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Inorganic Nutrient Fluxes Across the Sediment-water of Shallow Tropical Wetland

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Abstract

The aim of this study was to investigate the benthic nutrient fluxes in a tropical wetland of Chini Lake, Malaysia that has been infested by submerged Cabomba furcata vegetation. The role of this internal loading has been known to contribute to nutrient pool and enrichment of lakes worldwide. Despite its importance, the measurements of internal nutrient fluxes have not been taken into account in other studies in this Chini lake system. An experiment was performed in this shallow floodplain wetland measuring inorganic nitrogen and soluble reactive phosphate fluxes from intact cores collected in the pelagic areas. Pelagial nutrient fluxes showed dissolved inorganic nitrogen (DIN) fluxes were directed from the sediment toward the water column at most sites while dissolved reactive phosphate fluxes were low. Mean DIN was 0.75±0.55 *mmol/m/d. C.* furcata dominated sites were associated with silt, iron and organic carbon content ($p<0.01$). The results of this study indicated that internal loading specifically the nitrogen fluxes contributed to the nutrient enrichment of this wetland. Thus, there is a need to include the role of internal loading in the rehabilitation and management of wetland ecosystems.

Keywords: benthic fluxes; floodplain wetland; macrophyte; nutrient cycling; sediment-water dynamic

1. Introduction

Eutrophication has caused major challenges in shallow lakes worldwide due to nutrient input from external loading such as diffuse sources from agricultural areas in the surrounding catchment (Maberly et al., 2003) and pollutant discharges that flows into the main river (Furch and Junk, 1993). Internal loading resulting from nutrient release from lake sediment could also contribute to an increase in nutrient concentration (Howard-Williams, 1985), and had caused eutrophication in tropical waterbodies such as Kranji reservoir, Singapore (Gin and Gopalakrishnan, 2010). Among the factors that triggered nutrient release from sediment such as in the inshore macrophyte areas of the shallow Lake Illawarra, Australia were increase in water temperature and seagrass biomass (Qu et al., 2003). Photosynthetic activities of the plant-microphytobenthos-sediment community (Qu et al., 2007) and benthic organisms (Sundback et al., 1991) during the day affected diurnal variation of nutrient fluxes from the sediment. Seasonal variations in the biomass and growth of benthic communities, such as macroalgae and seagrasses, induced seasonal changes in nutrient fluxes (Qu et al., 2007). Release of nutrients also differs with sediment types, with higher release of nutrients such as nitrite and ammonium from muddy sediments compared to sandy sediments, especially during the dark (Sundback et al., 1991). Increased nutrient content in the lake system could promote either growth of phytoplankton (Duarte, 1995) or aquatic plant species that utilise nutrient pools in the water column (Howard-Williams, 1985).

In this paper, Chini Lake Malaysia was studied to ascertain the contribution of sediment nutrient fluxes. The shift from floating-leaved vegetation (*Nelumbo nucifera*) to submerged macrophyte (*Cabomba furcata*) production was observed in this shallow wetlands (Sharip et al., 2012b). From an ecological perspective, such shift in plant species can impact the soil nutrient dynamic, and alters habitat structure and the community assemblages and reduce biodiversity in the wetland (Ehrenfeld, 2003, Zedler and Kercher, 2004), subsequently impacting the ecological importance of this biosphere reserve. Nutrient enrichment of this lake remains as one of the major concerns for the lake management. Past studies have documented eutrophication in this floodplain system, which was thought to be attributed to run-off from agricultural areas and settlements (Shuhaimi-Othman et al., 2007). Mean phosphate concentration was reported to have rapidly increased over the last ten years (Sharip et al., 2012b). Higher phosphate concentrations were observed near the sediment surface during high flood levels, which could be induced by internal loading (Sharip et al., 2012a).

However, no studies are available to account for the nutrient exchanges at the sediment-water interface that may affect the nutrient cycling and contribute to the observed shift in macrophyte dominance in Chini Lake. This study is important as it attempted to characterise the contribution of the nutrient exchanges between the sediment and water, in particular the extent of internal loading in contributing to the nutrient pool and enrichment of the lake. By characterising the internal nutrient loading, this work provides better understanding of the sediment-water dynamic to aid in the management of the Chini Lake ecosystem. In this paper, the sediment nutrient fluxes was based on laboratory experiment and field survey to characterise the sediments and bottom waters.

