Tanner (1995) and Lario and others (2002).

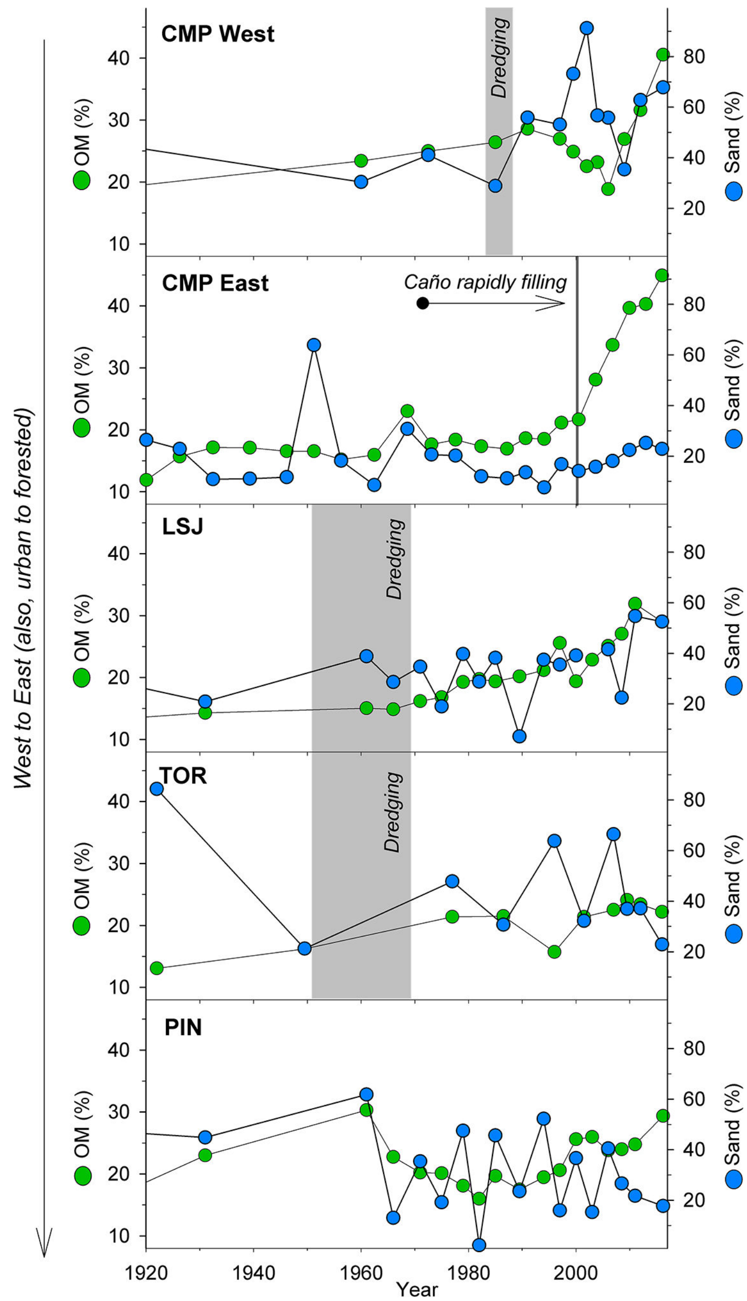

Fig. 4.

The percent organic matter (%OM), and sand content are presented from 1920 to 2016 for (from top to bottom): CMP west, CMP east, Laguna San José (LSJ), La Torrecilla (TOR), and Piñones (PIN). The gray filled areas indicate periods of active dredging and the arrow shown on the CMP east graph reflects a period of rapid infilling. Core locations are ordered from west to east, which also reflects a gradient from urban to forested.

