

Butyltin Contamination in Sediments and Lipid Tissues of the Asian Clam, *Potamocorbula amurensis*, near Mare Island Naval Shipyard, San Francisco Bay

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ABSTRACT

The former Mare Island Naval Shipyard, near Carquinez Straits in the northern reach of San Francisco Bay, California, has been a point source for introduction of butyltin compounds into the onshore and marine environment. Because tributyltin (TBT) is known to be a potent endocrine disrupting chemical, a study of butyltins in soil, benthic sediments, and lipid tissue of a common local bivalve, the Asian clam *Potamocorbula amurensis*, has been undertaken to evaluate the extent of the contamination. Soils from a sandblasting site at the shipyard contained low concentrations of mono-, di-, and tributyltin (0.3- 52 ng/g, total butyltin). Benthic sediments from nearby Mare Island and Carquinez Strait contained concentrations of total butyltin ranging from 1.3-8.1 ng/g. In contrast, clams accumulated much higher concentrations of di- and tributyltin (152-307 ng/g, total butyltin, with TBT and dibutyltin (DBT) making up from 54-85% and 15-46%, respectively, of the total butyl body burden of the clams). Biota Sediment Accumulation Factors (BSAFs) for butyltins in *Potamocorbula* were in reasonable agreement with literature values; they are greater than those of neutral hydrophobic compounds, suggesting that partitioning and binding processes may be involved in bioaccumulation. Therefore, there is potential for long-term chronic effects of TBT in San Francisco Bay.

INTRODUCTION

The Mare Island Naval Shipyard in San Francisco Bay, located at Mare Island, Vallejo, California (Figure 1), is a 6,000 acre U. S. Naval facility that repaired, overhauled, and maintained Navy vessels until April 1996, when the base was permanently closed. The Mare Island facility was the principal fleet supply base for the Pacific Coast. One important activity at the base was sandblasting and painting of submarine parts, ship hulls, vehicles, railroad cars, and small buildings. Over a period of years, a one-acre expanse of sandblast abrasives was generated from this activity at site IR04 on the northeastern shore of Mare Island (Figure 1). An estimated 400 cubic yards per year of spent sandblast abrasive material was stored and disposed of on the ground surface, in the tidal marsh areas along the shoreline of Mare Island Strait, and also in Mare Island Strait. The beach near site IR04 is referred to as "Green Beach"

because of the intense green color of the sandblast abrasives. Site IR04 sluices directly into Mare Island Strait, which is contiguous with

Figure 1. Map showing sampling locations near the former Mare Island Naval Shipyard, San Francisco Bay, California.

Carquinez Strait and San Pablo Bay. These sandblast abrasives and associated paint flakes contained the antifouling compound tributyltin (TBT). Tributyltin is the active ingredient of many bactericidal, fungicidal, insecticidal, acaricidal, and wood preservation products that have biocidal activity against a broad range of organisms. Tributyltin is used primarily as an antifoulant paint additive on ship and boat hulls, seawater piping systems, docks, fishnets, and buoys to prevent the growth of barnacles, algae, mussels, tube worms, and other marine organisms. Antifoulant agents discourage the growth of marine animals on ship-hulls by leaching out of the paint at a very slow rate, thus preventing attachment and growth of these organisms. About one million pounds of butyltin compounds are sold annually.

Prior to 1971, copper oxide was used as the primary antifoulant in marine paints. However, its use was discontinued because of its toxicity, and it was replaced by butyltin compounds. Since then, there have been numerous reports of contamination of aquatic and marine environments by butyltin compounds (Goldberg, 1986; Stang and Seligman, 1986; Clark and others, 1988; Gabrielides and others, 1990; Ritsema and others, 1991; Stewart and Thompson, 1994). Detrimental effects of TBT on biota include: high mortality on larvae and severe malformations of shells in oysters (Alzieu

and others., 1981-1982), imposex (male genitalia imposed on females) in dogwhelk populations (Bryan and others, 1986), growth retardation in mussels (Salazar and Salazar, 1991) and microalgae (Beaumont and Newman, 1986), and deformities in Fiddler crabs (Weis and others, 1987). Because of these environmental problems, several countries have adopted measures to control the usage and release of TBT into the environment. In the U.S. all of the organotins are regulated by the "Organotin Antifouling Paint Control Act of 1988".

