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# Control mechanisms on the reactive silicate fluxes by using on board resuspension experiments in the eutrophicated coastal environment

by

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## Abstract

This study aims to differentiate bio-mediated and biogenic $CO_3^{-2}$ precipitation or terrestrial $CO_3^{-2}$ input using onboard incubation techniques, to investigate the effects of resuspension in the coastal environment and to increase our understanding of predicted relationships between silicate releases and other biogeochemical variables in resuspension events. Relationships between dark silicate flux and BSi, $CO_3^{-2}$, OrgC, Mn (manganese) according to the seasons were examined. The silica flux is controlled by the $CaCO_3$ coating on the diatom skeletons due to the fact that diatom skeletons act as crystallization nuclei in the calcite precipitation that is biologically affected. The reduction in flux with BSi may be due to the reduction in the surface areas of larger diatom species. The negative linear relationships observed between silica fluxes and $CO_3^{-2}$ is indicative of RSi fluxes constrained by bio-mediated carbonate increase. Linear relationships which are the same in their slopes but differ in their intercepts, reveal the effect of the change in diatom size on silica flux. Smaller diatoms have more surface area per unit volume, meaning an increased silica flux. On the other hand, seeing different $CO_3^{-2}$ values at stations with the same orgC value have increased the confidence interval (CI) 95% in the linear relationship. The presence of different silica flux values in stations with the same carbonate value may be explained both by different orgC values and by diatoms containing different group sizes. The silica flux is controlled by the $CaCO_3$ coating on the diatom skeletons due to the fact that diatom skeletons act as crystallization nuclei in the calcite precipitation that is biologically affected. The main mechanism controlling the reactive silica flux is carbonate precipitation. The observation of different silica flux values in stations with the same carbonate values can also be explained by OrgC.

**Key words:** Resuspension; Reactive silica flux; Carbonate precipitation; Sediment; Biogenic silica; Organic carbon

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## 1. Introduction

Silica, a key nutrient in marine environments, is uptaken mainly by diatoms. Other taxa (silicoflagellates, radiolaria, etc.) cannot achieve high numbers in this environment. Diatoms take dissolved silica and transform it into solid phase skeletons and play a key role in the transformation of silica, as well as being closely related to biological carbon (Trequer et al., 2018). Once bloomed, diatoms are transported as export silica to sediment in a variety of ways, such as sinking and grazing (Tande and Slagstad 1985, Jacobson and Anderson 1986) and aggregation (Nelson et al. 1995, Brzezinski et al. 1997). An efficient food chain based on diatoms should give rise to a high vertical export of carbon (Svensen et al. 2001), either through aggregates or fecal pellets (Ryther and Officer 1981, Smetacek et al. 1984, Peinert et al. 1989, Passow et al. 1994). Packing the diatom skeletons in fecal pellets means their solubility decreases and they remain longer in the sediment of the bay. It thereby provides the silica needed for diatom reproduction in the water column (Fouillaron et al. 2007, Chauvaud et al. 2000).

Particulate silica rapidly dissolves in the water column in oligotrophic ocean gyres that have poor reactive silica content and reintegrates into the silica cycle (Bidle et al. 2003). In eutrophic seas the particle silica is rapidly transported to the sediment with increased productivity. Large amount of biogenic silica (BSi) accumulates in liminal zones and continental margins (DeMaster 2002). A large fraction of the BSi accumulating in the sediment dissolves in pore water and is transported in the overlying water and the water column. DSi flux from sediment in coastal regions and estuaries therefore supports diatom bloom in the water column. The DSi flux from sediment in the oceans is due to the degradation of clay minerals. Because between 90% and 99% of BSi produced in ocean surface waters dissolves without reaching the sediment-water interface. On the other hand, between 0.05% and 0.15% of BSi remains as a historical record in the sediment (Hurd 1973).

The main sources of silica dissolved in the seas are river discharge, transportion of dust from deserts by wind and dissolved silica flux from sediment. Depending on the degree of eutrophication in rivers, DSi (dissolved silica) from the river may be consumed by diatom blooms in rivers (Conley et al. 1993). It may therefore either be stored as BSi in river sediments or carried to estuaries. Physical mixing and transport processes in rivers and estuaries play an important role in BSi retention (DeMaster 1981, Trequer et al. 1995, Trequer and Dela Rocha 2013). In oligotrophic seas and oceans BSi re-dissolves into the water column, and its participation in the DSi reserve is a cyclical source (Trequer et al. 1995, Trequer and Dela Rocha 2013). In eutrophic marine environments BSi dissolution occurs in bottom waters and sediment as a result of the increase in sinking rate (Zhao et al. 2019).

One of the most important factors determining BSi dissolution is that the $CaCO_3$ crystal forms a cover on the diatom skeletons (Sturm et al. 1982). BSi plays a role as the crystallization nucleus in $CaCO_3$ precipitation. The greater the area of this covering on the diatom skeleton, the lower the dissolution of the BSi (RSi flux). Other factors limiting BSi dissolution are diatom size and BSi or biomass (Duarte et al. 1990). Agusti et al. (1989) report that smaller algae support higher maximal biomass than larger algae. The maximum diatom density that may be achieved in aquatic environments dominated by small diatoms is greater (Agusti and Kalff 1989). In such cases there will be an increase in the amount of dissolved silicate added to the water column. Duarte et al. (1990) report that observation of increased algal size as phytoplankton communities is denser and has two components: a tendency toward the replacement of small taxa by larger taxa and a tendency toward increased size of particular taxa as biomass increased. Growth rates of the diatom are controlled by nutrients and growth-limiting factors, such as self-shading of the diatom, grazing and sinking. Considering that nutrients in overlying water will not limit the growth rate of the algae, other constraining factors mentioned above are of great importance.

