

Freshwater marshes as dissolved silica recyclers in an estuarine environment (Schelde estuary, Belgium)

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Abstract

Compared to knowledge about N and P processing in the aquatic continuum of lakes, wetlands and estuaries, knowledge concerning transport and cycling of Si is only fragmentary. Furthermore, Si research in estuaries has mainly been focused on subtidal benthic sediments and uptake and recycling by diatom communities. The biogeochemical cycling of Si in tidal wetlands, which can contain large amounts of Si, has thus far been neglected. We have conducted several whole ecosystem Si mass-balances on a freshwater marsh located in the Schelde estuary (6 tidal cycles, 2 with BSi included). Our measurements show that the freshwater marsh acts as an important source of dissolved Si to the main river (1–18% more export than import, on average 0.114 g m^{-2}). This export is compensated by import of amorphous silica into the marsh (19–55% more import than export). The marsh was shown to act as silica recycler, resupplying biologically available dissolved Si to the estuarine ecosystem. Extrapolations show that during summer and spring months, when dissolved silica is depleted due to diatom growth, almost half of the total dissolved silica load in the main river channel could result from marsh recycling.

Introduction

In recent years, the transformation, retention and transport of nutrients through the vast continuum of rivers, lakes, wetlands and estuaries to coastal waters was the subject of many large research projects including the LOI-CZ-Programme (Land-Ocean-Interactions-in-the-Coastal-Zone-Programme), a core project of the International Geosphere-Biosphere Programme (IGBP), (Kondratyev & Pozdnyakov, 1996; Billen et al., 2001; Cave et al., 2003; Humborg et al., 2003). Compared to our knowledge concerning N and P processing, transport and cycling of dissolved silica in the aquatic contin-

uum is significantly less known (Conley et al., 2000). In contrast to N and P, with large human inputs, anthropogenic input of Si to estuarine systems is negligible. The amount of dissolved silica that eventually reaches coastal waters through estuaries is, however, essential in influencing the occurrence of eutrophication problems in the coastal zone. High anthropogenic inputs of N and P can eventually induce dissolved silica limitation of diatoms and subsequent succession of a phytoplankton community dominated by diatoms to a non-diatom phytoplankton community (Schelske et al., 1983; Smayda, 1990; Lancelot, 1995; Smayda, 1997; Billen, 2001).

Silicon research in estuaries has mainly been focused on subtidal benthic sediments and uptake and recycling by diatom communities (e.g. Yamada & D'Elia, 1984; Conley & Malone, 1992; Garnier et al., 1995; Muylaert et al., 2001). Intertidal systems have often been neglected in terms of their functioning within the estuarine Si cycle. Vegetated intertidal systems, which often represent a large amount of biomass, can contain a huge amount of amorphous silica (Conley, 2002). In the Cape Fear estuary, it was shown that the amorphous silica content in the upper sediment layers (10 cm) and the aerial portions of plants was about 36% of the yearly riverine input (Norris & Hackney, 1999).

In this paper, we present the first results of an integrated and detailed study, aimed at determining the role of freshwater intertidal marshes in estuarine Si cycling. We will demonstrate how freshwater intertidal habitats can act as an important area for recycling of Si in the estuarine environment. We conducted several tidal cycle mass balances in a tidal marsh, to quantify the export and import of DSi (dissolved silica) and BSi (biogenic silica and amorphous particulate silica) to and from the main river channel. Intertidal habitats were shown to be important sinks for particulate amorphous silica (plant phytoliths, diatoms, amorphous aluminosilicates) and significant sources of DSi, thus converting large amounts of amorphous silica to biologically available DSi.

