

# Radiocaesium dispersion and fixation in the lagoon systems of “Ria de Aveiro”, Portugal

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## Abstract

Radiocaesium ( $^{137}\text{Cs}$ ) dispersion and  $\text{Cs}^+$  fixation were studied in the sediments collected from the lagoon systems of “Ria de Aveiro”. The  $\text{Cs}^+$  sorption was tested for the fine mica grains and for the  $<2\ \mu\text{m}$  clay fractions extracted from silty clays. The  $\text{Cs}^+$  exchange is found strongly onto mica-rich fractions than smectite-rich fractions. The distribution coefficient increases if the silty material is constituted by rich-mica clay fractions or if the non-clay minerals are removed from the silty-clay material. The samples studied behave as multisite ion exchange, where  $\text{Cs}^+$  engages in ion-exchange reactions with hydrated cations on planar sites on expansible layer silicates. Higher concentrations of the  $^{137}\text{Cs}$  were found associated with mica-rich silty clays. The  $^{137}\text{Cs}$  ranges from 3.2 to 3.9  $\text{Bq kg}^{-1}$  in the  $<38\ \mu\text{m}$  fractions and from 2.9 to 3.3  $\text{Bq kg}^{-1}$  in the  $<64\ \mu\text{m}$  fractions.

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## 1. Introduction

Large concentrations of  $^{137}\text{Cs}$  were released to environment around the world in the last 50 years. The  $^{137}\text{Cs}$  with half-lives of 30.2 years found out in sediments is connected to the worldwide fallout, resulting from atmosphere nuclear tests and the Chernobyl accident (Ukraine). Also, it is an important constituent of radioactive wastes held in storage by several nuclear potentially countries.

The migration of the  $^{137}\text{Cs}$  to the biosphere and its subsequent bioavailability depends on the mechanisms of clay minerals adsorption (Higgo, 1987) and organic matter (Staunton et al., 2002). The interface of river–

ocean, via estuaries or lagoon systems, acts as sinks for natural and anthropogenic radionuclides.

Weathering effects on the structure of mica-type clay mineral is a sensitive consequence of the relative  $^{137}\text{Cs}$  concentrations in highly selective fashion to “frayed edge” sites (Jackson, 1963). The  $^{137}\text{Cs}$  may also be viewed as a potential radioisotope to data very recent sedimentation rates and ages of contaminated core (Siegel et al., 1994). The aim of this study is focused on the  $^{137}\text{Cs}$  dispersion,  $\text{Cs}^+$  ion-exchange reaction and estimation of the sedimentation rates in the living ecosystem of “Ria de Aveiro” based on the dispersion of  $^{137}\text{Cs}$ .

## 2. Materials and methods

The so called “Ria de Aveiro” is a barrier type lagoon located in the central north-western littoral of

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Portugal (Fig. 1). The lagoon covers an area of approximately 50 km<sup>2</sup> developed from the Atlantic Ocean to the estuary of the river Vouga. The genesis of lagoon is assumed to have taken place on top of a favourable geological structure, started less than 1000 years ago when a littoral sandy spit grew southwards, and isolated the estuary of river Vouga from the Atlantic Ocean (Delgado et al., 1992). The lagoon extends parallel to the coast, forming several tidal channels. The lagoonar environment is of the transition type, where both fluvial and marine effects may be observed. The silting up of the lagoon to the east caused the continuous diminishing of the wet areas

due to the transport of terrigenous sediments from the drainage basin of the river Vouga and the effluents. Silty clays and sands occur at the upper level of lagoon.

Samples studied were collected from 2 sites located in western part of lagoon and from 4 sites located to the eastern part of lagoon, where the interface rivers–lagoon is more evident (Fig. 1). Sediments were sampled in channels and interfluvies down to depths from 10 to 30 cm. The mineralogy of selected samples was determined by X-ray diffraction (XRD) analysis using a Philips X'Pert machine equipped with a CuK $\alpha$  anticathode. The samples were run in the range 2–50° 2 $\theta$  and ana-