Resuspension is a common physical process that occurs everywhere in marine environments, both in shallow liminal areas and in the deep sea (Thomsen et al. 1994, Vangriesheim and Khripoonoff 1990, Tengberg et al. 2003). Silica flux experiments obtained before resuspension are both smaller values and higher variation than silica flux values obtained according to resuspension experiments. Onboard resuspension experiments provide a number of advantages. Firstly, more accurate results may be obtained due to higher silica flux values (Tengberg et al. 2003). The resuspension event tends to bring a bias to the silica flux values before resuspension. In addition, both bio-mediated inorganic carbonate and biogenic carbonate precipitation may be distinguished due to the dispersion of all particles of the sediment into the water in the resuspension event and each particle equilibrates with overlying water. The presence of $CO_3^{-2}$/JRSi (carbonate/reactive silicate flux) negative relationships indicates bio-mediated inorganic carbonate precipitation. Lack of a relationship between these two parameters indicates biogenic carbonate exudation or terrestrial carbonate. Biogenic carbonate deposition is independent of BSi solubility, as it precipitates as a separate solid phase from other parameters such as silt, sand, diatom skeletons, etc. On the other hand, if these components of the sediment are of the same origin, there should be a positive relationship between them. Ti is generally an element of terrestrial origin. Since Ti is a terrestrial element, revealing the source of $CO_3^{-2}$ will therefore depend on the negative/positive relationship between the two parameters. When the relationship between $Ti/CO_3^{-2}$ is negative, it therefore indicates that $CO_3^{-2}$ is of marine origin. In addition to biogeochemical parameters of sediment, data obtained from onboard-Si flux trials may provide information about the source of $CO_3^{-2}$ precipitation. If $CaCO_3$ precipitation is autogenic, $CaCO_3$ depends on two different processes: bio-mediated (diatom and cyanobacteria) primary productivity or biogenic precipitation (exudation from dinoflagellates cyctes or haptophyt scales) (Brown et al. 1991, Riding 2006, Olsen et al. 2006). Revealing the functions that control silica may also provide an important advantage in controlling the eutrophication of the water column. We learn about the stations where certain diatom size groups that provide this silica flux, $CaCO_3$ exudation groups (*S. trochoidea*) and bio-mediated groups for the inorganic precipitation of $CaCO_3$ occur. The formulation of the silicate flux and the $CO_3^{-2}$ coating that limits this flux at the cell level may therefore be demonstrated by onboard resuspension trials. By determining flux in resuspension, each sediment particle is thought to equilibrated in the water column. Permeability is therefore eliminated in resuspension studies, because in normal flux trials the permeability of the sediment participates to control the process as another variable.As a matter of fact, it was initiated by Tengberg et al. (2003) that the silica flux is variable without a resuspension event.

This study aims to distinguish bio-mediated carbonate from biogenic or terrestrial carbonate using onboard incubation techniques, to investigate the effects of resuspension in the coastal environment and to increase our understanding of predicted relationships between silicate releases and other biogeochemical variables in resuspension events. This study also provides an algorithm to distinguish the source of carbonate precipitation in liminal environments.

## 2. Materials and methods

### 2.1. Study area

The Gulf of Izmir is a large natural bay in the Mediterranean, located between latitudes 38°20′N and 38°40′N and between longitudes 26°30′E and 27°10′E. It has a semi-closed basin and extends along the west coast of Turkey into the Aegean Sea. The average depth of the Bay is 15 meters and its total area is 500 $km^2$. It has been contaminated with domestic and industrial waste for the last 30 years. The bay waters have therefore eutrophic features. The quality of the water and the sediment of the inner bay is seriously threatened by industrial waste and pollutants discharged into rivers. In terms of its hydrographic and topographic structure, the Gulf is divided into three parts: the inner, the middle and the outer bay (Güven & Akıncı 2008, Ozkan 2012). The area of our study is limited to the inner bay rather than the entire Gulf of Izmir (Ozkan et al. 2008). The city of Izmir is extending both into the inner and outer bays and is exposed to a wide variety of pollutants, such as domestic and industrial waste. The eastern and northern parts of the inner bay, which constitute the research area, form the river storage shores and the southern part the rift (Başoğlu 1975).

### 2.2. Sampling

Sediment samples were taken from 16 stations seasonally 4 times between February 2015 and November 2015. Field studies in the winter and spring periods were carried out with the PiriReis RV; during the summer period with the Dokuz Eylül1 RV and the autumn period with the Dokuz Eylül3 RV.

There is a mixture of materials, both terrestrial from the north and south at the western border of the inner bay and from different sources in the inner harbor (Ozkan et al. 2012). Sampling stations are as shown in Fig. 1.

