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Source: Journal of Coastal Research, 36(sp1) : 118-123

Published By: Coastal Education and Research Foundation

URL: https://doi.org/10.2112/1551-5036-36.sp1.118

Journal of Coastal Research	SI 36	118-123	(ICS 2002 Proceedings)	Northern Ireland	ISSN 0749-0208

Distribution of Fe, Mn, Cu and Cd in Upper Sediments and Sediment-Trap Material of Ria Formosa (Portugal)

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ABSTRACT

In shallow highly productive coastal environments intense biogeochemical activity is concentrated in the upper sediment layers. However, pore water composition of permeable inter-tidal sediments change as water flows over the areas during ebb and flood tides. In order to examine metal post-mobilisation, inter-tidal sediment cores of 4 cm length and particles settled in sediment-traps over several periods during 10 months were collected in Ria Formosa (SW Iberian Peninsula). Concentrations of Al, Fe, Mn, Cu and Cd, loss on ignition and the proportion of fine fraction were determined in sediment layers of 0.5 cm thickness and in sediment-trap material. Levels of Mn in sediments were similar to those in sediment-trap material, although enrichment in the topmost sediment layer (0.1 mm) was observed as MnO_2 is formed. Although Fe in sediments and sediment-trap material ranged within similar intervals, two relationships with Al were found showing that sediment-trap material are impoverished in Fe in comparison to sediments. This suggests that Fe is mainly cycled inside the sediment. Copper and Cd exhibited different patterns. Levels in sediment-trap material were not correlated to Al or LOI, probably due to local contamination or uptake by plankton. These values were lower than levels in the topmost sediment layer, suggesting that Cu and Cd that reach the sediment surface are rapidly released to the water column. Concentrations in sediments, including the topmost layer, exhibited two relationships to Al, for both Cu and Cd. One corresponding to background values and the other found in stations closer to the anthropogenic sources. In these cases Cu and Cd are incorporated into the sediments that is facilitated by AVS values close to the sediment surface.

ADDITIONALINDEXWORDS: *Surface sediments, heavy metals, geochemistry, coastal lagoon, Portugal.*

INTRODUCTION

The equilibrium between pore water and sediment solids in shallow highly productive environments is greatly influenced by the presence and activity of benthic organisms (ALLER, 1977), the pressure variation induced by wave motion (SHUM and SUNDBY, 1996), and the mixing linked to the tidal excursion (HEMMOND *et al*., 1984; AGOSTA, 1985). These disturbances occur in short-time scales and thus chemical equilibrium are frequently modified and reset. Equilibrium in inter-tidal permeable sediments of macro- and meso-tidal environments is repeatedly altered by the tidal flushing, which causes a partial renewal of pore waters and the export of solutes to the water column twice a day (FALCÃO and VALE, 1995). For example, NH_4^+ weakly sorbed to the sediment particles and of Fe, a redox sensitive element, change dramatically their concentrations during tidal inundation (CAETANO *et al*., 1997; HEUTTEL *et al*., 1998). When sediment temperature increases during exposure to the atmosphere, solute concentrations change due to density gradient currents (ROCHA, 2000).

Ria Formosa is a mesotidal coastal lagoon permanently connected to the sea located in the south of Portugal in which approximately 50% of the flat areas, corresponding to one third of the lagoon area, are alternatively exposed to the atmosphere for several hours and inundated by the tide on semi-diurnal tidal cycles. The lagoon is highly productive, in particular due to clam production on extensive inter-tidal sediments (SPRUNG, 1994). Nutrients are intensely pumped from inter-tidal sediments to water by the tide and the activity of benthic organisms (FALCÃO, 1997). The lagoon receives no permanent freshwater input, and untreated domestic effluents from two cities (Faro and Olhão) are discharged in inner channels. In this highly dynamic ecosystem products of post-depositional reactions are thus poorly recorded in pore waters. Due to these specific conditions the approach followed in this study was to examine the distribution of Fe, Mn, Cu and Cd concentrations in suspended material settled in sediment traps and in the first 4-cm of inter-tidal sediments with 0.5-cm depth resolution.