2. Materials and Methods

2.1 Site description and experimental set up

Chini Lake, a shallow freshwater wetland located in the Pahang River floodplain, was designated as a UNESCO biosphere reserve in 2009. The lake is characterised as 12 small open water bodies (surface area ~2 km^2) with an average depth of 2 m during normal season. The lake expands its size and depth depending on the flooding of the Pahang River during the rainy season.

Nutrient fluxes experiments were performed at Chini Lake before the monsoon season. The experiment was carried out in September 2009 to investigate the sediment characteristics and the spatial differences of nutrient fluxes between sites. Sediment and water quality samples were collected at five pelagic sites as shown in Figure 1. Additional sample cores were collected April 2010 in two locations: S6 (dominated by floating-leaved *N. nucifera*) and S7 (dominated by submerged *C. furcata*). The open water bodies where submerged *C. furcata* was sampled was reported to have been dominated by the species since it was first detected in early 2000. The shoreline and vegetation in the water bodies was not disturbed prior to the sampling.

2.2 Sediment and water quality sam pling

Undisturbed sediment core samples were collected at each location using PVC tubes (110 mm diameter and 600 mm long). Each sampling tube was inserted to a depth of approximately 200 mm. The tube was carefully removed and a PVC cap inserted at the bottom to preserve the sediment structure during sampling. The core tubes containing the sediment samples and the overlying water were labelled and placed in a transportation box and transported to the laboratory within 12 hours of sampling.

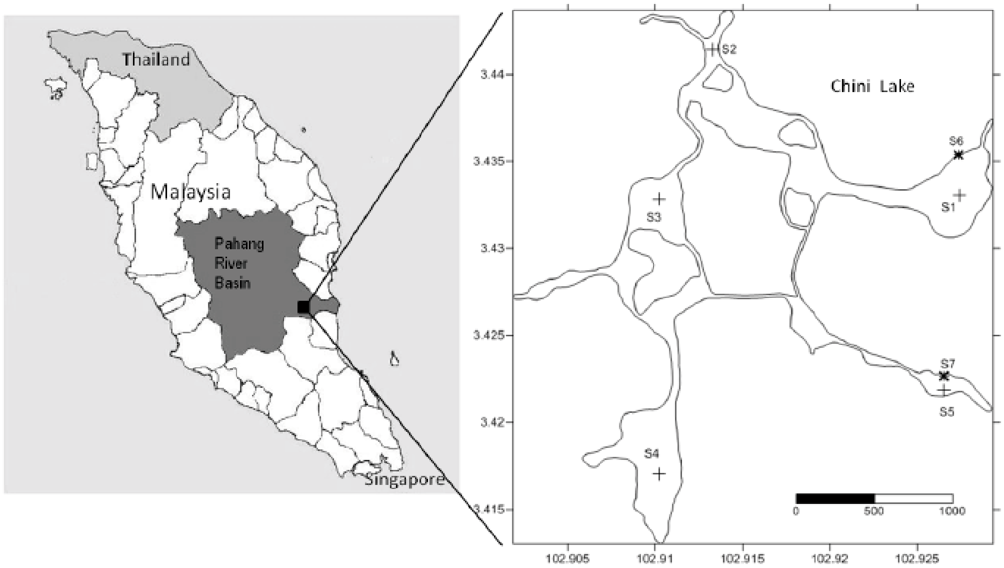

Figure 1. Map of Lake Chini, Malaysia and the sampling locations.

Additional sediment samples were taken using a Van Veen grab sampler and sent to laboratory for analysis of sediment textures and pH. An additional 20 L volume of overlying water was collected from each of the sampling locations. The overlying water was poured into clean 20 L carboys which had been washed in 10% hydrocloric acid (HCL) and rinsed with deionised water. The bulk overlying water reservoirs were kept in the dark at approximately 4 °C to avoid exposure to light.

Measurement of temperature, pH and dissolved oxygen (DO) at mid-depth of the water column were recorded in-situ using a multi-parameter Sonde (YSI 6600, YSI Incorporated) at each sampling location. Detection limit for each parameter: DO - 0 to 50 mg/L, pH - 0 to 14 units, temperature - -5 to 50 °C. Water samples were collected and analysed for phosphate (PO_4), nitrate (NO_3^-), ammonium (NH_4^+), total nitrogen (TN) and total phosphorus (TP) according to APHA (1995).