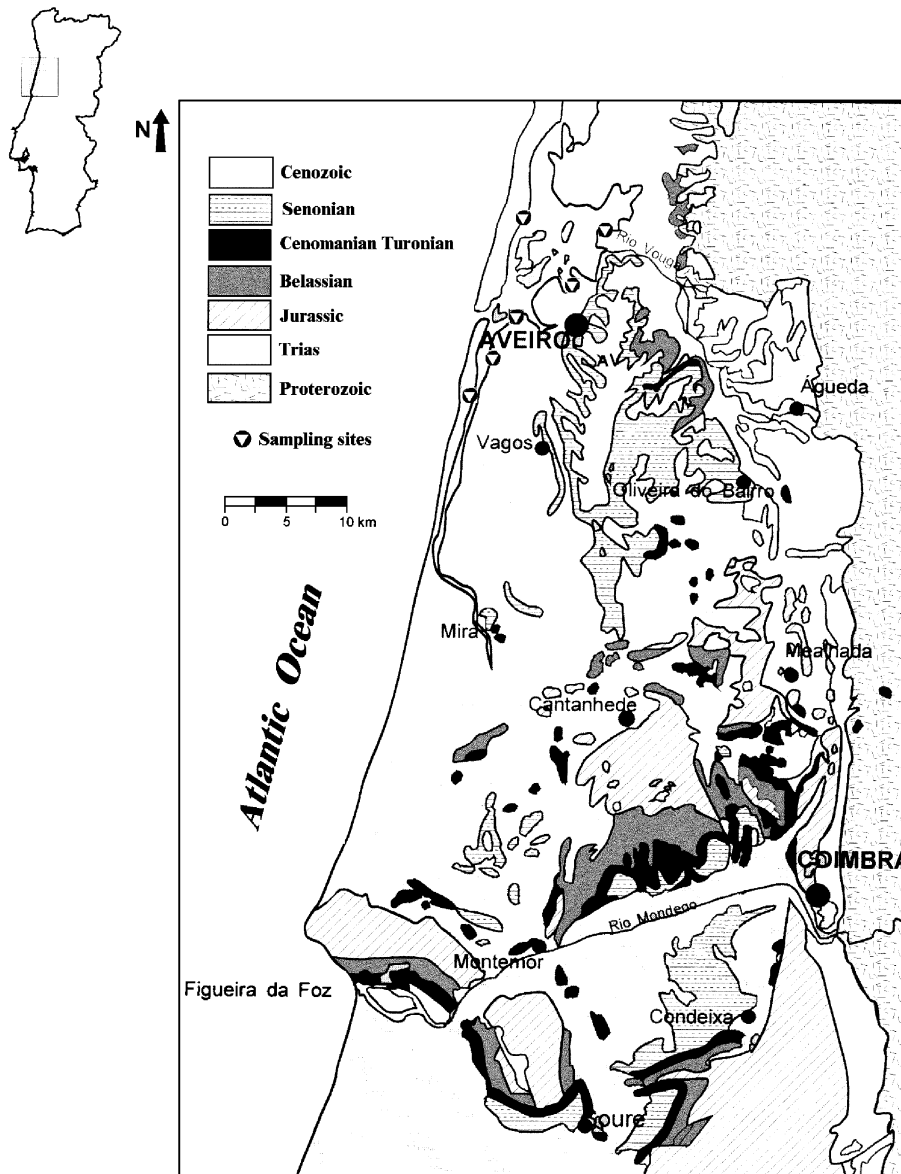


Fig. 1. Geological map of the Aveiro region and localization of samples studied.

lysed in air dried (AD) and ethylene glycol (EG) or glycerol solvated states.

Grain size distribution of the sampled sediments collected from different depths was carried out using a set of standard sieves. The  $<2\ \mu\text{m}$  clay fractions were separated by sedimentation. Previously, organic matters, carbonates and iron oxides were removed according to Jackson (1975). Organic matter was removed because it may cause the reduction of  $\text{Cs}^+$  sorption on clay minerals (Dumat et al., 1997). In order to differentiate high-charge from low-charge smectite, both clay fractions were saturated with  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ , using 0.1 M  $\text{MgCl}_2$  and  $\text{CaCl}_2$  solutions. Cation exchange capacity (CEC) of the samples selected was determined according to Worrall (1975).