SAMPLING AND METHODS

Five sediment cores of 4 cm length were collected in July 1993 in stations A, B, C, D and E located in inter-tidal areas of Ria Formosa (Fig. 1). Stations A, B and C are located nearby the channels where the domestic sewage are discharged. Stations D and E showed no vegetation cover, and the other stations were colonised by *Zostera marina*. Visual inspection of all the collected sediments revealed no presence of macro fauna. The sediments were collected with a small box-corer of 15x15 cm at low tide in order to minimise perturbations of the sediment surface during sampling. The non-compacted topmost sediment layer, with an approximate thickness of 1 mm, was collected by direct aspiration into pre-cleaned syringes. Immediately after cores were sliced in 0.5 cm layers and stored in plastic vials under a N_2 atmosphere. Suspended particulate matter settled into sets of six sediment-traps, with 5 cm diameter and 20 cm, which were placed in sub-tidal areas in front of stations A, C and D. Samples were collected from April 1992 to February 1993 during the following periods: 15/04-26/05/92, 26/05-01/07/92, 01/07-17/08/92, 17/08-26/10/92, 11/12/92-08/01/93 and 08/01-25/02/93. Sampling over this period allows better characterising of the material that circulates in suspension in Ria Formosa and deposited in the inter-tidal areas. Due to the shallowness of the lagoon, sediment-trap material includes plankton and resuspended sediments resulting from water excursion during ebb and flood spring tides, waves and wind. Retained particles in the six traps placed at each station were combined in composite samples.

Sediment samples were sieved at 63 µm to determine the percent of silt and clay. Sediment samples were freeze-dried, grounded, homogenised with an agate mortar for determination of loss on ignition and metals (Al, Fe, Mn, Cu and Cd). LOI was determined at 450ºC for 2 hours (CRAFT *et al.*, 1991). Approximately 200 mg of sediment was weighted and transferred into a Teflon bomb, followed by 6 ml of fluoridic acid, 1 ml of Aqua Regia ($HCl:HNO_3$, 3:1) and digested at 100 ºC for 1 hour. Subsequently, the bombs content was poured into a 100-ml volumetric flask containing 5.6 g of boric acid and filled up with Milli-Q water (RANTALA and LORING, 1975). Concentrations of Al, Fe and Mn were determined by flame atomic absorption spectrometry with air-acetylene flame apart from Al that was with a nitrous oxide-acetylene flame. Concentrations of Cu and Cd were determined by graphite furnace atomic absorption spectrometry with deuterium background correction. The detection limits of Al, Fe, Mn, Cu and Cd were 0.11, 0.14 %, 12, 3.7 and 0.02 µg g-1, respectively. International certified standards were used to ensure the accuracy and precision was determined by analysing replicate samples. The precision expressed as relative standard deviation was 1% for Al, Fe and Mn and 2% for Cu and Cd.