2.3 Nutrient flux measurements

Nutrient flux was estimated as the rate of change of nutrient concentrations in the water overlying the sediment core samples. An increase in nutrient concentration in the overlying water is assumed to be a release from the sediments, while a decrease in nutrient concentration in the overlying water is assumed to be due to the uptake of nutrients by the sediments. Sediment cores in their PVC tubes were placed in a water bath, the temperature of which was adjusted to within about 1 °C of the ambient water temperature at the time of sample collection. Sediment samples were then allowed to settle overnight and the overlying water above each sediment core was carefully siphoned off and replaced with 2 L of the bulk overlying water collected from the respective sites in the morning

Daytime incubations were simulated under reasonably bright overhead laboratory lighting with the sediment water aerated with a portable air pump via an air-stone without unduly re-suspending surface sediment particles. Water samples (about 30 mL) were collected from the overlying water above each sediment core and filtered through a 0.45 μm filter into a 100 mL polypropylene container. The samples were analysed for NH_4^+, nitrate-nitrite N (NO_x^--N), and filterable reactive phosphate (FRP), by discrete analyser where samples were automatically loaded into the system and mixed with the reagent solution to form a coloured complex which was then calorimetrically determined by a UV/VIS detector. Water samples were collected hourly for over eight hours.

Once the eight hour incubations were completed, the overlying waters were carefully siphoned off and replaced with the water from the respective bulk water storage. The entire eight hour procedure was then repeated for dark or night-time experiments, where each acrylic tube was wrapped in aluminium foil to eliminate light. To mimic natural conditions of a low wind night-time environment, the overlying waters were manually stirred at approximately 20-minute intervals without causing sediment re-suspension to retain sufficiently mixed water. The concentration of DO and temperature in the overlying waters was recorded at the start and at the end of incubation. After the completion of the night-time incubation, the overlying water in the tubes was discarded and the sediment cores transferred to plastic zip-lock bags and stored at 4 °C prior to sediment characterisation testing.

Sediment pore water was obtained by centrifuge and analysed for NH_4^+, NO_x^-, FRP, TN and TP concentrations. Bulk sediment samples were analysed in inductively coupled plasma optical emission spectroscopy for trace metal contents such as iron and aluminium, and total organic carbon (TOC) using the methods in USEPA (1996). Total organic matter was determined by the ashing method where samples were dried at 550 °C. The bulk samples were also analysed for particle size distribution in accordance to the British Standard No. 812-103.2 (British Standards Institution 1990). Additional grab samples that were collected at each locations were also analysed for particle size distribution.

2.4 Nutrient fluxes calculations

Nutrient flux (F) of NH_4^+, NO_x^--N, and FRP across the sediment-water interface were calculated according to eq. 1 as described in Qu et al. (2003).

$$F = \frac{\alpha . V}{A} \quad (1)$$

Where α is the slope of the linear regression obtained by plotting the concentration of the relevant nutrient parameter as a function of incubation time (mg/L/h), V is the volume of the water column (L), and A is the sediment core surface area (m^2).

2.5 Data analysis

Pearson's correlation was used to analyse the relationship between dissolved inorganic nitrogen (DIN) and sediment characteristics and water column quality. The Kruskal-Wallis test (n = 5) was used to determine spatial differences in the DIN flux rates. All tests of differences and multivariate analysis were performed using PASW Statistic. Environmental variables namely PO_4, NO_3, NH_4+, TN and TP were log-transformed to improve normality.

3. Results and Discussion

The main purposes of this work were to assess the sediment-water interaction and contribution of the nutrient exchanges between the sediment and water in relation to the reported shift in plant species in this wetland. were extracted (hobbies, smoking, past ear problems) to determine the relationship between hearing impairment with distance traveled per day through Pearson Chi-Square test. The significance level of probability (α) was set as 0.05 for all analysis.

3.1 Sediment and water column quality

The mean nutrient concentration in the water column and pore water is shown in Table 2. The surface TN concentration was stable around 0.5 mg/L while surface TP ranges between 0.02–0.04 mg/L. Phosphate concentration was not detected in the pore water possibly due to oxic environment during the experiments. Each parameters N = 5.