Materials and methods

Study site

The Schelde estuary (Fig.1), located in Northern Belgium (Flanders) and the southwest of the Netherlands, has a history of extensive anthropogenic pollution (Wollast, 1988; Boderie et al., 1993; Baeyens, 1998; Van Damme et al., this issue). It is known as extremely eutrophic and receives large inputs of inorganic nutrients from non-point as well as point sources (Heip, 1988). Tidal influence reaches inland up to Ghent, 155 km from the mouth of the estuary. A full gradient from salt to fresh tidal water is present along the estuary. A large freshwater tidal area characterizes the Schelde. This is approximately situated between Ghent (km 155, i.e. 155 km upstream of the estuarine mouth) and Temse (km 100). The total surface area of freshwater marshes along the Schelde is approximately 285 ha. Our mass-balance studies were conducted in a freshwater marsh near Tielrode, at the confluence of Durme and Schelde. The total area of this marsh is approximately 10 ha. The study area receives water through one main creek. Summer dikes along the river prevent water flowing in over the edges at high tide. All water thus enters the marsh through the creek. All major vegetation types, characterizing the freshwater marshes along the Schelde (i.e. pure *Phragmites australis* vegeta-

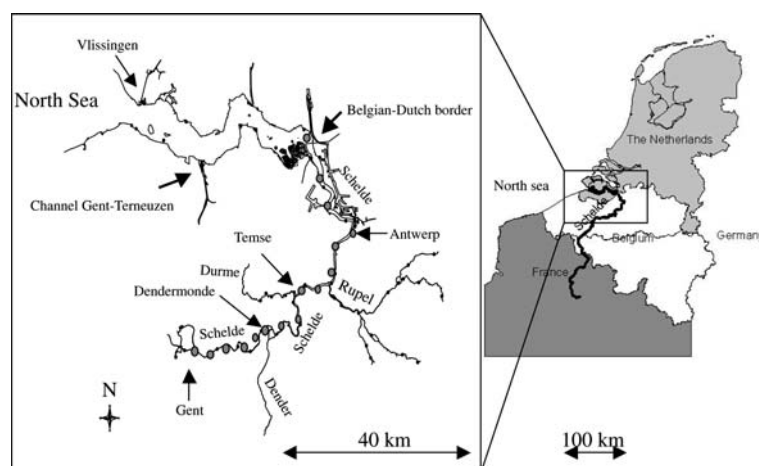


Figure 1. The Schelde estuary and its tributaries. The study area is near the confluence of the Durme and the Schelde (latitude 51°06', longitude 4°10').

tion, rough vegetation dominated by *Urtica dioica*, *Impatiens glandulifera* and *Epilobium hirsutum*, a mixed reed-rough vegetation and a *Salix* shrubs and tree vegetation), are present in the study area (unpublished data). Groundwater input from the surrounding polders to the marsh is very unlikely; the marsh surface is several meters above the surrounding polder surface.

Field measurements

In 1997–1998, four intensive study periods were conducted for the whole marsh area in the main creek (\varnothing ca. 16 m) entering the Tielrode marsh in order to compute mass-balances. In 2002, two intensive studies were conducted on an artificially isolated study area of approximately 3500 m² within the marsh, fed by one single creek (\varnothing ca. 4 m). Artificial isolation by dikes ensured water could only enter the isolated study area through this creek at high tide, and not over the marsh edges.

For both creeks, detailed flow models were developed, covering the angle of water flow to the banks and temporal, vertical and horizontal flow variations during bulk tidal phase (Struyf et al., in prep, Van Damme et al., in prep.). Water velocity was continuously measured with OTT-mills and a Valeport Model 801 electromagnetic flow meter. Vertical (bottom and surface OTT-mill) and lateral profiles (electromagnetic flow meter, 10 lateral points) of water velocity were continuously carried out. This allowed us to make an accurate water balance, an essential condition to construct detailed mass-balances. Detailed error calculation on water-balances indicated that relative error on both inflowing and outflowing water was about 10% of the water volume exchanged during flood and ebb respectively. Discharged volumes were calculated by multiplying flow velocity and cross surface area (subdivided into more than 40 lateral subsections) every minute during the bulk tidal phase and every hour during the seepage water phase. Bulk tidal phase is the period of approximately 3 h (on average 75 min inflow, 105 min outflow) during which large amounts of water flow in and out the marsh through the creek (around high water in the main river). Seepage water is exported out of the marsh between two bulk tidal phases, when the tide in the main river is

approaching low tide or rising to the threshold water level where water starts flowing into the marsh (=bulk tide). The seepage water is water leaving the sediments and includes no or very little surface drainage.