#### 2.2.1. Benthic flux incubation trials in resuspension conditions onboard experiments

The sediment liners taken from the research vessel with core sampler were incubated for between 4 and 6 hours in an incubation tank, which was continuously added by sea water to keep the temperature constant. During incubation in dark conditions, the loose upper layers of the sediment were continuously ventilated with air hoses in order to mix with the water column. As the silica flux is independent of the oxygen concentration in the overlying water, aeration is

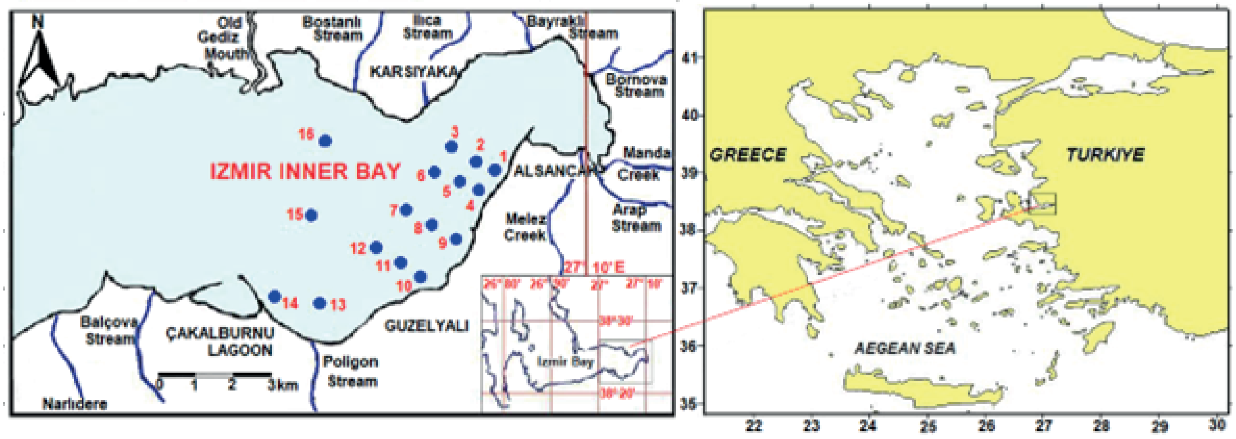


**Figure 1**

Sampling stations in the study area

performed in order to create the resuspension (Yamada & D'Elia 1984). Time was recorded at the beginning and end of the incubation experiment and samples were taken from the water in each core sample. The same process was also applied to the control cores filled with bottom water in trials conducted in dark conditions. The water depth above the sediment in the core was recorded before the experiment.

Over four seasons, net silicate fluxes containing incubation results were obtained and contributions of processes in sediment overlying water were determined. A 100 ml sample taken was filtered using GF/C filter paper. Polycarbonate filter papers were used in silicate analysis. Silicate analysis was performed according to Strickland & Parsons (1972) in water samples which were filtered and diluted with distilled water.

Flux calculations were made in accordance with the following equation:

$$\textbf{Flux} = ([\text{Nutrient}]_{test} - [\text{Nutrient}]_{control}) \times [\text{water level in core sample(m).}] \times 1000 \times 24/\Delta t$$

where Δt: incubation time in hours, h: water height in the core as meter,

$$\textbf{nutrient concentration: } \mu\text{g-at/L } (=\text{mg-at/m}^3) \times 1000$$

is the factor of conversion mg-at/$m^2$ to µg-at/$m^2$.

### 2.2.2. Sediment analysis

**Determination of biogenic silica in sediment**

According to DeMaster (1981), the timed dissolution method was used to determine the biogenic silica in sediment. Between 10 mg and 50 mg of sediment samples from each station were taken and transferred to 50 ml teflon tubes, and 10 ml of 1M NaOH was added. The mixture in the tubes was homogenized with ultrasonic homogenizer and placed in the oven. It was kept at 100°C for 24 hours. 5 ml samples were taken from the samples after 30 minutes, 1 h, 1.5 h, 3 h, 6 h, 8 h, 12 h and 24 h. The samples were placed in 50 ml polypropylene tubes and 30 ml of pure water was added. $HNO_3$ was added until pH = 6. The cooled samples were filled to 50 ml. Dissolved silicate measured with ICP-MS within 24 hours.

**Determination of carbonate in sediment**

The carbonate in the sediment was determined using the gasometric method based on the measurement of the partial pressure of the $CO_2$ gas released by the treatment of the sediment with 10% HCl (Martin, 1972). $\Delta P_{CO2}$ mmHg was determined for 1g $CaCO_3$ (0.001mol). RT/V constant is determined.

$$\Delta P_{CO2} / [RT/V] = n \text{ (mol)}. \ \%CO_3^{=} = n*60*100 / W_{sed}$$

*(R = gas constant = 62300 ml mmHg/mole.degree; T = room temperature = 273+°C; n = mole for $CO_2$; w = sediment weight)*

The distinction between bio-mediated $CO_3^{-2}$ and biogenic carbonate was determined by the presence of a negative linear relationship in the JRSi/$CO_3^{-2}$ scatter plot. Bio-mediated carbonate crystallizes directly on diatom skeletons, reducing silica solubility. The silica flux decreases with increasing carbonate precipitation. The relationship between JRSi/$CO_3^{-2}$ may not be observed in some seasons. This may be attributed to biogenic carbonate precipitation. $CaCO_3$ secreted on dinoflagellate cysts forms a separate solid phase.