The  $<2\ \mu\text{m}$  clay fractions were used for sorption experiments. Clay fractions were treated under homoionic conditions with 1 M NaCl, prior to their size fractionation and then, dialysed. We used 50 mg of sample with 5 ml of solution with  $\text{Cs}^+$  stable concentrations on the order of  $0.1\text{--}6.0 \times 10^{-6}$  M and 0.04 M  $\text{NaNO}_3$  solutions as a background electrolyte. The selectivity coefficient ( $k_s$ ) was calculated either  $\text{K}^+$  or  $\text{Cs}^+$  according to Sawhney (1970). Samples were saturated with 0.01 M KCl and 0.01 M  $\text{CaCl}_2$  solutions during five sequences of wetting–drying cycles in order to test the selective uptake by mica, I–S–V and S. The  $\text{Cs}^+$  speciation in solution was tested on samples studied by calculation the concentrations of  $\text{Cs}^+$  adsorbed ( $X_{\text{Cs}}$ ) ( $\text{mol kg}^{-1}$ ) and remaining in solution [ $\text{Cs}^+$ ] ( $\text{mol dm}^{-3}$ ). The distribution coefficient ( $K_d$ ) was calculated as ratio of concentration of  $X_{\text{Cs}}$  and [ $\text{Cs}^+$ ], assuming the same distribution for  $^{137}\text{Cs}$  (Staunton, 1994; Staunton and Roubaud, 1997). The selective  $\text{Cs}^+$  uptake is expressed as  $K_d$ .

The  $^{137}\text{Cs}$  was quantitative determined either the  $<63\ \mu\text{m}$  sandy clays fractions or the  $<38\ \mu\text{m}$  silty clays fractions using high-resolution  $\zeta$ -ray spectrometry.

### 3. Results

#### 3.1. Sediments mineralogy

##### 3.1.1. Samples from the eastern part of lagoon

The  $<63\ \mu\text{m}$  fractions are predominant constituted by feldspars, quartz, iron oxides, carbonates, mica and small amounts of kaolinite. The  $<38\ \mu\text{m}$  fractions are constituted of illitic material (mica, illite and mixed layer illite-smectite), small amounts of kaolinite, chlorite and smectite and non-clay material: quartz, feldspars and carbonates (Fig. 2a). Higher amounts of smectite were identified only in one sample (Fig. 2b) collected from the central part of lagoon close to the

Aveiro University. Randomly oriented specimens of detrital mica separated from silty clays were analysed by XRD (Fig. 2c).

Oriented specimens of detrital mica separated from both fractions of the  $<63\ \mu\text{m}$  and  $<38\ \mu\text{m}$  were recorded in AD, EG solvated and  $\text{Mg}^{2+}$ -saturated. No expandable layers were identified after EG salvation. Nevertheless, two segregated layers of illite–vermiculite (high-charge) associated to the “open” mica structure were identified for the  $\text{Mg}^{2+}$ -saturated and glycerol solvated samples.

Illitic material, smectite and minor amounts of kaolinite, chlorite and quartz were found in both  $<2\ \mu\text{m}$  fractions. Illitic material is composed of detrital mica and illite–smectite mixed layers (I–S) with 15% smectite (%S). The XRD patterns for  $\text{K}^+$ -saturated, heated at  $150\ ^\circ\text{C}$  and EG solvated confirm the presence of segregated three components of illite–smectite–vermiculite (I–S–V).

##### 3.1.2. Samples from the western part of lagoon

Samples collected from the top part are more sandy rich in quartz grains, which are characteristics features for eolian or marine deposits. However, few dispersed interbeddings with small amounts of mica grains and rich-organic matters were identified at depth ranging from 20 to 25 cm.

#### 3.2. Sorption, fixation and distribution coefficient

The  $\text{Cs}^+$  sorption was tested for the fine mica grains and for the  $<2\ \mu\text{m}$  fractions with high amounts of illitic material and high amounts of smectite. The sorption of  $\text{Cs}^+$  by selected clays after 24 h is shown in Table 1. More  $\text{Cs}^+$  was adsorbed by the mica exchange sites, than illite or smectite.