It is estimated that in seawater 93% of the TBT exists mainly as the neutral hydroxide (TBTOH), with smaller amounts of the chloride (TBTCl; 2-3%) and cation (TBT⁺; 4-5%) (Arnold and others, 1997). In addition, the TBT⁺ cation may complex with other organic ligands such as naturally occurring carboxylic acids and amino acids in sediments, cellular components of microorganisms, and tissues. Because of its hydrophobic ($\text{Log } K_{ow} = 4.1$; K_{ow} is the octanol/water partition coefficient) and ionic characteristics, TBT tends to accumulate in the lipid tissues of many aquatic species (Davies and McKie, 1987; Wade and others, 1988; Iwata and others, 1994; Kannan and others, 1995; Kannan and others, 1996). TBT also binds to macromolecules such as the protein glutathione in organs such as kidney and liver (Kannan and Falandysz, 1997). Because of the unique physicochemical properties of butyltin compounds, it has been postulated that significant amounts of TBT may be associated with particulate material and suspended sediments in coastal plain estuaries, and that TBT contaminated sediments may act as sources for dissolved TBT (Unger and others, 1987). Therefore, the potential exists for significant amounts of TBT to be leached out of contaminated sediments at the Mare Island site and to contaminate neighboring Mare Island Strait, Carquinez Strait, and San Pablo Bay. This area of the San Francisco Bay is the state's richest "nursery" for young Dungeness crabs, whose numbers have declined significantly in the last few decades. It is known that juvenile Dungeness crabs in San Francisco Bay feed on fish, crustaceans, bivalves, and other food sources, and also that they accumulate hydrophobic contaminants such as PAHs, DDE, and PCBs (California Department of Fish and Game, 1983). Because juvenile crabs may be vulnerable to toxic contaminants such as

butyltins, it is important to assess the extent of contamination of sediments and benthic organisms in the vicinity of the sand-blasting site IR04.

The Asian clam *Potamocorbula amurensis* was introduced to San Francisco Bay in 1986, presumably in ballast water from cargo ships (Carlton and others, 1990). Since then the clam has spread throughout the Bay, displacing much of the former benthic community. It is now an important food source for San Francisco Bay biota such as diving ducks, sturgeon, and Dungeness crab. This suspension-feeder has the potential to alter completely the food-web dynamics in the Bay (Nichols and others, 1990). Because of this clam's grazing habits, and its ability to filter large volumes of water (1-5L per day), it also has the potential of being a biomonitor of pollutants in the Bay (Pereira and others, 1992). Bivalves, unlike fish and other species, are deficient in degradative enzymes such as microsomal oxidases and mixed-function oxidases which are responsible for the degradation of organic contaminants. Therefore, bivalves can serve as integrators and biomonitors of pollutants.

A study was initiated in 1995 to determine if TBT and its degradates have contaminated Mare Island Strait, Carquinez Strait, and possibly San Pablo Bay. The objectives of this investigation were to determine the extent of contamination of benthic sediments near Mare Island, and to investigate the bioavailability of TBT and its degradates to *Potamocorbula amurensis*.

FIELD AND LABORATORY METHODS

Sample collection

Soil samples (IR04-A, -B, -C, Dike 14, IR05) were collected at five locations on Mare Island (Fig. 1). Surficial bottom sediments (MI-1 to MI-6) were collected at six sites from Mare Island and Carquinez Straits (Fig. 1) using a Van Veen grab sampler. The upper 8 cm of sediment were sampled with a stainless steel pipe to include the depth to which the *Potamocorbula* clams burrow (~1-2 cm) and also any sediment immediately below this that may influence the clams, possibly from bioturbation and mixing of the underlying sediments. Sediments and soils were stored in a freezer at -15°C prior to analysis. Clams [MI-1(T) to MI-6 (T)] were collected in the same

general vicinity as the sediment grab samples using the Van Veen grab sampler, followed by screening. Clams were allowed to depurate in ambient water for 48 hours to clear sediment from the digestive tract (Brown and others, 1995), rinsed with distilled water, and stored in a freezer at -15°C until analysis.