Prymnesiophytes form $CaCO_3$ scales. These scales form a separate phase independent of diatom skeletons when deposited in sediments. From the negative relationship between Ti and $Ca^{+2}$ or $CO_3^{-2}$ in sediment we may also assume a marine origin of $Ca^{+2}$ or $CO_3^{-2}$ due to the terrestrial origin of titanium. This negative relationship explains the dilution of parameters with different sources.

#### The determination of organic carbon in sediment

The determination of organic carbon in sediment was carried out via the Walkley-Black Method (Gaudette et al. 1974) which was based on the back titration of dichromate, which remained in the phenylamine indicator, using $Fe^{+2}$ ammonium sulfate.

#### The analysis of metal in sediment

The analysis of metal in sediment was carried out by accredited ACME laboratories.

#### The determination of chlorophyll-*a* in sediment

The values for the chlorophyll-*a* in sediment were calculated according to Strickland & Parsons (1972). A few grams of wet sediment were placed into a 100 ml beaker and were then extracted in 50 ml of 90% acetone for 12 h at 4°C in a refrigerator before being centrifuged for 5 min to clarify to supernatant, before measuring absorbances (665, 645, 630 and 750 nm). The chlorophyll-*a* content was calculated by measuring the absorbance of the supernatant with a Hatch Lange DR4000 spectrophotometer and by weighing the dried sediment.

### 2.2.3. Statistical analysis

The whole data set was analyzed for simple linear regression Analysis was performed using STATGRAPHICS Centurion XV version 15.1.02 statistical software for Windows.

## 3. Results and discussion

### 3.1. Distribution of sediment parameters by seasons

The $CO_3^{-2}$ values of the east coast (stations 1, 2, 4, 5, 9, 11) and the south coast (station 13) are more than two times the west coast (stations 14, 15, 16) in winter (Fig. 2). A maximum $CO_3^{-2}$ value of 10% was observed at sta. 4. In the western region $CO_3^{-2}$ value decreases to < 2.5%. It is observed that in the spring stations 3, 4, 9, 10, 11, 12, 13 and 16 have relatively high $CO_3^{-2}$ concentrations as far as the north and south coasts compared to the winter period (Fig. 2).

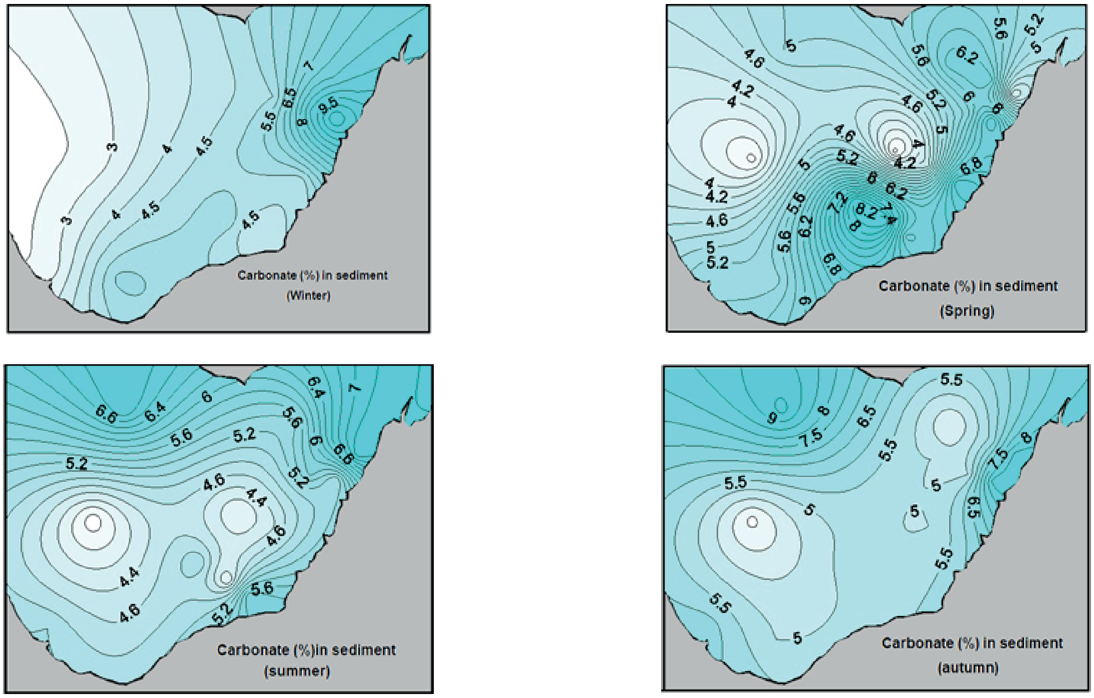


**Figure 2**

Seasonal $CO_3^{-2}$ distributions in sediment in the Gulf of İzmir Inner Bay

While there is less than 4.4% $CO_3^{-2}$ in stations 7, 11 and 15 in the interior of the study area during summer, there are higher $CO_3^{-2}$ values in other stations (coastal stations) surrounding these stations. In the stations on the north coast especially $CO_3^{-2}$ values have reached more than 6.6% (Fig. 2). The amount of $CO_3^{-2}$ increased at the stations on the northern coast in autumn compared to summer and $CO_3^{-2}$ values greater than 9% were observed. At stations 3, 6, 7, 12 and 15, the $CO_3^{-2}$ values were less than 5.5%.