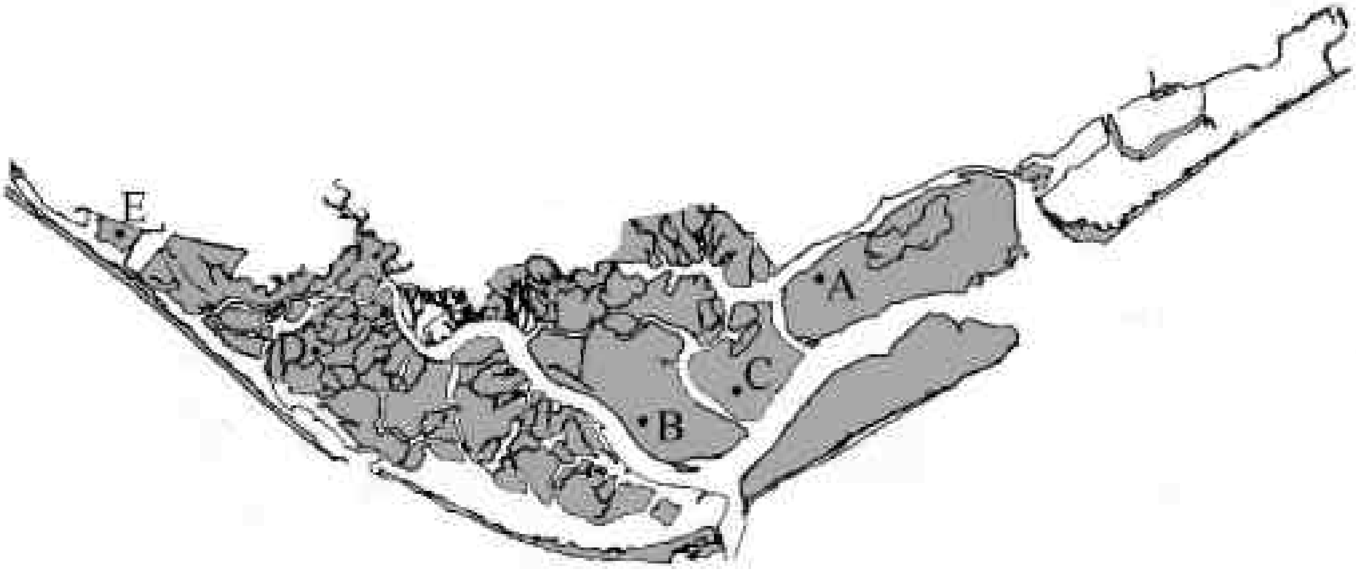

Figure 1 Map of Ria Formosa with the location of the five sampling stations (A, B, C, D and E).

RESULTS

The proportion of fine fraction (<63 µm), Al, Fe, Mn, Cu and Cd concentrations and LOI in sediments and sediment-trap material are presented in Table 1. The first 3-cm of sediments from stations A, B, C and D contained a larger proportion of the fine fraction (53-94 %) than deeper layers and sediments from station E. Aluminium concentrations were higher in sediment-trap material (3.8-7.7%) than in sediments (2.1-6.7%). Aluminium in sediments of stations C, D and E varied irregularly with depth. This variation agrees with the grain size data and indicates the existence of different mixtures of coarse and fine-grained material in inter-tidal sediments. Coarse material transported from nearby clam-culture grounds by tidal currents and driven-wind waves possibly contributed to the variability in grain size distribution. Because stations A and B are located far from clam grounds the grain size was more regular with depth. The Al content covaries with the percentage of fine fraction (FF) in the sediment at a significant level ([Al] = 0.05 [FF] + 0.64; $r^2 = 0.89$; $p<0.001$) pointing to Al as a good indicator of the fine sediment distribution. Loss on ignition was higher in fine sediments ([LOI] = 0.18 [FF] – 4.4 ($r^2 = 0.86$; $p<0.001$) indicating that particulate organic matter is deposited together with fine particles.

Manganese showed enrichment in the topmost sediment layer (1º mm) followed by a decrease with depth (Table 1). Excluding this thin layer, sediments presented similar levels (77-315 µg g^{-1}) to sediment-trap material (101-312 µg g^{-1}). Iron ranged in broader interval in sediments (0.89-4.1 %) than in sediment-trap material (1.6-3.5 %). Enhanced levels of Fe were found in sediments from stations A and B that presented also higher Al content. In all stations but B, Fe showed slight enrichment in the upper sediment layers. Copper in sediment-trap material from stations A (22-46 µg g^{-1}) and D (19-33 µg g^{-1}) were comparable to concentrations recorded in sediments (10-41 µg g^{-1}), while in station C sediment-trap material contained more Cu (35-149 µg g^{-1}) than sediments (14-30 µg g^{-1}). Copper was higher in station A that exhibited enhancements in the first 3-cm. Cadmium concentrations in sediment-trap material from stations A, B and C ranged in similar intervals in the three studied stations (0.16-0.52 µg g^{-1}). Concentrations in sediments (0.045-0.31 µg g^{-1}) were lower displaying an irregular variation with depth. As observed for Cu, sediments from station A presented higher Cd contamination.

DISCUSSION

In order to examine the Mn distribution in Ria Formosa concentrations were plotted against Al content (Fig. 2). A linear relationship ($p<0.001$) was found for sediments and sediment-trap materials, excluding the point's corresponding to the topmost sediment layer (1º mm) that are located above the regression line. This indicates that Mn is deposited and sediment-trap material is mainly related to the aluminosilicate fraction, except at the sediment-water interface that is enriched in diagenetic manganese. In fact, Mn(II) in pore waters of Ria Formosa exhibited a maximum at subsurface layers (0.5-cm) over all year (CAETANO *et al.*, 1995), which indicates that Mn(IV) in the topmost sediments is generated through upward diffusion of dissolved Mn, as commonly observed in marine sediments (SUNDBY *et al*., 1986). Low Mn/Al ratio in sediment and