The selective coefficient is strong onto mica than onto smectite (Table 2) despite its lower CEC of mica than those for smectite. The difference in CEC between the last two clays is less evidenced. The  $\text{Cs}^+$  sorption on clay fractions selected is shown in Fig. 3, where the adsorption isotherm of  $\text{Cs}^+$  adsorbed. More  $\text{Cs}^+$  remains in solution when rich-smectite sediments do occur. The calculated  $K_d$  decreases as [ $\text{Cs}$ ] increases. Kaolinite and chlorite adsorb  $\text{Cs}^+$  less than illite. Impurities such as quartz, carbonates or feldspars associated to illitic material have a low affinity for  $\text{Cs}^+$ .

##### 3.3. Dispersion of $^{137}\text{Cs}$ in the “Ria de Aveiro” lagoon

Higher concentration of  $^{137}\text{Cs}$  determined in the  $<38\ \mu\text{m}$  fractions is about  $3.9\ \text{Bq kg}^{-1}$  (dry weight), being

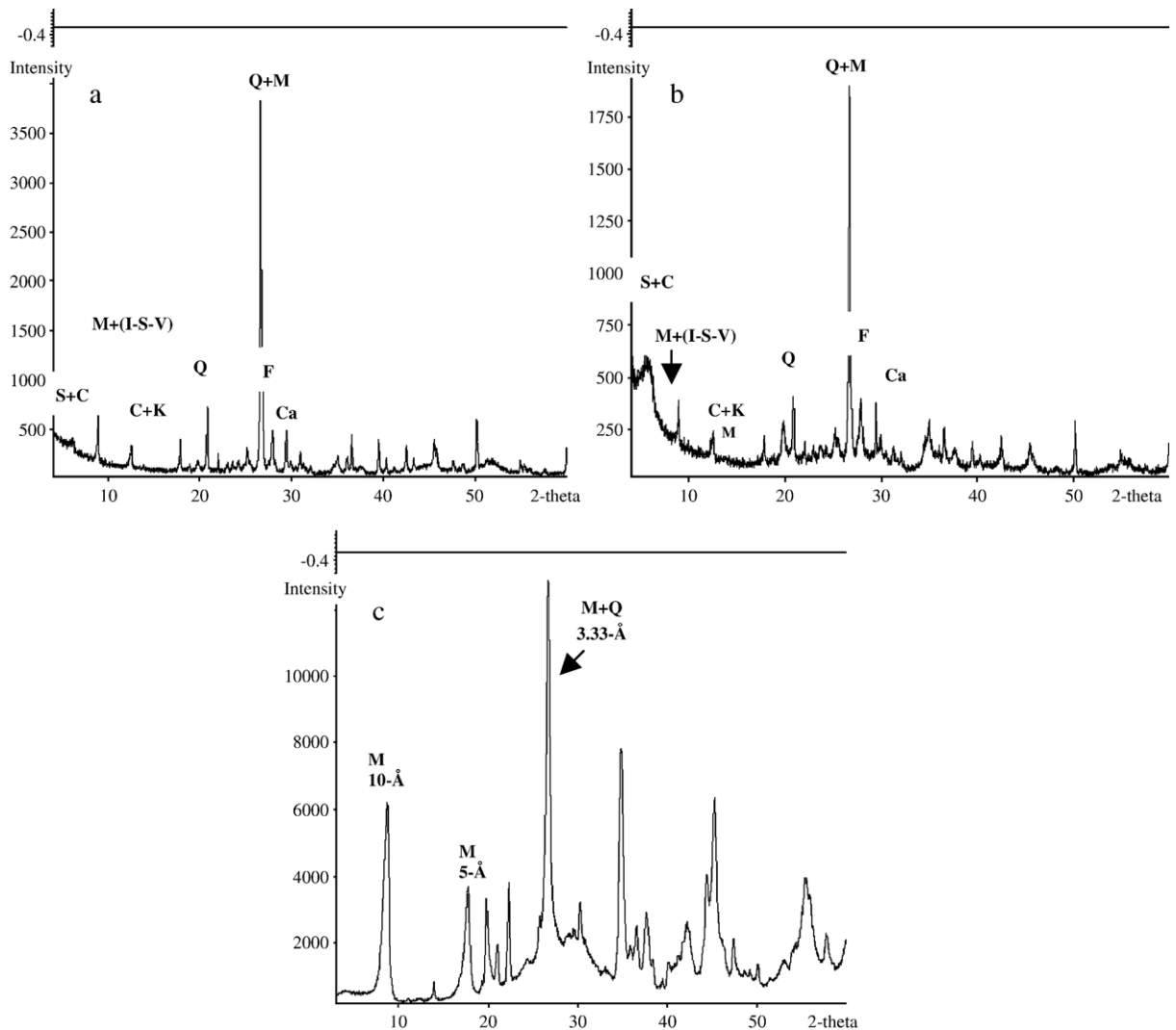


Fig. 2. Randomly oriented XRD patterns of the  $<38 \mu\text{m}</math> fractions (a, b) and mica grains (c) where  $^{137}\text{Cs}$  was determined (S: smectite; M: mica; I-S-V: illite-smectite-vermiculite; K: kaolinite; C: chlorite; Q: quartz; F: feldspars; Ca: calcite). The positions of the  $d_{hkl}$  reflections (not shown) in the XRD pattern of mica grains correspond to 1 M polytype.$

identified in silty clays (Fig. 2a) located at  $-30 \text{ cm}$  depth from the eastern part of lagoon. The samples collected at  $-20 \text{ cm}$  depths show nearly  $^{137}\text{Cs}$  values ranging from  $3.2$  to  $3.6 \text{ Bq kg}^{-1}$ . In the  $<64 \mu\text{m}</math> fractions collected at  $-20 \text{ cm}$  depths, the  $^{137}\text{Cs}$  ranges from  $3.1$  to  $3.3 \text{ Bq kg}^{-1}$ , whereas the samples collected at depths from  $-5$  to  $-10 \text{ cm}$  are characterized by the$