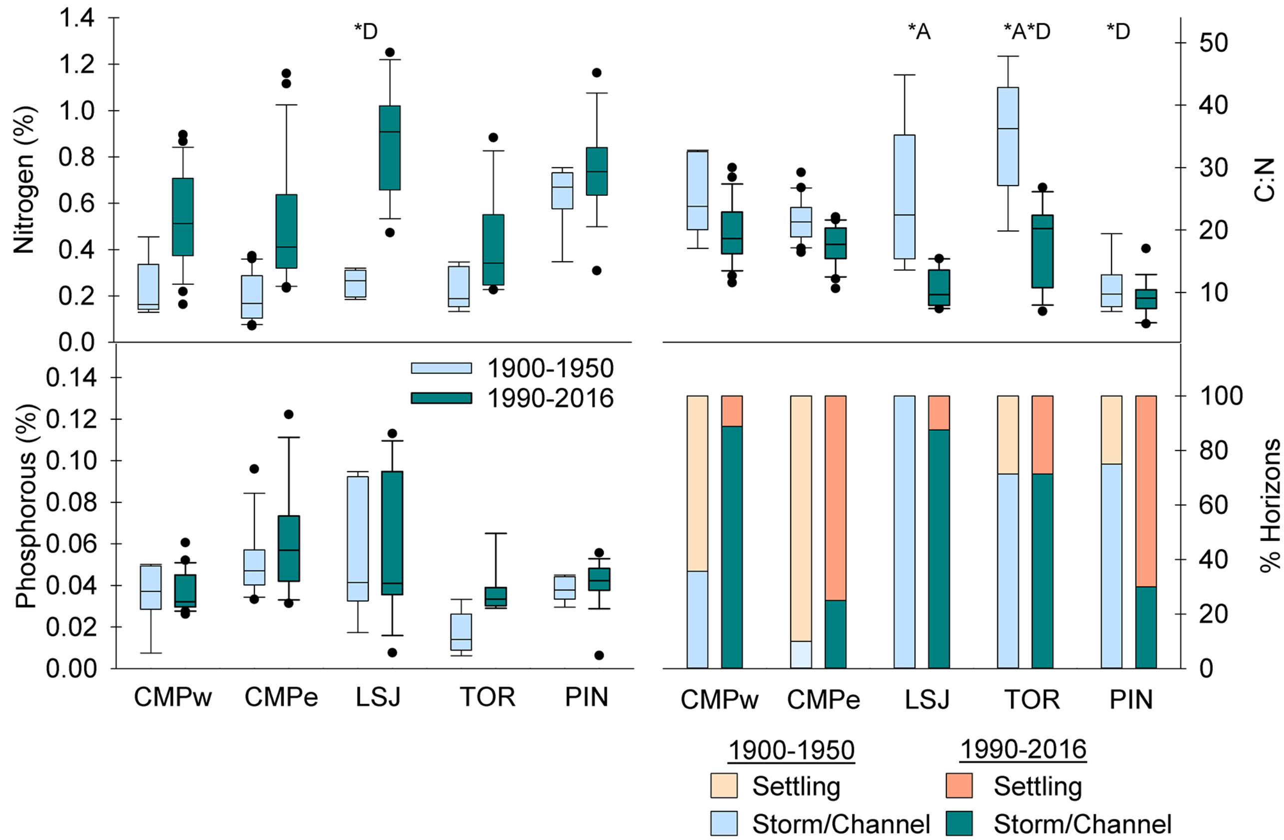

Fig. 5.

Box-and-whisker plots of %N, %OP, and molar C:N in sediment deposited between 1900 and 1950 and between 1990 and 2016 for CMP west (CMPw), CMP east (CMPe), San José (LSJ), La Torrecilla (TOR), and Piñones (PIN) for all cores from each site. Lighter colored bars and boxes represent older sediments (1900–1950) while brighter colors represent more recent data (1990–2016). Significant differences between time periods for all the core data (*A) and for just the dated cores (*D) are noted. The bar graph gives the particle size distribution depositional domain for each site where the number of horizons plotting in either a storm/channel (coarser sediments) or settling domain (more fine-grained sediments) were normalized to the number of horizons in each time period (1900–1950 and 1990–2016).