In 1997–1998, DSi samples were taken every half hour. In 2002, BSi was added to the variables analyzed. DSi and BSi samples were taken every 15 min during the bulk tidal phase, and every hour in the seepage water. All samples were surface samples, taken in the middle of the creek.

Analysis

To analyse for BSi in 2002, three 30 ml samples were filtered from a well-mixed total sample of 200 ml onto a 0.45 μ -polycarbonate filter. BSi was extracted from the filters in a 0.1 M Na₂CO₃ solution at 80 °C. Subsamples were taken at 80, 120 and 160 min. Blank extractions were conducted to correct for possible DSi released from the filters or from DSi in the chemicals. Blank concentrations were very small (<0.2 mg l⁻¹). BSi was calculated by extrapolating the linear line through the three extraction points in a time-extracted silica plot (DeMaster, 1981). DSi was analyzed spectrophotometrically on an IRIS ICP.

Results

Water balances

Water balances for all tidal cycles are shown in Table 1. Incoming and outgoing water volumes were nearly conservative during 5 out of 6 of the intensive studies. In April 1998, the exported water volume greatly exceeded the incoming volume. A possible reason is that water that entered the marsh during the previous tidal cycle had not completely flowed out of the marsh yet. This is more likely to occur at higher tides and the April 1998 studies were carried out at a higher tide than the other whole marsh samplings (Table 1). Water volumes exchanged between the main river and marsh varied according to the maximum water height. Water height during tidal cycles varied between 533 and 597 cm TAW (“Tweede Algemene Waterpassing”, the Belgian national water reference level).

Table 1. Water balances during all tidal cycles conducted, with separate indication of seepage-, bulk inflowing and bulk outflowing water. Maximal water height is indicated in cm TAW, the Belgian national tidal reference. The balance is indicated as percentual import (+) or export (–)

Date	Max. water height (cm TAW)	Bulk incoming (m ³)	Bulk outgoing (m ³)	Seepage (m ³)	Balance	
					(m ³)	(%)
<i>Whole marsh</i>						
1/07/1997	541	9834	−9601	−750	−517	−5.3
7/10/1997	562	12,649	−11,415	−1090	144	1.1
27/01/1998	533	10,221	−9843	−99	279	2.7
29/04/1998	570	26,000	−23,501	−6066	−3567	−13.7
<i>Isolated area</i>						
26/05/2002	597	1700	−1642	−61	−3	−0.2
30/05/2002	589	1376	−1305	−65	6	0.4

Concentration profiles

DSi concentrations were lowest during the bulk tidal phase, i.e. both in the main inflowing and in the main outflowing water (from 4.1 mg l^{–1} in October 1997 to 6.4 mg l^{–1} in January 1998). DSi concentrations strongly increased in the seepage water phase during 5 out of 6 mass balances (Fig. 2a,b,d–f) and reached an eventual value of around 9–10 mg l^{–1}, a two- to threefold increase. Only in January 1998 was DSi concentration increase in the seepage water minor and only rose from 6.2 to 8 mg l^{–1} (Fig. 2c).

Contrary to DSi concentration patterns, BSi concentrations were zero during the seepage water phase, and at their maximum (up to 1.2 mg l^{–1}) during the early inflowing bulk water (Fig. 2e, f). BSi concentrations fairly constantly lowered during the bulk tidal water, until reaching the zero level of the seepage water.

Si balances

Mass balances for DSi and BSi are shown in Table 2. During 5 out of 6 tidal cycles DSi was net exported from the marsh. Only in January 1998, no net exchange of DSi between the marsh and the main river was observed. All net DSi export occurred almost completely during the seepage phase, during which DSi concentrations were maximal. The percentage difference between import and export was highest in October 1997 and April 1998 (up to 17.5%). DSi exchange per

square meter was between 0.01 g in January 1997 and 0.43 g in April 1998. BSi exchange per square meter was in the same order of magnitude as DSi exchange. Contrary to DSi, BSi was net imported into the marsh during the 2002 tidal cycles. This is in accordance with the BSi concentrations dropping to zero throughout the bulk tidal phase. In between 18 and 56% of the total imported BSi during flood was deposited on the marsh surface.