Sample preparation and analysis

Soils and sediments were air dried and ground using a clean porcelain mortar and pestle. The samples were passed through a 32 mesh stainless steel sieve. Clams were shucked, excess moisture removed with a clean filter paper, and the sample ground and homogenized. Sediment samples were extracted four times with 0.2% tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one) in methylene chloride by the method of Wade and others (1990) and McGee and others (1995). Tissue samples were extracted three times by maceration with 0.05% tropolone in methylene chloride in the presence of sodium sulfate by the method of Garcia-Romero and others (1993). A surrogate (tripropyltin chloride) was added to all samples prior to extraction and was used for the determination of analyte concentrations. The sample extracts were concentrated by Kuderna-Danish technique and the solvent exchanged to 10 ml of hexane. Organotin compounds were hexylated with Grignard Reagent (n-hexylmagnesium bromide) and the derivatized extract was purified using silica gel/alumina column chromatography. The hexylated organotin compounds were analyzed by high resolution capillary gas chromatography using flame photometric detection (GC/FPD) with a 610 nm filter for tin specific analyses. This method quantitatively determines tetrabutyltin (4BT), TBT, DBT, and monobutyltin (MBT). All concentrations are reported as ng Sn/g dry weight. Quality control samples (blanks, matrix spikes, and matrix spike duplicates) were processed with each batch of 20 or less samples in a manner identical to the actual samples. No butyltins were detected (peaks with area greater than three times the signal to noise ratio) in any of the blanks (tissues or sediment/soils). The recoveries of analytes in the matrix spike and matrix spike duplicates were acceptable (80-130 %), except MBT in sediments (22-46% recoveries). The detection limit, based on

peaks with a signal/noise ratio of at least 3, is 0.2 ng Sn/g for sediments and 10 ng Sn/g for tissues.

TOC Analyses

TOC in soils and sediments was determined by MSI Analytical Laboratories, Santa Barbara, CA. The method involved acid treatment to remove inorganic carbon, followed by combustion to CO₂ with thermal conductivity detection on a Control Equipment Corporation instrument.

Lipid Analyses

Lipids in tissue samples were determined by methylene chloride extraction, followed by solvent evaporation, and determination of the weight of the extract.

RESULTS AND DISCUSSION

Total organic carbon and nitrogen in soils from Mare Island and sediments from Mare Island Strait and Carquinez Strait, along with the lipid content of *Potamocorbula amurensis* are shown in Table 1. In general, the organic carbon and nitrogen content of the benthic sediment were similar at the six sites, resulting in a relatively

Table 1. Total organic carbon and nitrogen in soils and sediment and lipid content of *Potamocorbula amurensis*, Mare Island, California.

Site	Weight %*		C/N ratio
	C	N	
<u>Benthic Sediment</u>			
MI-1	1.27	0.15	8.58
MI-2	1.34	0.15	9.21
MI-3	1.31	0.15	9.04
MI-4	1.23	0.13	9.64
MI-5	1.18	0.14	8.61
MI-6	1.18	0.14	8.49
<u>Soils</u>			
IR04A	0.29	0.03	11.30

IR04B	0.06	0.03	2.48
IR04C	0.04	0.03	1.30
IR05	0.30	0.02	13.2
Dike 14	1.36	0.10	13.3

<u>Potamocorbula</u>	% Lipid*
MI-1 (T)	19.1
MI-2 (T)	26.7
MI-3 (T)	6.7
MI-4 (T)	9.2
MI-5 (T)	8.7
MI-6 (T)	11.4

* On a dry weight basis

uniform C/N ratio that is characteristic of values in the range between terrigenous organic inputs [C/N 12~14, Prahl and others (1980)] and inputs from marine phytoplankton [C/N ~6, Muller (1977)]. The C/N ratios within the soils from sites IR04A, IR05, and Dike 14 gave values showing mainly terrigenous input. Soils from sites IR04B, and IR04C, which were very sandy and therefore had much lower organic content in general, gave much lower C/N values. Site IR04A had a much greater TOC value than sandy sites IR04B and IR04C, which, as will be seen later, resulted in sorption of greater amounts of butyltins. The lipid content of *Potamocorbula amurensis* varied between 6.7 and 26.7 % (dry weight basis); lipid content is dependent on the physiological condition of the clam communities at the different sites.