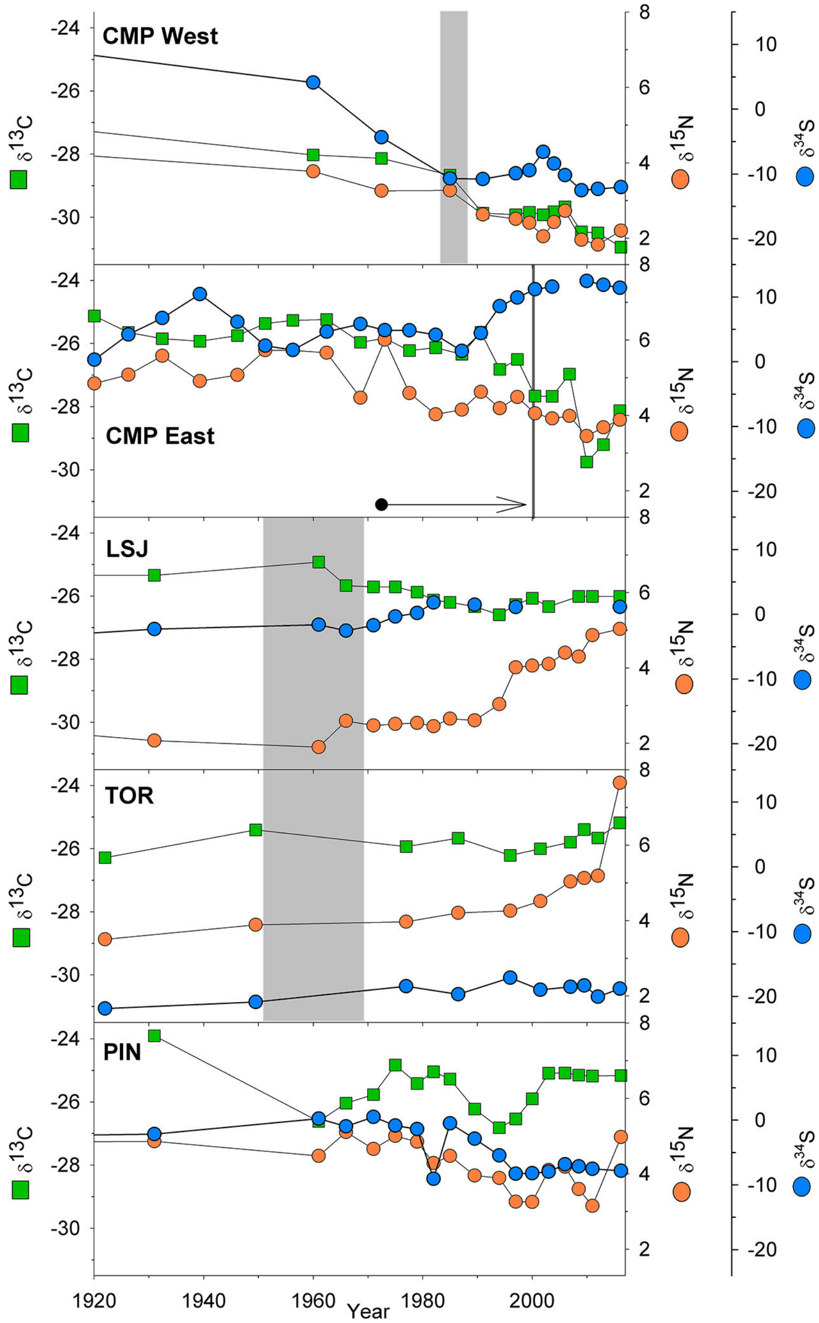

Fig. 6.

Results of isotope analyses for carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), and sulfur ($\delta^{34}S$) are presented in the same manner as in Fig. 4, where LSJ indicates Laguna San José, TOR is La Torrecilla, and PIN is Piñones. Core data are arranged (from top to bottom) west to east, gray areas represent periods of dredging, and the arrow on the CMP east graph denotes a period of rapid infilling.

Table 1.

Horizon dates for each core (Location) derived from Pb-210_{ex} profiles, with 1 sigma error ranges given, where CMP West is Caño Martín Peña west, CMP East is Caño Martín Peña East, LSJ is Laguna San José, Tor is La Torrecilla, and Pin is Piñones.