Table 3 presents the total organic matter content, sediment pH and sediment texture at the different sites.

The mean percentage of organic matter and sediment pH was 20.1±6.2% and 5.14±0.15 respectively. The mean percentage of sediment composition from core samples was 43% clay, 58% silt and 8% sand. The silt-clay ratio in sample S1-S4 was around 1.00 while in sample S5 was 32.5. Sample S5 had the highest percentage of sand c. 30% compared to other samples <10%.

T-test analysis showed significant variability in TOC content between sites ($p < 0.01$). Organic content was highest in sample S5 with the TOC almost double that of other samples. The mean TOC (9.58±4.58) was consistent with TOC measurement in 2007 (Bakhtiari et al., 2009).

Combining the grab sediment samples, the mean silt-clay ratio was 0.19±0.26 in S1 and 16.9±22.0 in S5 (Table 4).The mean percentage of silt content and sediment pH in this study were significantly higher ($p < 0.001$) than the mean percentage of silt content and sediment pH reported in a past study (Abas et al., 2005). The sediment has a high iron content; the iron/P ratio ranged from 2 to 17.5. The mean iron/P ratio was 6.6±6.2.

High phosphate concentration in the water column of the pelagic region of this study indicates a nutrient-rich environment at all five lake sub-basins. The sediment characterisation results indicate high silt content in all samples compared to findings in 2004 (Abas et al., 2005) which could be originated from run-off from within the catchment. Higher sand content in sediment core S5 compared to sediment from grab samples S6 indicated variability of

Table 2 Mean nutrient (±SD) concentrations of the water column and pore-water

Parameter	Water column (mg/L)	Pore water (mg/L)
Ammonium as N	0.03±0.02	2.78±0.88
Nitrate as N	0.14±0.07	0.04±0.01
Total nitrogen	0.50±0.00	5.00±0.80
Phosphate as P	0.02±0.01	n.d
Total phosphorus	0.03±0.01	0.13±0.13

Note: n.d – not detected

Table 3 Characteristics of sediment-core samples

Lake	pH	Total organic carbon (%)	Total organic matter (%)	Particle types (%) (gravel/sand/silt/clay)	Silt/Clay ratio
S1	4.9	6.9	15.7	0/1/52/47	1.11
S2	5.2	7.5	16.7	0/8/56/36	1.56
S3	5.2	7.3	17.5	0/1/55/44	1.25
S4	5.3	8.5	19.7	0/2/60/38	1.58
S5	5.1	17.7	30.8	3/30/65/2	32.5
Mean S1-S5	5.1	9.6	20.08	1/8/58/43	1.35

Table 4 Characteristics of sediment samples

Lake	Particle types (%) (gravel/sand/silt/clay)	Silt/Clay ratio
S1 [a]	0/1/52/47	1.11
S1 [b]	0/1/42/57	0.74
S5 [a]	3/30/65/2	32.5
S5 [b]	0/7/53/40	1.335

Note: a – Core sample, b – grab sample

sediment within the lake. Different input sources for the top and bottom layers of the sediment have been reported in Bakhtiari et al. (2009); analysis based on N-alkanes of the sediment samples indicated that the recent formation of the sediment at the top layer was influenced by higher plant waxes and bacteria (Bakhtiari et al., 2011) that could be attributed to plant decomposition by the sediment community. Alteration of plant community structure can change organic matter conversion (Viaroli et al., 1996). Substantial decomposition of labile submerged vegetation such as *C. furcata* in Chini Lake could contribute to the accumulation of organic carbon content and silt material subsequently and induce dystrophic conditions that affect benthic processes. Visual observation on the sediment cores taken at the two littoral sites (S6 and S7) indicated differences in colour and texture, with darker texture and higher organic content in S7 compared to S6. The decomposition process of submerged C. *furcata* was found to contribute to high organic carbon pool due to the species high organic content as reported in the Oleo Lagoon, Brazil (Peret and Bianchini, 2004).