Discussion

It is clear that the freshwater marsh studied here acts as an important source of DSi to the main river. Furthermore, our measurements indicate that this export is compensated by the import of amorphous silica. Thus, the marsh seems to act as Si recycler, resupplying biologically available DSi to the estuarine ecosystem, despite the high potential uptake of DSi by marsh plants and sediments.

Diatoms living on the marsh surface can take up DSi and transform it into BSi, which is finally buried in the marsh sediments. Sediments and plants have been shown to be important sinks for DSi in an estuarine marsh (Norris & Hackney, 1999; Hackney et al., 2000). After the marsh plants take up DSi, it is deposited in the plant tissue as solid amorphous silica in structures of various shape and ornamentation, known as opal phytoliths (Kaufman et al., 1981). Wetland graminace

(e.g. *Phragmites australis*), heavily abundant in the marsh and along the Schelde estuary (up to 14 ton ha⁻¹, worldwide up to 26 ton dry biomass ha⁻¹, Meyerson et al., 2000), can contain Si in concentrations up to 5–15% of total dry weight

(Conley, 2002, Struyf, unpublished data). DSi taken up by vegetation must be dissolved to become available again to the estuarine ecosystem. Plant phytoliths are resistant to decomposition and have been used as indicators for reconstructing

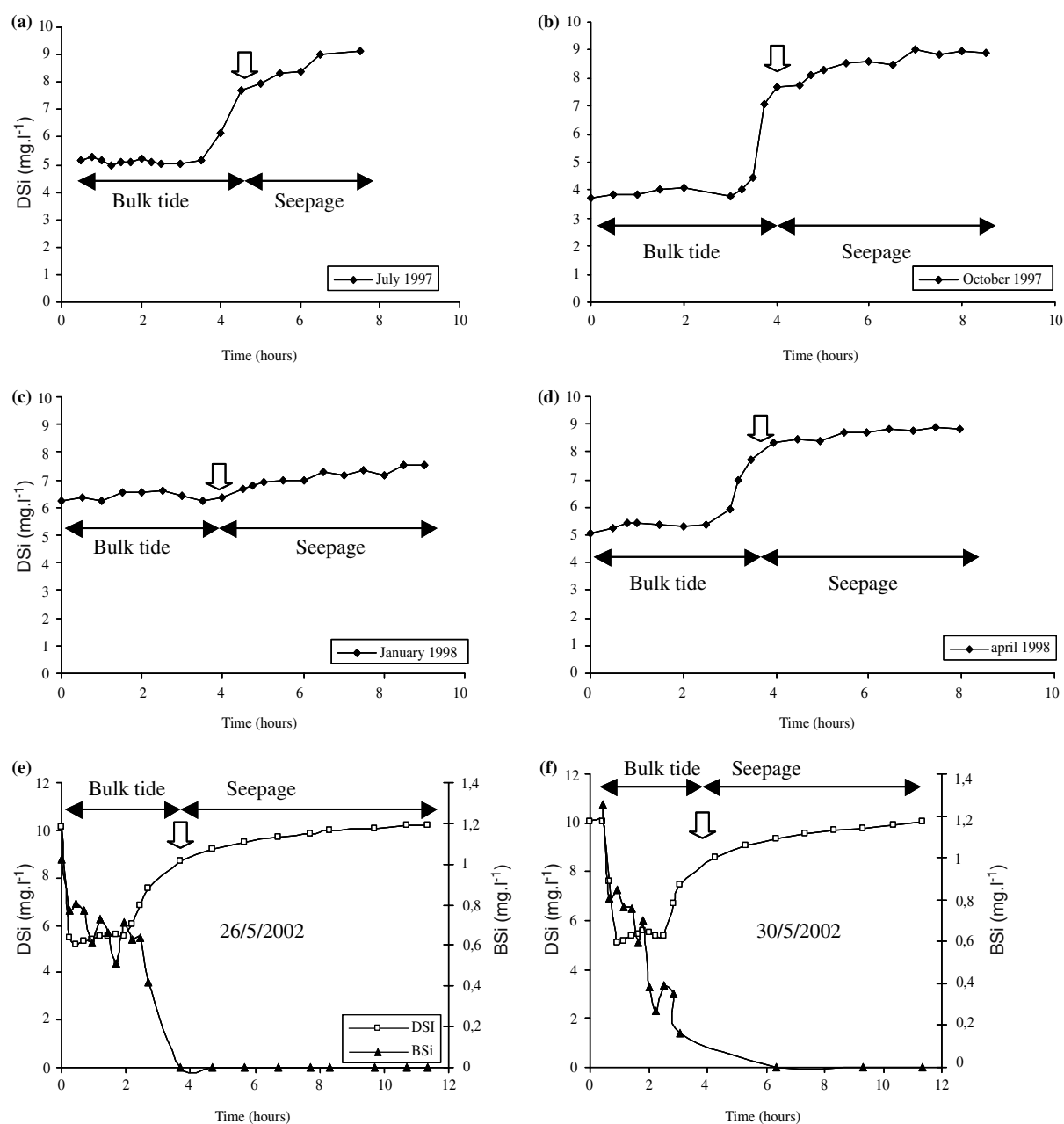