As a result, while a max $CO_3^{-2}$ deposit is observed in the east in winter, this deposit expands towardsthe north and the south in spring. While $CO_3^{-2}$ deposits reaches max values on the northern shores in summer, a similar trend is observed in autumn (Fig. 2).

In winter at stations 9 and 10 in the eastern and southern parts of the study area high orgC values of > 5% (Fig. 3) were recorded. The high values of OrgC in spring were observed in the northern, southern and eastern parts of the study area. In summer in the eastern and southern regions high orgC values were unchanged, while in the northern and western regions, there was a reduction in orgC values. OrgC values of < 3.4% at stations 2 and 6 in the north of the study area are worthy of note. In autumn the orgC values in the northern reaches of the study area are < 3.2%. In the south orgC values were found at < 2.4% only in station 10. The highest orgC value was observed at station 4 to the east of the study area (5.2%) (Fig. 3). When we compare Figures 2 and 3 in stations where $CO_3^{-2}$ is increased in general, the orgC value is lower. OrgC takes control of the silicate flux in stations with the same $CO_3^{-2}$ values.

Mn concentrations in sediment are relatively high at stations 4, 8, 11, 12 and 13 during winter (Fig. 4). Mn values are lower in spring than in winter (except for station 4). The high Mn value of up to 2217 ppm only at station 4 is remarkable. Station 4 therefore seems to be the most important source of Mn for the sediments of the Gulf of İzmir Inner Bay. It is understood that mn spreads from this station into the environment. This is only valid for station 4 in spring. High Mn values at stations 6, 7, 12 parallel to the east coast in summer indicate the manganese that has been mobilized from inner part of the sediment into the water, possibly due to the reduction of sediment conditions (Burdige, 1993). Mn values are relatively low at the east and west stations in summer (Fig. 4). Mn distribution in autumn shows a similar situation to that of summer. It may be said that the majority of Mn accumulates in a line closer to the shore due to water movement.

The BSi distribution patterns are similar throughout the four seasons (Fig. 5). While BSi values were observed quantitatively at their highest values in winter, they reached the lowest values in summer. It may be said that high BSi values in winter are caused by benthic diatom blooms. Stations 13, 14, 15 and 16 in the west have the lowest BSi values during all seasons