$^{137}\text{Cs}$  values ranging from  $2.9$  to  $3.1 \text{ Bq kg}^{-1}$ . The  $^{137}\text{Cs}$  concentration in rich smectite fractions (Fig. 2b) is about  $2.9 \text{ Bq kg}^{-1}$ . Sandy and silty samples collected from the near surface ( $-10$  and  $-15 \text{ cm}$ ) of the western part of the lagoon correspond to the  $^{137}\text{Cs}$  values below the detection limit ( $\sim 0.5 \text{ Bq kg}^{-1}$ ). The data obtained

Table 1  
 $\text{Cs}^+$  sorption by clays from the lagoon of "Ria de Aveiro"

Samples	CEC (meq/100g)	mg Cs/g clays	meq Cs/meq exchange
Mica	21	0.096	$34 \times 10^{-4}$
I-S-V-rich fractions	34	0.062	$13 \times 10^{-4}$
Smectite-rich fractions	56	0.076	$10 \times 10^{-4}$

Table 2  
Selectivity coefficient of clay samples for  $\text{K}^+$  and  $\text{Cs}^+$

Samples	nK, Cs/nCa	(m1/2Ca)/mK, Cs	$K_s$
Mica	0.463	0.7241	0.335
I-S-V-rich fractions	0.368	0.1495	0.055
Smectite-rich fractions	0.310	0.1318	0.041

Each value is an average of 5 analyses. Errors calculated from replicates are about 10%.

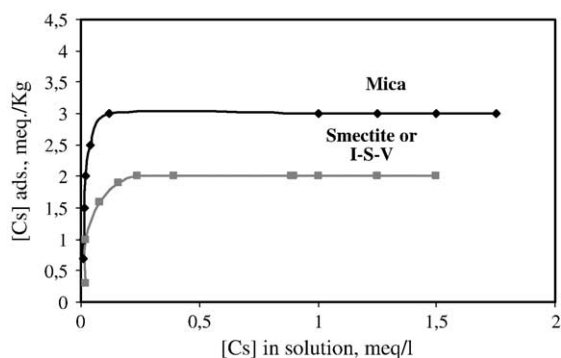


Fig. 3. Adsorption isotherm of  $\text{Cs}^+$  adsorbed ( $X_{\text{Cs}}$ ) and remaining in solution  $[\text{Cs}]$ . The lines are the fits of the experimental data to the Langmuir equation.

confirms that the  $^{137}\text{Cs}$  occurs just in the eastern part of lagoon, where the sediments of the lagoonal system are rich in silty clay materials.