Soils: Concentrations of butyltin compounds in soils from Mare Island and in sediments and *Potamocorbula amurensis* from Mare Island Strait and Carquinez Straits are shown in Table 2. Soils from sites IR04A, IR04B, and IR04C within the sand-blasting zone all contain TBT and its degradates DBT and MBT. Of these three sites, site IR04A, which had the highest organic carbon content, also contained the highest levels of butyltins, suggesting that the sorption of these compounds, especially in the case of TBT, is controlled mainly by a partitioning process into the organic carbon of the soils (Chiou and others, 1983). At site IR04A, concentrations of the individual butyltins were in the order of decreasing lipophilicity, with TBT > DBT > MBT. The lipophilic t-butyl groups of TBT control sorption via a partitioning process into organic carbon. At

sites IR04B and IR04C, the sandy soils, this order generally was reversed with concentrations of MBT > DBT > TBT at IRO4B, and MBT>TBT>DBT at IRO4C. This phenomenon occurs probably because the more ionic MBT and DBT are bound to the sand particles by ionic and ion-dipole bonds. Here, the ionic properties of the molecule may control the sorption process. It is reported that the dominant interaction of triorganotin (TOT) compounds with mineral surfaces is sorption of TOT⁺ cations to negatively charged surfaces by cation exchange (Wiedenhaupt and others, 1997). These lipophilic and ionic properties of butyltins probably have important implications for the bioavailability and fate and transport of these compounds in estuarine systems. The presence of DBT and MBT also indicates that abiotic or microbiological degradation processes of TBT are occurring in soils at site IR04. Thus,

Table 2. Concentrations of butyltin compounds in soils, sediments, and the Asian clam *Potamocorbula amurensis*, from Mare Island (ng Sn/g dry weight).

TBT is progressively dealkylated and detoxified in soils, resulting in the formation of the less toxic DBT and MBT. Soil IR04-A from site IR04 also contained trace levels of 4BT, an impurity in commercial TBT. Site IR05, which is outside the sand-blasting zone, contained trace levels of TBT. Soil from the Dike 14 area, also outside the sand-blasting zone, contained no detectable amounts of butyltin.

Sediment: All the benthic sediments from Mare Island and Carquinez Straits (Table 2; MI-1 to MI-6) contained relatively low concentrations of TBT and its degradates, with concentrations of these compounds in the order TBT > DBT > MBT, except in the case of MI-3 where concentrations of butyltins were very low and in the order DBT > MBT > TBT. The reason

Site	Monobutyltin	Dibutyltin	Tributyltin	Tetrabutyl tin	Total Butyltin
Soils					
IR04-A	13.6	15.5	22.0	0.5	51.6
IRO4-B	2.8	0.9	0.8	nd	4.5
IRO4-C	2.0	0.9	1.3	nd	4.2
Dike 14	nd	nd	nd	nd	-
IRO5	nd	nd	0.3	nd	0.3
Benthic sediment					
MI-1	1.6	2.2	2.8	nd	6.6
MI-2	2.0	2.5	3.6	nd	8.1
MI-3	0.4	0.6	0.3	nd	1.3*
MI-4	1.4	1.8	2.7	nd	5.9
MI-5	0.5	1.7	2.7	nd	4.9
MI-6	1.5	2.0	2.1	nd	5.6
<i>Potamocorbula</i>					
MI-1(T)	nd	29.4	123.0	nd	152.4
MI-2(T)	nd	46.0	142.5	nd	188.5
MI-3(T)	nd	26.9	158.5	nd	185.4
MI-4(T)	nd	141.0	166.0	nd	307.0
MI-5(T)	nd	39.3	151.7	nd	191.0
MI-6(T)	-	-	-	-	-

nd- not detected, * data point is suspect.

for this anomaly at site MI-3 is not understood at this time. In addition, as discussed later, an anomalously high Biota Sediment Accumulation Factor (BSAF) for TBT was obtained at site MI-3, in spite of the low concentration of butyltin in benthic sediment. In general, concentrations of butyltins in benthic sediment are controlled primarily by a partitioning process into the sediment organic carbon, with ionic interactions probably playing a minor role in the sorption process. Microbiological processes also may be responsible for transformation of TBT to DBT and MBT in marine benthic sediments. Ratios of TBT/DBT were relatively constant in all the benthic sediments, except for site MI-3, and ranged from 1.1-1.6 indicating relatively uniform and similar microbiological activity in benthic sediment at these sites. The data in Table 2 also indicate that TBT and its degradates, which are leached by precipitation and tidal action, are in the waters around Mare Island and into Carquinez Straits, and, by implication, possibly into San Pablo Bay. The benthic sediment data also suggests that a contamination gradient does not exist near Mare Island, and that the butyltin contamination problem is more diffuse in nature. The diffuse nature of this contamination probably is a result of the hydrodynamics of the Bay and remedial operations in progress at the Naval Base.