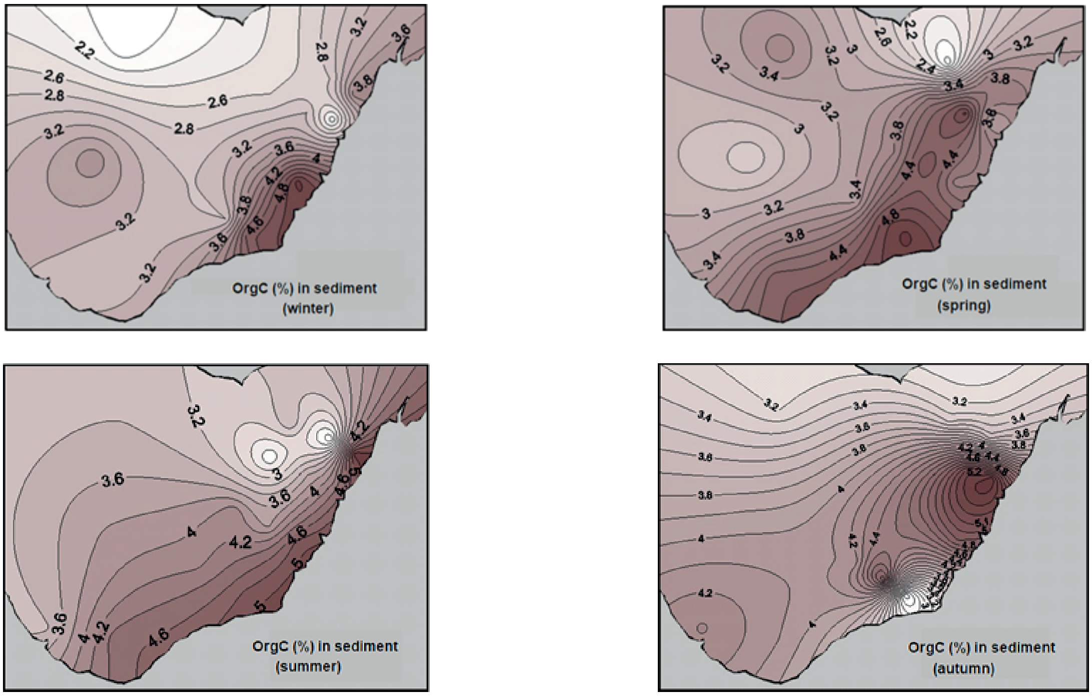


**Figure 3**

Seasonal orgC distributions in sediment in the Gulf of İzmir Inner Bay

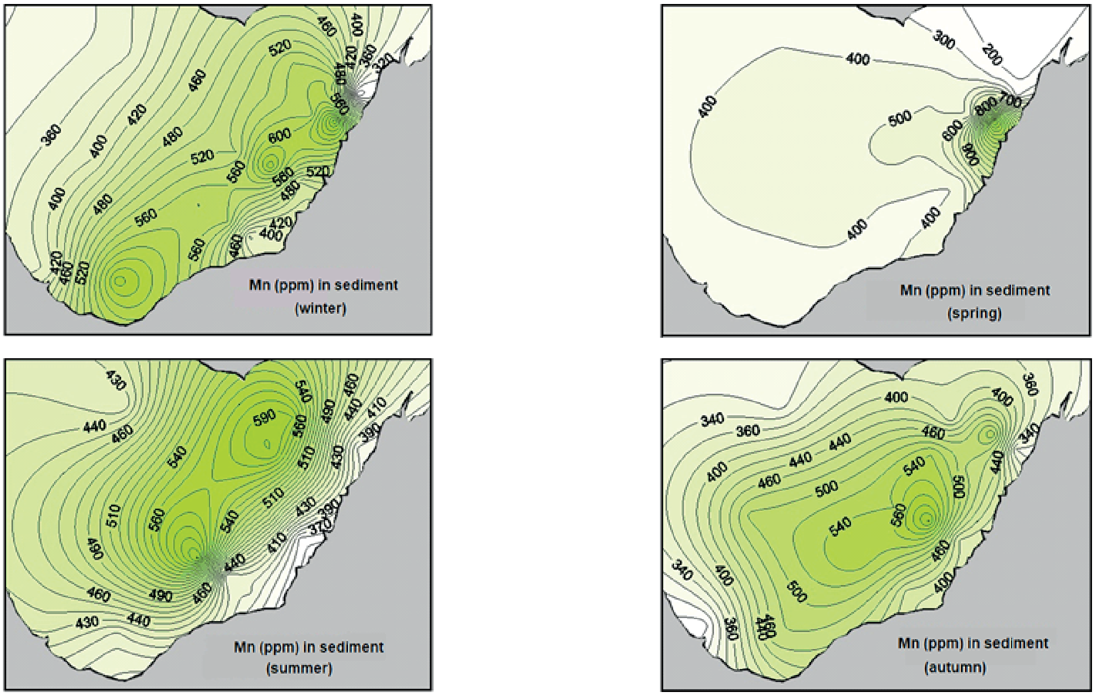


**Figure 4**

Seasonal Mn distributions in sediment in the Gulf of İzmir Inner Bay

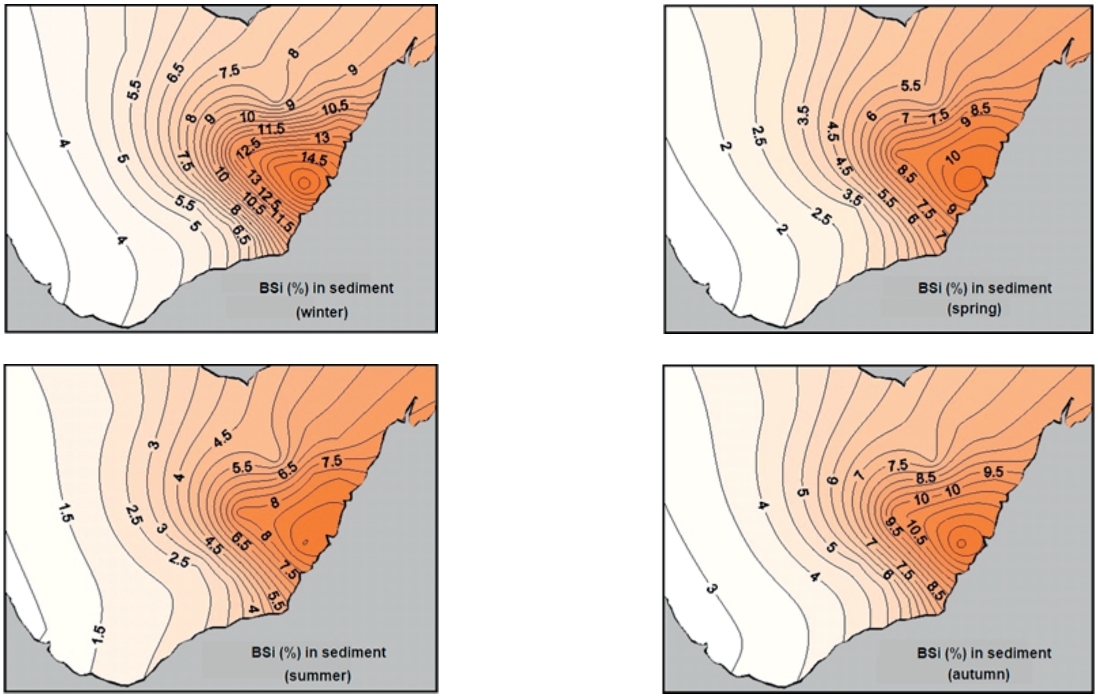


**Figure 5**

Seasonal BSi distributions in sediment in the Gulf of İzmir Inner Bay

(Fig. 5). The sediment of station 9 has the highest BSi value in all seasons, so it is a source of RSi (reactive silicate) for the water column for diatom blooms.