	Depth (cm)		Decimal Date		
Location	**Minimum**	**Maximum**	**Bottom**	**+ 1σ**	**− 1σ**
CMP West	0	0	2016.178	-	-
	0	3	2011.9	2013.7	2010.1
	5	7	2005.8	2007.9	2003.7
	9	11	2001.8	2004.2	1999.5
	13	15	1997.1	1999.9	1994.3
	17	19	1984.9	1988.8	1980.9
	21	23	1960.5	1968.5	1952.5
	25	27	1861.5	1924.7	1798.3
CMP East	0	0	2016.178	-	-
	0	3	2013.1	2014.7	2011.5
	5	7	2006.8	2008.8	2004.8
	9	11	2000.5	2002.9	1998.1
	13	15	1994.1	1997.0	1991.2
	17	19	1987.2	1990.7	1983.6
	21	23	1977.6	1982.3	1972.9
	25	27	1968.6	1974.7	1962.5
	29	31	1956.3	1964.9	1947.7
	33	35	1946.2	1957.5	1934.8
	37	39	1932.4	1948.5	1916.4
	41	43	1920.1	1941.6	1898.5
	45	47	1916.8	1940.0	1893.6
	49	51	1907.0	1935.6	1878.4
LSJ	0	0	2016.172	-	-
	0	3	2014.9	2016.1	2013.8
	5	7	2011.2	2012.5	2009.9
	9	11	2005.4	2007.0	2003.9
	13	15	1996.5	1998.5	1994.5
	17	19	1986.8	1989.4	1984.1
	21	23	1974.4	1978.2	1970.5
	25	27	1957.8	1964.0	1951.5
	29	31	1941.1	1951.0	1931.1
	33	35	1940.4	1950.5	1930.2
	37	39	1936.4	1947.6	1925.1
	41	43	1918.9	1936.4	1901.5
TOR	0	0	2016.172	-	-
	0	3	2012.3	2014.6	2010.0

	Depth (cm)		Decimal Date		
Location	**Minimum**	**Maximum**	**Bottom**	**+ 1σ**	**− 1σ**
	5	7	2006.8	2009.5	2004.1
	9	11	1995.8	1999.6	1992.1
	13	15	1977.4	1983.8	1971.0
	17	19	1921.6	1947.7	1895.4
PIN	0	0	2016.175	-	-
	0	3	2010.6	2011.5	2009.6
	5	7	2006.0	2007.1	2005.0
	9	11	1999.9	2001.1	1998.6
	13	15	1994.3	1995.8	1992.8
	17	19	1984.6	1986.6	1982.6
	21	23	1979.2	1981.6	1976.8
	25	27	1970.6	1973.7	1967.6
	29	31	1960.7	1964.8	1956.7
	33	35	1900.9	1921.1	1880.7

Date of collection (3/3/2016, 3/4/2016, or 3/5/2016) assigned to surficial sediment (depth = 0 cm).

Table 2.

ANOVA results for dated cores only where CMPe is Caño Martín Peña east, CMPw is Caño Martín Peña west, LSJ is Laguna San José, Tor is La Torrecilla, and Pin is Piñones (see Fig. 1 for core locations). Early refers to core horizons deposited from 1900–1950 and late is 1990–2016.