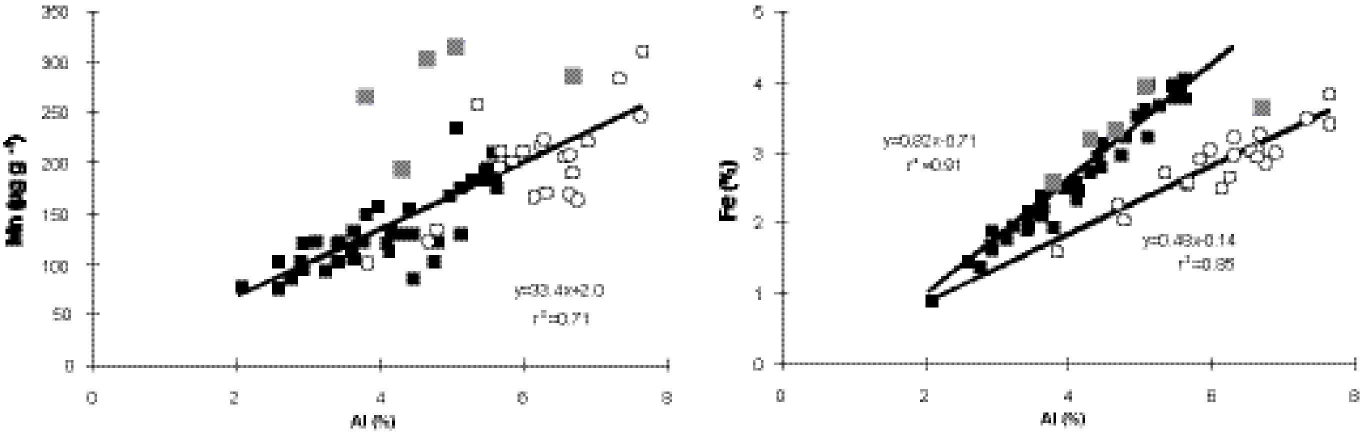

Figure 2 Manganese and Fe concentrations in sediments and sediment trap material versus Al content. Solid line represents the regression line. Black and grey squares represent sediments and 1º mm sediment layers, respectively, for all stations. Open circles represent sediment-trap material.

Table 1 Proportion of fine fraction (<63 µm) Al, Fe, Mn, Cu and Cd concentrations and loss on ignition (LOI) in sediments cores and sediment-trap material collected at Ria Formosa.