3.2 Nutrient fluxes

The results from this study show a general positive flux for NH_4^+ and a negative flux for NO_x^--N (Figure 2). Flux is positive when nutrient concentrations were released from sediments and negative when they were taken up by the sediments. The flux results for NH_4^+ for sediment from S4 were negative for both day time and night time incubations (Figure 3). These results were considered to be highly skewed due to an apparent rapid increase in the NH_4^+ concentration within several minutes of addition of the 2 L of overlying water. Mean release rate of NH_4^+ was 1.277±0.657 m mol m^{-2} d^{-1} and mean sinking rate of NO_x^--N was 0.567±0.283 mmol/m_2/d under dark condition. Kruskal-Wallis analysis showed DIN fluxes were not statistically different between sites (p >0.05); the mean DIN was 0.75±0.55 m mol/m_2/d. With the exception of fluxes in sediment cores from S4, all fluxes of DIN (NH_4^+ + NO_3^-) were directed from the sediments toward the water column, indicating that the sediment was a nitrogen source for primary production. The highest rate of efflux of nutrients from the sediment to the water column was in S3. The flux of DIN from S4 was directed from the water column to the sediment surface, indicating that the sediment was a nitrogen sink leading to a net removal of inorganic nitrogen from the water above the sediment. The pore-water contains high NH_4^+ and NO_3^- concentration in all samples. DIN values were significantly correlated to iron, TP and TN (p <0.05). PO_4^{2-} was not detected in any of the sediment core incubation or below the detection of 0.01 mg/L. FRP was also found undetectable in the pore water at all sites. The low PO_4^{2-} and FRP values could be due to oxic conditions.

This study showed the importance of nitrogen cycling between the sediment and water column of Chini Lake, Malaysia. DIN fluxes were dominated by the release of NH_4^+ fluxes consistent with findings from studies in Lake Illawarra, Australia (Qu et al., 2003). At most of the sites, fluxes of NH_4^+ were positive (i.e., from sediment to water). High efflux of