Measure	R-squared	Period x Core		Period		Location/Core		Period differences *	Location/Core differences **
		F	p-value	F	p-value	F	p-value		
$\delta^{15}N$	78%	**12.46**	**>0.0001**	0.02	0.9792	**20.68**	**>0.0001**	CMPe,CMPw: early>late; LSJ,Tor: late>early	early: LSJ>CMPe; late: CMPe>CMPw, CMPe<Tor
$\delta^{13}C$	80%	**7.57**	**>0.0001**	**22.60**	**>0.0001**	**28.73**	**>0.0001**	CMPe,CMPw,Pin: early>late	early: Pin>CMPe; late: CMPe>CMPw, CMPe<LSJ, Tor
$\delta^{34}S$	89%	**9.87**	**>0.0001**	0.89	0.4173	**86.77**	**>0.0001**	CMPe: early<late; CMPw: early>late	early: CMPe>Tor; late: CMPe>CMPw, Pin, Tor
%N	59%	**2.21**	**0.0364**	**21.18**	**>0.0001**	2.42	0.0564	CMPe, LSJ: early<late	none
%P	47%	0.89	0.5306	0.81	0.4479	**6.99**	**0.0001**	none	CMPe>CMPw,Pin,Tor
%S	62%	**4.51**	**0.0002**	1.52	0.2270	**7.25**	**>0.0001**	CMPe: early<late	early: none; late: CMPe>Tor
%OM	56%	1.64	0.1296	**18.38**	**>0.0001**	1.04	0.3911	early<late	none
Log (OM:N)	65%	**4.29**	**0.0003**	**10.40**	**0.0001**	**11.37**	**0.0001**	CMPe: early>late	early: CMPe>Pin; late: CMPe>Pin, LSJ
%C	51%	**3.80**	**0.0010**	**6.74**	**0.0021**	0.60	0.6641	CMPe: early<late; LSJ: early<late	early: CMPe<Tor; late: CMPe>Pin, Tor
Log(C:N)	69%	**3.54**	**0.0018**	**17.61**	**>0.0001**	10.63	**>0.0001**	Pin: early>late; Tor: early>late	early: none; late: CMPe>Pin, LSJ

* Comparing early (1900–50) to late (1990–2016) only, based on Bonferroni pairwise comparisons (site-specific if interaction is significant)

** Comparing sites to MPE only; Bonferroni pairwise comparisons if interaction is significant, Dunnett's if not

Table 3.

ANOVA results for all cores. Age models from dated cores were applied to undated cores to estimate time periods (early is 1900–1950, late is 1990–2016). For the undated core models, replicate cores were treated as a random nested effect within the fixed location variable and F-tests were adjusted so that the core random effect term was used in the denominator. The Abbreviation CMPe is Caño Martín Peña east, CMPw is Caño Martín Peña west, LSJ is Laguna San José, Tor is La Torrecilla, and Pin is Piñones. Early refers to core horizons deposited from 1900–1950 and late is 1990–2016.

Measure	R-squared	Period x Location		Period		Location		Period differences *	Location differences **
		F	p-value	F	p-value	F	p-value		
$\delta^{15}N$	75%	2.25	0.1642	0.36	0.5683	1.00	0.4676	none	none
$\delta^{13}C$	52%	**4.25**	**0.0466**	13.72	**0.0076**	0.22	0.9202	CMPw: early>late	none
$\delta^{34}S$	66%	2.49	0.1385	0.57	0.4766	**30.95**	**0.0002**	none	CMPe>CMPw,Pin,Tor
%N	69%	2.61	0.1265	**78.45**	**<0.0001**	**6.08**	**0.0196**	early<late	CMPe<Pin
%P	41%	2.07	0.1892	**7.43**	**0.0295**	**5.18**	**0.0292**	early<late	CMPe>Tor
%S	21%	2.05	0.1921	0.06	0.8188	**5.47**	**0.0256**	none	CMPe<Pin, Tor
%OM	41%	**6.75**	**0.0150**	24.95	**0.0016**	0.91	0.5079	CMPw: early<late	early: CMPe<Tor
Log (OM:N)	59%	**5.44**	**0.0260**	**91.28**	**<0.0001**	22.69	**0.0004**	CMPw, LSJ, Tor: early>late	early: CMPe>Pin, CMPe<Tor; late: CMPe>LSJ
%C	53%	2.89	0.1047	**14.91**	**0.0062**	0.88	0.5210	early<late	none
Log(C:N)	62%	**5.40**	**0.0264**	**99.99**	**<0.0001**	**7.69**	**0.0106**	LSJ: early<late; Tor: early<late	early: CMPe>Pin; late: CMPe>Pin, LSJ

* Comparing early (1900–50) to late (1990–2016) only, based on Bonferroni pairwise comparisons (site-specific if interaction is significant)

** Comparing sites to MPE only; Bonferroni pairwise comparisons if interaction is significant, Dunnett's if interaction is not significant