Station	Depth	Fraction	Al	Fe	Mn	Cu	Cd	LOI
	(cm) (%)	<63 µm	(%)			(µg g-1)		(%)
A	ST	--	3.8 - 7.6	1.6 – 3.4	101 - 246	22 - 46	0.16 – 0.38	6 - 14
	0-0.1	--	5.1	3.9	315	37	0.20	--
	0.1-0.5	88	5.1	3.6	235	38	0.25	11
	0.5-1.0	94	5.6	4.1	184	43	0.26	12
	1.0-1.5	92	5.0	3.5	167	40	0.28	10
	1.5-2.0	81	4.8	3.2	122	40	0.28	10
	2.0-2.5	74	4.7	3.0	102	41	0.28	7.9
	2.5-3.0	72	4.4	2.9	156	34	0.26	8.0
	3.0-3.5	73	4.5	3.1	131	33	0.31	8.5
	3.5-4.0	67	4.4	2.8	85	32	0.28	7.1
B	0-0.1	--	6.7	3.6	287	29	0.22	--
	0.1-0.5	83	5.6	3.8	175	30	0.19	13
	0.5-1.0	88	5.4	3.9	184	27	0.19	12
	1.0-1.5	87	5.6	3.9	209	25	0.18	11
	1.5-2.0	86	5.3	3.7	184	22	0.18	12
	2.0-2.5	82	5.1	4.0	174	27	0.17	12
	2.5-3.0	88	5.1	4.0	130	27	0.20	12
	3.0-3.5	86	5.5	3.8	193	22	0.16	12
	3.5-4.0	90	5.5	4.0	194	27	0.17	12
C	ST	--	5.3 - 7.7	2.5 – 3.8	190 - 312	35 – 149	0.22 – 0.51	11 - 15
	0-0.1	--	4.3	3.2	195	30	0.15	--
	0.1-0.5	60	4.1	2.3	113	25	0.19	8.2
	0.5-1.0	66	4.1	2.6	121	27	0.18	6.6
	1.0-1.5	60	3.4	2.1	122	25	0.15	6.7
	1.5-2.0	61	3.6	2.1	113	28	0.21	6.1
	2.0-2.5	53	3.6	2.4	131	28	0.21	6.7
	2.5-3.0	56	3.1	1.8	122	23	0.17	6.4
	3.0-3.5	51	3.8	1.9	122	23	0.22	4.1
	3.5-4.0	28	2.1	0.9	77	14	0.09	2.9
D	ST	--	5.7 - 7.3	2.5 – 3.5	163 - 283	19 - 33	0.17 – 0.52	9 - 11
	0-0.1	--	4.6	3.3	304	24	0.11	--
	0.1-0.5	54	3.6	2.2	104	17	0.07	4.6
	0.5-1.0	58	4.1	2.5	131	16	0.07	6.0
	1.0-1.5	67	3.8	2.5	149	20	0.08	4.7
	1.5-2.0	64	4.3	2.7	131	20	0.09	4.8
	2.0-2.5	75	5.1	3.2	130	23	0.09	7.2
	2.5-3.0	64	4.0	2.5	158	20	0.06	5.5
	3.0-3.5	45	3.4	2.0	122	14	0.04	3.2
	3.5-4.0	38	2.8	1.4	86	10	0.08	2.4
E	0-0.1	--	3.8	2.6	267	19	0.09	--
	0.1-0.5	35	2.9	1.7	102	12	0.09	3.3
	0.5-1.0	38	2.9	1.6	122	14	0.08	4.0
	1.0-1.5	49	2.6	1.5	77	12	0.10	3.6
	1.5-2.0	53	3.4	1.9	103	15	0.12	3.9
	2.0-2.5	57	2.9	1.9	94	14	0.11	4.0
	2.5-3.0	51	3.4	2.0	121	17	0.13	3.7
	3.0-3.5	51	3.2	1.9	94	15	0.09	3.8
	3.5-4.0	49	2.6	1.4	104	11	0.07	2.5

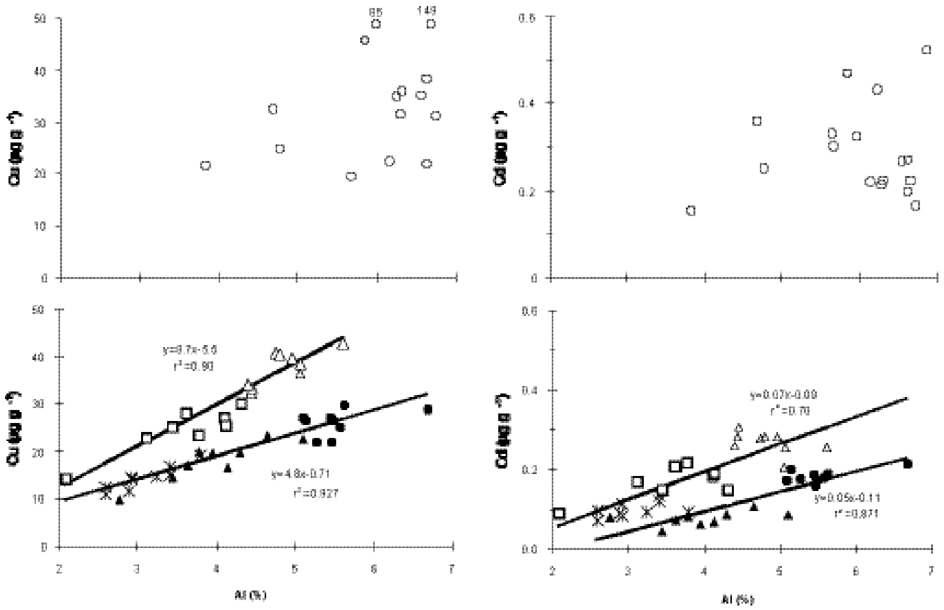

Figure 3 Copper and Cd concentrations in sediments and sediment trap material versus Al content. Solid lines represent the regression lines. Open triangles, black circles, open squares, black triangles and asterisks represent sediments from stations A, B, C, D and E, respectively. Open circles represent sediment-trap material.