The distribution patterns of chl-*a* values throughout the seasons are similar in sediment. It is also closely related to BSi (Fig. 6). This situation may

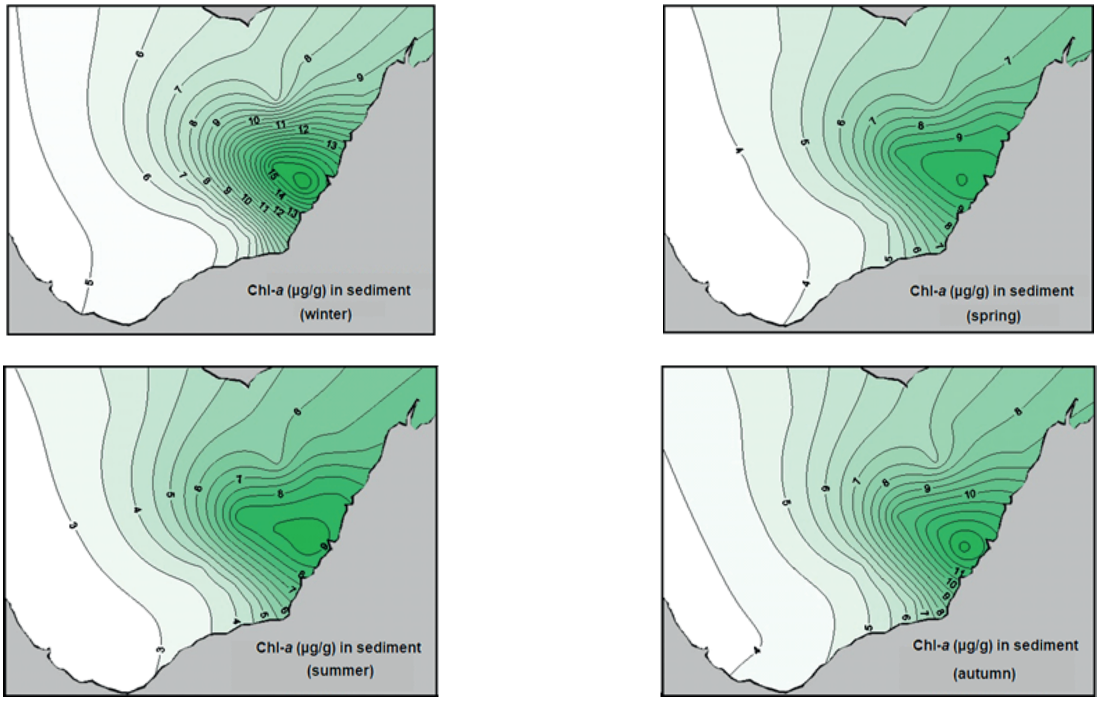


**Figure 6**

Seasonal chl-*a* distributions in sediment in the Gulf of İzmir Inner Bay

be explained in two ways: first, Chl-*a* is likely to show the content of live benthic microalgae. The second possibility is that chl-*a* may have been preserved in the sediment by carbonate precipitation (Strickland & Parsons, 1972). As a matter of fact, in determining chl-*a* in sea water, an $MgCO_3$ solution is added in order to prevent chl-*a* from turning into feopigment and filter paper is provided. With the grazing of zooplankton, chl-*a* also turns into feopigment in the acidic conditions of the digestive system. Precipitation of calcium and magnesium carbonate in the basic environment may therefore stop a decrease in the pH. Chl-*a* values, which increase in autumn, reach their maximum in winter. Spring chl-*a* values decrease and reach the lowest value in summer (Fig. 6) and nitrogen determines the growth rate of phytoplankton in the inner bay (Sunlu et al. 2005) due to low productivity in summer, so the amount of organic matter that sinks to the sediments and the decomposition of organic matter is also less. This will limit the development of benthic microalgae.

The BSi and chl-*a* distributions in the sediment are similar. Controlled entry of dissolved silicate by $CO_3^{-2}$ in the study area ensures that the silicate remains longer in the region and supports the productivity of benthic diatom. Due to the primary productivity of benthic microalgae in the bottom water/sediment interface, $CO_3^{-2}$ precipitates onto the sediment surface. The $CO_3^{-2}$ that sinks crystallizes on silica skeletons, reducing the solubility of the silica. In summer especially, when river mouths are low, the sediment supports the productivity of diatom by providing dissolved silicate to the water column. In winter high primer productivity (PP) and high chl-*a* biomass in the study area may reflect relatively weak feeding activity with benthic suspension. Hily (1991) states, however, that the feeding activity of benthic grazers from Brest Bay might explain the paradox between high PP and low chl-*a* biomass in summer. It was also concluded that dissolved silica from diatom skeletons in these pellets was slowly diffused into the water column, leaving the fecal pellets of the gastropod *Crepidula fornicata* with benthic microalgae. It was therefore emphasized that the productivity of diatom was supported in summer.