Biota: There is a paucity of information about butyltins in San Francisco Bay, and virtually no information available on the accumulation of butyltins in *Potamocorbula amurensis*. One study reported concentrations of TBT of 111-127 ng Sn/g dry weight in transplanted oysters (*Crassostrea gigas*) in the vicinity of our study area, whereas concentrations of TBT in these organisms and other bivalves ranged from 1-73 ng Sn/g in other locations of the Bay (San Francisco Estuary Institute, 1995). The National Oceanic and Atmospheric Administration (NOAA) National Status and Trends (NS&T) Mussel Watch Project reported in 1989-90 concentrations of total butyltins in bivalve mollusks in the range of 184-867 ng Sn/g and the concentrations of TBT in the range of 94-373 ng Sn/g at three locations in San Francisco Bay (Uhler and others, 1993). The concentrations of total butyltins for these three NS&T sites in 1995 ranged from 38-84 ng Sn/g (GERG, Texas A&M University, unpublished

results), suggesting that the levels of organotins in biota in San Francisco Bay have decreased significantly since 1989 when limitations in the usage of TBT and (or) use of lower release rate paints were instituted. Concentrations of butyltins in lipid tissues of *Potamocorbula amurensis* from our study are shown in Table 2. Only TBT and lesser amounts of DBT were present in tissue samples. MBT was not detected in the tissues. The absence of MBT in the clam tissue probably indicates that this compound is bioaccumulated less efficiently or depurated more rapidly than TBT and DBT. Concentrations of TBT ranged from 123-166 ng Sn/g (ppb) and concentrations of total butyltins ranged from 152-307 ng Sn/g (ppb). TBT made up from 54-85% of the total butyltin burden of these bivalve mollusks, and DBT from 15-46% of the total butyltin burden. Ratios of TBT/DBT in *Potamocorbula amurensis* in the study area ranged from 1.2-5.9. The ratio of TBT/DBT in *Mytilus edulis* from the east and west coasts of the United States has been reported as 2.6 ± 1.0 (Uhler and others, 1993). The wider range in the ratios of TBT/DBT in our limited data set probably is due to various complex physiological processes that affect the uptake and depuration of butyltins in *Potamocorbula*. Although relatively small concentrations of butyltins were present in benthic sediment from Mare Island Strait at site MI-3 (which is in the vicinity of site IR04, the sand-blasting site near Green Beach), the largest concentrations of butyltins in *Potamocorbula* were found in sample MI-4(T). Concentrations in *Potamocorbula* at this site are on the order of about sixty times greater than those in sediment. This observation suggests that butyltins probably are gradually leached out from contaminated sediments into the water column. Because *Potamocorbula* filter very large volumes of water (about 5L/clam/day), the major routes of accumulation of TBT probably are by bioconcentration from the water column or uptake from suspended particulates including phytoplankton in the water column, with lesser amounts of accumulation from the benthic sediment.

Biota Sediment Accumulation Factor (BSAF): In order to describe the preference of hydrophobic organic contaminants for lipid tissues of the organism relative to sediment

organic carbon, BASFs for butyltins were calculated using the method of Lee and others (1989) and McFarland and others (1994) (Table 3). BSAF is the ratio of the tissue contaminant concentration (normalized to the lipid content) of the organism to the sediment contaminant concentration (normalized to organic carbon) to which the organism is exposed, at equilibrium. Normalization of the sediment contaminant concentration to the organic carbon content reduces variability in sediment characteristics, and normalization of the tissue contaminant concentration to the lipid content reduces variability in tissue concentrations among individuals of the same species as well as between different species. The BSAF when multiplied by the organic carbon normalized sediment contaminant concentration

Table 3. Biota Sediment Accumulation Factors of butyltin compounds at Mare Island, San Francisco Bay, California.