#### 4. Discussion and conclusion

The study of sediment profiles provides information on the  $^{137}\text{Cs}$  contamination history and long term potential environmental impacts. The analytic data shows that sediments from the Aveiro lagoon are good traps and promote the sink of radionuclides. Illite and mica are the main components of the inorganic part of the sediments that are filling up continuously the Aveiro lagoon, changing the characteristics of the ecosystem.

Samples studied exhibit structural heterogeneity characterised by three distinct layers (I–S–V) showing a great layer charge density. Mica with the frayed edges and illitic material with lower layer charge density and CEC than montmorillonite exhibits greater selectivity for  $^{137}\text{Cs}$  sorption. This structural heterogeneity arrangements identified in clay material is a consequence of the weathering effect due to wetting–drying cycles and geomicrobiological activity in the “Ria de Aveiro” lagoon. Weathering effects on the structure of mica-type clay mineral is a sensitive consequence of the relative  $^{137}\text{Cs}$  concentrations in highly selective fashion to frayed edge sites and at the edges of high-charge smectite (vermiculite) interlayers. Thus, the samples studied behave as multisite ion exchange, where  $\text{Cs}^+$  engages in ion-exchange reactions with hydrated cations on planar sites on expansible layer silicates.

The  $K_d$  remains a basic parameter in prediction of the  $^{137}\text{Cs}$  behaviour in aquatic system. The  $K_d$  increases if the silty material is enriched in clay or the non-clay minerals are removed.

The maximum value of the total caesium ( $^{137}\text{Cs}$  and  $^{134}\text{Cs}$ ) deposition in Portugal following the Chernobyl

accident was estimated at about  $0.012 \text{ kBq m}^{-2}$  (Sagerstahl, 1991). The sediment inventory of the  $^{137}\text{Cs}$  determined in the Aveiro lagoon is lower than expected from cumulative fallout. Increase in  $^{137}\text{Cs}$  retention is confirmed by increased weathering of micaceous minerals, which restricted its mobility. The detritic material deposited at  $-30 \text{ cm}$  depth from the western part of lagoon is characterized by higher  $^{137}\text{Cs}$  values. By contrast, lower  $^{137}\text{Cs}$  values were determined at the top ( $-10 \text{ cm}$ ). The  $^{137}\text{Cs}$  appear to increase with increasing contents of clay particles. Vertical transport of radionuclides in the water column by adsorption onto sinking organic matter was described in several studies (i.e., Fowler et al., 1987). Subsequent sorption and fixation of the  $^{137}\text{Cs}$  in clays sites was realised during natural wetting and drying cycles.

Radiocaesium has also been viewed as a potential radioisotope to date very recent sedimentation rates and ages of contaminated core. Studies on the  $^{137}\text{Cs}$  dating of the tidal flood sediments (located to southwestern part of lagoon, close to Mira channel way) in the barrier–island system of Aveiro establish four hypothetical isochrones (Daza et al., 1998) corresponding to 1950 years ( $^{137}\text{Cs}=57\text{--}73 \text{ }\mu\text{Bq/g}$ ), to 1960 years ( $^{137}\text{Cs}=884 \text{ }\mu\text{Bq/g}$ ), to 1970 years ( $^{137}\text{Cs}=280 \text{ }\mu\text{Bq/g}$ ) and to 1980–1996 years ( $^{137}\text{Cs}=365 \text{ }\mu\text{Bq/g}$ ). Based on these results the authors estimated the sedimentation accumulation rates on the intertidal flat at about  $0.6 \text{ cm year}^{-1}$ . Preliminary data obtained in this study show that the  $^{137}\text{Cs}$  tracer indicates a strong relationship with clay-sized particles. High concentrations of radionuclide levels should always be associated with mica-rich sediments than non-clay sediments. Hence, the  $^{137}\text{Cs}$  is not a very suitable isotope for quantification of sedimentation accumulation rates in lagoonal environments.

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