Figure 2. Concentration profiles of DSi (a-f) and BSi (only in 2002, e-f) during all tidal cycle measurements conducted. Bulk tide and seepage water are indicated with arrows. The block arrow indicates the beginning of seepage water. DSi = dissolved silica, BSi = biogenic silica.

Table 2. DSi and BSi mass-balances during all tidal cycles conducted, with separate indication of seepage-, bulk inflowing and outflowing water (both absolute flux and g m^{-3}). DSi mass-balances are shown above, BSi mass-balances are shown underneath. The balance is indicated as percentual import (+) or export (-), for both the observed mass-balance and a conservative mass balance. Net whole balance exchange per square meter is indicated. The conservative mass balance is the mass balance corrected for import or export of water

Date	Bulk incoming		Bulk outgoing		Seepage water		Balance		Balance import/export	
	(g)	(g m^{-3})	(g)	(g m^{-3})	(g)	(g m^{-3})	(g)	(g m^{-2})	(%)	Conservative (%)
DSi-balance										
<i>Whole marsh</i>										
1/07/1997	50400	5.1	-49467	-5.2	-6533	-8.7	-5600	-0.06	-11.1	-5.9
7/10/1997	51800	4.1	-50867	-4.5	-9053	-8.3	-8120	-0.08	-15.7	-16.8
27/01/1998	65333	6.4	-63467	-6.4	-700	-7.1	1166	0.01	1.8	-0.9
29/04/1998	136267	5.2	-126933	-5.4	-51940	-8.6	-42606	-0.43	-31.3	-17.5
<i>Isolated area</i>										
26/05/2002	9422	5.5	-9444	-5.8	-568	-9.3	-590	-0.17	-6.3	-6.1
30/05/2002	7641	5.6	-7372	-5.6	-560	-8.6	-291	-0.08	-3.8	-4.2
BSi-balance										
<i>Isolated area</i>										
26/05/2002	1261	0.7	-1023	-0.6	0	0	238	0.07	18.9	19.1
30/05/2002	1066	0.8	-468	-0.4	0	0	598	0.17	56.1	55.7