sediment-trap material of Ria Formosa (33.4) in comparison to marine sediments (Mn/Al≈50; WINDOM *et al.*, 1989) reflects the absence of permanent freshwater inputs. When Fe concentration is plotted against Al content two relationships (Fig. 2) were found at significant level ($p<0.001$). Sediments, including the 1º mm, fit the regression with higher slope (0.82). This was higher than the slope for sediment-trap material (0.48) and the value 0.48 reported for the natural abundance of Fe in marine sediments (WINDOM *et al.*, 1989). The excess Fe in sediments reflects the dominance of internal cycling, reactive iron being mainly retained in the upper sediment layers. The retention may result from the interaction of Fe (II) with O_2 and MnO_2 (BURDIGE, 1993) at the topmost sediment layer that works as a chemical barrier slowing down the flux of Fe(II) exported from sediments to the water column. As shown in previous work (CAETANO *et al.*, 1997), this barrier is effective for Fe even during tidal flushing of inter-tidal sediments due to the fast kinetics of Fe(II) oxidation. Besides the formation of Fe-oxides, the presence of high concentrations of AVS (Acid Volatile Sulphides) below the sediment surface suggests that Fe(II) precipitates in the form of sulphides due to the production of HS^- (MADUREIRA, 1997). The linear Fe-Al relationship indicates that reactive Fe is retained more efficiently in fine sediments, due to their lower permeability to tidal water flushing.

Copper and Cd showed different patterns when concentrations are plotted against Al content: (i) significant correlations were found for sediments, including the 1º mm layer, but not for sediment trap material, and (ii) sediment values are combined in two relationships (Fig. 3). The lack of correlations between Cu, Cd and Al or LOI in sediment trap material indicate those particles act as a vehicle for those elements to the sediments due to contamination or uptake by plankton. This particulate material enriched in Cu and Cd is spread inside the lagoon due to the large water mass exchanged over semi-diurnal tidal cycles between Ria Formosa and the sea (SPRUNG, 1994; FALCÃO, 1997). The high Cu/Al and Cd/Al ratios in sediment trap material relative to upper sediments, including the topmost layer, suggest that Cu and Cd are transported from the water column to sediments being rapidly remobilised from the solids and transferred back to the water column. Transport towards the pore waters appears to be less effective, since incorporation in solid sediments did not increase with depth, although precipitation as sulphides would be favoured by the presence of AVS just below the sediment-water interface (MADUREIRA, 1977). Presumably tidal flushing, before any reactions sequestering them in the solid fraction, pumps dissolved Cu and Cd in the topmost sediment layers out. This appears to be the case in stations that presented a Cu-Al relationship slope (4.8) similar to background values (LAANE, 1992). Higher slope (8.7) recorded in two stations indicates high Cu retention in finer sediments, either due to faster sequestering processes and/or contamination due to the proximity to anthropogenic sources. Cadmium showed a similar behaviour to Cu, however, the slopes for two groups of stations (0.05 and 0.07) are not significantly different ($p<0.05$) and the two lines are parallel. This means the addition of relatively constant quantities of Cd in coarser and fine sediments closer to the anthropogenic sources.

Similar relationships were also obtained for Mn-LOI since particulate organic matter is preferentially deposited in areas of fine sediments (higher Al). Metal concentrations in sediments covered with Zostera marina (stations A, B and C) were not significantly different (ANOVA-Scheffé; $p<0.05$) from stations with no vegetation cover, suggesting that in this case root-sediment interactions have weak implications on the sediment chemistry (CAÇADOR *et al*., 1996).

In summary, the results obtained in this study point out to different metal cycles in Ria Formosa. Whereas Mn and Fe are recycled mainly inside the upper sediment layers responding to changes on redox conditions, Cu and Cd cycles involve the water column. Copper and Cd are incorporated in suspended particulate matter, derived from anthropogenic sources or uptake by plankton, and when particles reach the sediment these elements are rapidly remobilised to the water column. Only in the proximity of anthropogenic sources is incorporation in the sediment solids evident.

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