Site	Dibutyltin	Tributyltin
Mare Island*		
<i>(Potamocorbula amurensis)</i>		
MI-1	0.96	2.32
MI-2	0.36	1.93
MI-3	8.7	96.3
MI-4	10.6	7.97
MI-5	3.19	7.78
San Francisco Central Bay **		
<i>(Macoma nasuta)</i>		
	0.86	8.19
<i>(Mytilus edulis)</i>		
	3.48	5.85
Oakland Inner Harbor Turning Basin **		
<i>(Macoma nasuta)</i>		
	0.09	0.11
<i>(Mytilus edulis)</i>		
	0.90	0.85

* Field study

** Data from Mc Farland and others, 1994 (28 day laboratory study)

predicts the lipid normalized tissue residue concentration.

Data for Mare Island in Table 3 indicate that BSAFs of TBT ranged from 1.93-7.97 (except in the case of site MI-3), and those of DBT from 0.36-10.6. Because several grab samples of sediment had to be collected in order to obtain a sufficient number of clams, the anomalously high BSAF obtained at site MI-3 probably indicates that the clams from this site were not directly associated with this sediment sample or they were not in equilibrium with the sediment sample collected at this site. BSAFs determined in a 28-day laboratory bioaccumulation study in *Macoma nasuta* and *Mytilus edulis* (McFarland and others, 1994), are included in Table 3 for comparison. Differences in BSAFs, for example in the case of *Macoma nasuta* in San Francisco Central Bay and Oakland Inner Harbor Turning Basin, may be due to differences in sediment. The San Francisco Central Bay sediments were surficial sediments, whereas the Oakland Inner Harbor Turning Basin sediments were undisturbed virgin sediments that were collected from a depth of about 40 feet. However, several of the BSAFs reported in this field study for *Potamocorbula amurensis* are in closer agreement with the BSAF values reported in the laboratory study for San Francisco Central Bay than those reported for the Oakland Inner Harbor Turning Basin. These differences in BSAF values could be due to differences in the organisms under investigation (*Potamocorbula* vs. *Mytilus edulis* and *Macoma nasuta*), a field vs. laboratory study, or lack of equilibrium conditions in a dynamic estuary.

The BSAFs obtained in this field study also tend to be much larger than values reported for neutral hydrophobic compounds such as PAHs and PCBs (BSAF, ~ 0.9) in laboratory studies (McFarland and others, 1994). One possible explanation for the larger BSAFs of the organotin compounds over the neutral hydrophobic PAHs and PCBs may be due to processes other than simple partitioning of the neutral species into lipid, such as ionic binding to the -SH and =NH groups of proteins (Kannan and Falandysz, 1997) or ion pairing with other natural organic ligands which could enhance bioaccumulation.

In addition to the contamination problem from the Mare Island site, it is also possible that additional sources of TBT contamination are involved in the study area. These could include TBT from ships undergoing salvage operations at marinas in Mare Island Strait, as well as bay-wide

transport of fine sediment containing TBT. Recent data from the San Francisco Estuary Institute (1995), and NS&T studies for mussels, clams and oysters also indicate that organotin contamination is widespread throughout San Francisco Bay; however, levels of organotin compounds in biota from San Francisco Bay have decreased significantly since 1989, when limitations on usage of butyltins and/or use of low release rate paints were instituted.

CONCLUSIONS

The results of this field study clearly indicate that soils from the sandblasting site at the former Mare Island Naval Shipyard, and benthic sediment and *Potamocorbula amurensis* from Mare Island and Carquinez Straits are contaminated with organotin compounds. This organotin contamination problem is now diffuse and has spread into Carquinez Strait and possibly into San Pablo Bay. Although benthic sediments contain low levels of these compounds, the clams bioaccumulate significant amounts of di- and tributyltin. Because *Potamocorbula amurensis* is an important food source for diving ducks, sturgeon, Dungeness crab, and other biotic species in San Francisco Bay, the organotin compounds have the potential for biomagnification in the food chain. Tributyltin is extremely toxic to marine organisms, and it is classified as a potent endocrine disrupting chemical. Further studies are necessary to determine the environmental effects of the organotin compounds on biota in San Francisco Bay.

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