past environments (Piperno, 1988). Twiss (1983) reported that some phytoliths of plants do not decompose in the soil after the plants decay. More labile components of the plant tissue such as organic carbon and nitrogen leach from the plant during decomposition leading to higher relative Si contents in the dead plants (Gallagher et al., 1976, Eleuterius & Lanning, 1987). Recent studies have shown that Si released from weathering of plant phytoliths buried in the soil was twice that of Si released from lithogenic silicate mineral weathering (Alexandre et al., 1997), considered inert at biological timescales. It was shown from our dataset that despite the high potential of freshwater marshes with high plant biomass to act as a DSi sink, DSi was exported from the marsh site to the main river channel in all but one of the six mass balance studies carried out. The DSi export was due to the doubling or tripling of DSi concentrations in the seepage water. The seepage water has been in intimate contact with the surface layers of the marsh sediment. Particularly in summer and spring, when DSi concentrations in the main river were depleted due to diatom growth, the sediments could act as a source of DSi for the tidal river water entering the marsh, due to the steeper gradient in DSi concentration between the marsh pore water, which was enriched in DSi concentration and the DSi depleted flood water. Regeneration of DSi from recently deposited amorphous silica in bottom sediments is known to play an important role in marine and estuarine systems (Long Island Sound, Chesapeake Bay, Cape Hatteras) (Aller & Benninger, 1981; D'Elia et al., 1983, Wollast, 1988, Willey & Spivack, 1997) and, although less studied, was also observed in freshwater sediments (House et al., 2000). The pore water comes into contact with BSi (dead diatoms, phytoliths, amorphous aluminosilicates) in the sediments in between two tidal flooding events. Dissolution of DSi from the marsh soil sediments could furthermore occur directly into the floodwater.

BSi was imported into the marsh site over all tidal cycles, mainly due to the absence of suspended matter in the seepage water phase. Diatoms are imported into the marsh in summer and spring and deposited in the marsh during the flood tide. In addition, import of plant phytoliths from the main river, originating from decaying plant

material in the river basin, could be a source of amorphous silica. The BSi imported into the marsh, contributes to the potential of the marsh surface sediments to enrich seepage water with DSi.

We extrapolated the exported and imported amounts of Si as observed at our study site to the entire area of freshwater marshes along the Schelde. This is reasonable because the study site was chosen as a good representation of freshwater marshes along the river. We used the data from the isolated area to perform our extrapolation for both BSi and DSi. The average export of DSi from the isolated marsh was around 400 mg over one tidal cycle. This gives an exchange of 0.114 g m^{-2} . The exchange per square meter was of the same order of magnitude over the tidal cycles performed at the main creek, although much higher in April 1998 (0.43 g m^{-2}). The total area of freshwater marshes along the Schelde is about $2,850,000 \text{ m}^2$. Over one tidal cycle, this area would export 325 kg. If we would assume the export of silica over $\frac{1}{2}$ tidal cycles on a yearly basis (300), which is a fair assumption considering the observations on the main creek (export in spring, summer and autumn), this would give a total yearly export of 100 tons of DSi. A similar calculation for BSi shows that this export of DSi is accounted for by a similar import of BSi. Although these exports are low (1–2%) compared to the total yearly DSi discharges in the main river (6000 tons in 1997), the export could still provide a very important source of DSi, especially in spring and summer, when DSi concentrations in the main river are lowest due to DSi uptake by diatoms and DSi export from the marsh was highest (e.g. May 2002: export of DSi estimated at 10–20 tons, while DSi-discharge in the river in summer and spring months can drop below $50 \text{ tons month}^{-1}$). In more natural river-marsh systems, where tidal areas cover larger areas than those in the heavily modified Schelde, the recycling function of marsh ecosystems could have an even bigger influence.

Although these extrapolations are rough (no evaporation included), they do show that freshwater marshes (and flooded areas in general) along estuaries could play an important role in resupplying DSi to the water column, especially during the diatom growing season. To be able to understand the role of freshwater marshes, and marshes

in general, in the estuarine Si cycle, it will be necessary to perform additional tidal cycle mass balances of DSi and BSi in different seasons in estuarine regions around the globe. Furthermore, it will be necessary to quantify different Si sinks and sources in the marshes (vegetation, sediment, pore water) along these estuaries and to quantify the fluxes between these compartments. This should allow us to gain an understanding of the important role these flooded areas play in the estuarine biogeochemical Si cycle, a role that has not received much scientific attention up to now (Hackney et al., 2000). This understanding is of major scientific importance, as currently it is accepted by most estuarine scientists that microalgae, for which DSi is an essential nutrient, are the most important energetic source for estuarine food chains (Peterson & Howarth, 1987, Sullivan & Moncreiff, 1990).

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