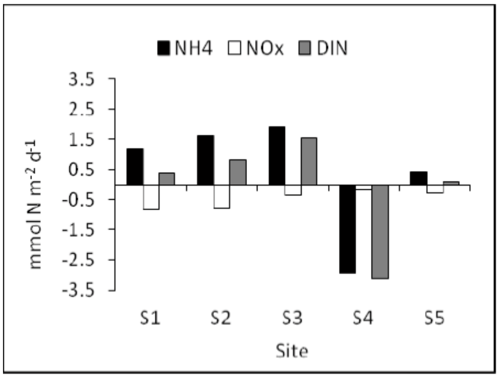

Figure 2. Daily fluxes of NH_{4+}, NO_x and DIN

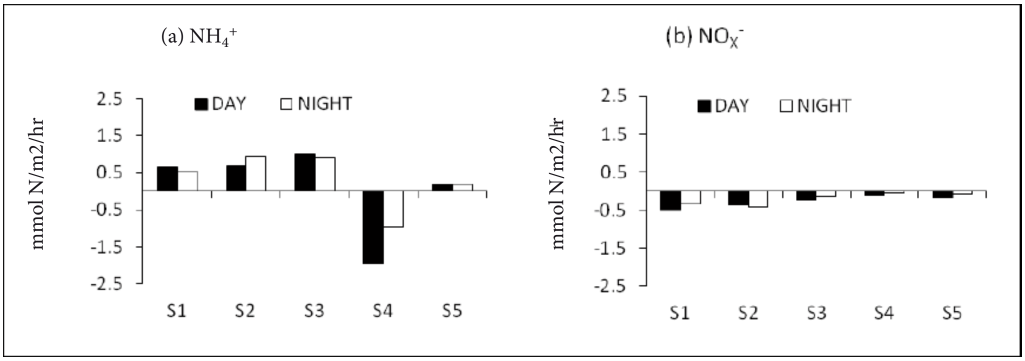

Figure 3. Day and night fluxes of (a) NH_4^+ and (b) NO_x^-

NH_4^+ from sediment to water could be associated with increased decomposition of organic matter and mineralisation of the plants in the sites. Seasonal variations of DIN were apparent with higher efflux of NH_4^+ in the summer attributed to the decomposition of organic matter and release of NH_4^+ from the reducing condition in sediments (Qu et al., 2007). High particulate organic matter was observed in Chini Lake which may be attributed to plant decomposition due to very low water column chlorophyl-a content (Sharip and Jusoh, 2010). Subsequently, the sediment in most of the sites acted as a significant nitrogen source. Daily negative efflux of NO_x at all sites indicates NO_x were taken up by the sediment. Organic matter decomposition could contribute to the higher NH_4^+ release and low NO_3^- + NO_2^- uptake. Higher NH_4^+ release and all fluxes of DIN (NH_4^+ + NO_3^-) were directed from the sediments toward the water column, indicating that the sediment was a nitrogen source for pelagic primary production. High nitrogen in porewater analysis of the six sediment samples supported the flux data. In contrast to the other sediment samples, the higher sand content in sample S5 could contribute to the lower flux rates for NH_4^+ and NO_x-N. However, sample S5 has the highest TOC and organic matter content which could be attributed to the observed appearance of decaying leaf matter in the sample. The availability of nutrients through the efflux of nitrogen from the sediment to the water column could promote the growth of *C. furcata*.

Past studies hypothesised the contribution of internal eutrophication (Sharip et al., 2012a) to the increase in phosphate concentration in Chini Lake. Anoxic conditions at the sediment-water interface enhanced P-mobilisation (Boers and Zedler, 2008) and the release of P into the water column. However, in this study phosphate concentration was found undetectible in all sediment-core samples which could be associated to oxic conditions. Low FRP fluxes at the sediment-water interface and in porewater have been associated with relatively oxidised conditions in the surface sediments (Boynton and Kemp, 1985). Under oxic conditions, active iron in the wetland sediment in the form of Fe^{3+} sorp and bind P to sediment, while under anoxic and hypoxic conditions, active iron in the wetland sediment in the form of Fe^{2+} reduces P sorption and cause P releases from the sediment (Sondergaard, 2001). High iron content and the Fe:P ratio (by weight) exceeding 15 as found in this system is consistent with the other studies (Sondergaard, 2001), that support high sediment retention capacity that prevent internal P loading. High phosphate concentration in the surface water may have originated from nutrient rich inflow from the tributaries or horizontal exchange.

This study only investigates the nitrification rates in separate sub-basins of Chini Lake. High nitrate levels was reported in this system with anoxic layers formed as stratification increases during increases in water levels (Sharip et al., 2012b). Various studies have illustrated that denitrification becomes important in high nitrate systems with denitrification rates increasing in association with an increase in nitrate concentration and anoxic layer (Rysgaard et al., 1994; Schaller et al., 2004). Future study should address denitrification in this wetland, in particular in the Cabomba dominated system, to quantify the contribution of denitrification and the assimilation by aquatic plants in the removal of nitrate from the wetland ecosystem.

Few studies have reported that plants can shape aquatic habitat by altering biogeochemical processes (Eviner, 2004; Farrer and Goldberg, 2009). Thus, the increasing density and overall production of *C. furcata* across the lake sub-basins could affect the chemical and biological processes and subsequently benthic fluxes in the wetland. This study suggests that the shift in plant dominance to non-native *C. furcata* could have alters the sediment characteristic by increasing the organic carbon content, silt material and sediment pH. Decomposition analysis of *C. furcata* showed that the species high carbon content efficiently contributes to the dissolved organic matter pool in the Oleo Lagoon, Brazil (Peret and Bianchini, 2004). In this study, the release of DIN into the water column in the pelagic areas could be attributed to sediment nitrification or organic matter mineralisation. Sediment nitrification was shown to contribute to the release of DIN in nutrient fluxes measurement in the un-vegetated sediment (Pinardi et al., 2009; Qu et al., 2007). The findings from this study may have implications for the rehabilitation and management of this tropical wetland such as limited success in reducing nutrient levels in the water bodies due to unaccounted nutrient inputs from sediments in existing rehabilitation measures. Other implication includes continual challenges in controlling or eradicating the expansion of submerged non-native *C. furcata* sustainably due to incessant availability of nutrients from the sediments for their growth.

4. Conclusions

This study provides the first estimation of sediment-water interaction at Chini Lake, Malaysia. Net DIN effluxes at all sites in the pelagic water suggested contribution of internal nitrogen loading to Chini Lake. Organic content, sediment pH and silt material significantly increased at all sites with the highest organic carbon found in sites dominated by *C. furcata*.

Acknowledgements

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