When looking at the dark net Si flux, the direction of flux is from water to sediment in stations 5 and 6 in winter and in stations 6, 8, 11, 12, 13, 14, 15 and 16 in autumn (Fig. 7). In these stations the silicate flux calculated from the control samples containing only bottom water comes mainly from the dissolution of the diatom skeletons in the bottom water. The change of net silicate flux to negative values should therefore result from the uptake of silica by benthic microalgae. In spring and summer the net dark silicate flux direction is from sediment to water. In the control trials conducted in these seasons, negative silicate flux

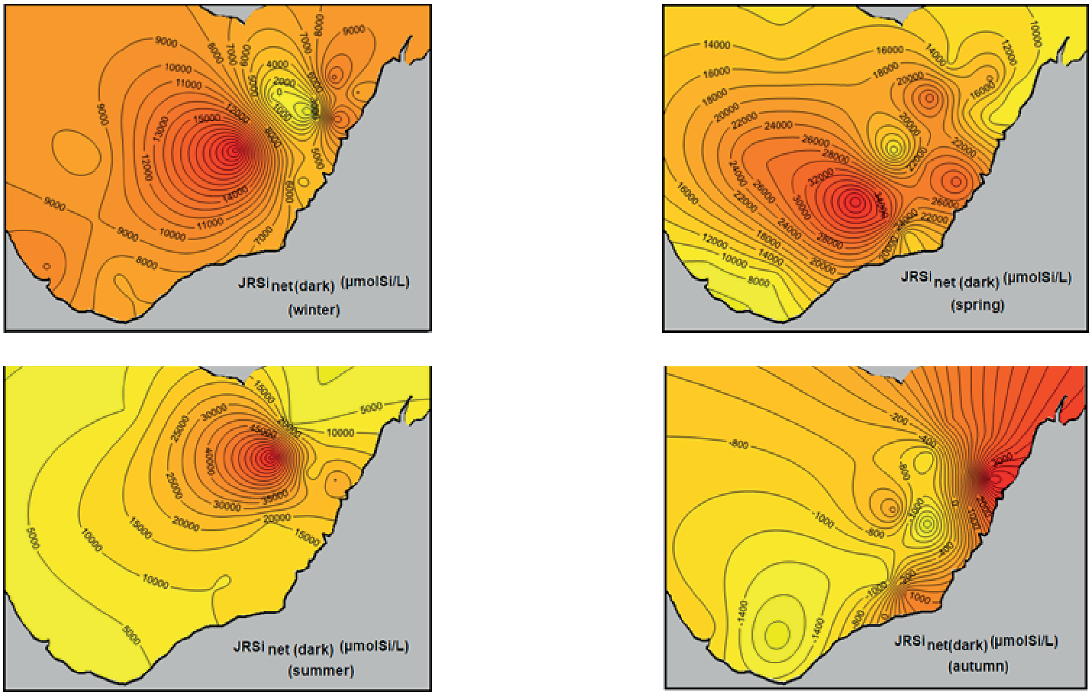


**Figure 7**

Distributions of dark-net silica fluxes in sediment in the Gulf of İzmir Inner Bay

values were determined at certain stations. This may be explained by dark silicate uptake of the diatoms in the overlying water, because dissolved silicate is not scavenged (Koschinsky et al. 2001). The dark silica fluxes determined in the resuspension event were found approximately between 4 and 10 times higher than the values obtained by Büyükışık et al. (2015) without resuspension.

### 3.2. Statistical relations of variables

A negative linear relationship was observed between the silicate concentrations in pore water and reactive silica (RSi) fluxes from the sampling conducted in January 2008 in still weather conditions (Büyükışık et al. 2015). The main factor determining the silicate flux from the sediment was the permeability of the cement material (clay, fine silt) in the sediment (Fig. 8). Increased pore water silicate concentrations indicate reduced permeability.

Where the permeability is minimum the pore water silicate value is 300 μM (Fig. 8). This 300 μM value increases with temperature. It is impossible to differentiate other variables that may control the flux under stagnant weather conditions. The variation of the data obtained from silica fluxes from sediment in stagnant weather conditions is higher than the variation of silica flux data obtained from resuspension of the sediment made in this study (Tengberg et al. 2003).

In this study resuspension of the sediment in stormy weather conditions eliminates permeability, which provides control of the silicate flux. Each sediment particle is equilibrated separately with the water column. In order to simulate stormy conditions, the intensity of the air bubbling was increased and the sediment upper layer (0-5 cm) was allowed to mix into the water column in the core liner.

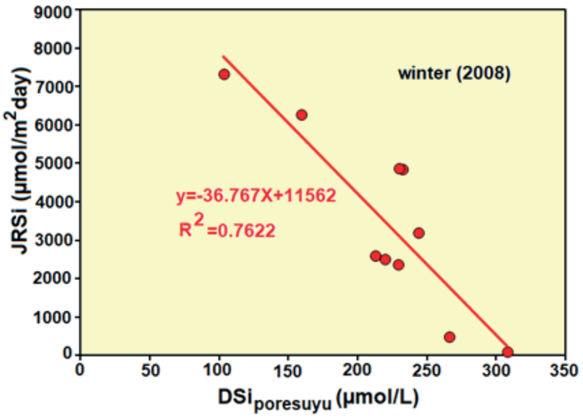


**Figure 8**

Relationships of silica flux in sediment and pore water silicate concentrations (Büyükışık et al. 2015)

An increasingly positive linear relationship between BSi and $CO_3^{-2}$ was observed in the sediment in most stations during winter. As the abundance of benthic diatoms increases, consuming $CO_2$ for photosynthesis causes carbonate precipitation (Fig. 9). At the same time, the increase in the abundance of the benthic and planktonic diatom communities increases the inorganic carbonate deposits as it makes the marine environment more alkaline. It is therefore expected that a linear relationship between these two parameters in the winter season be observed, a process we may define as *bio-mediated inorganic carbonate precipitation*. Due to the positive relationship between these two parameters, it may be assumed that the source of calcium carbonate in the sediment is marine because the biogenic silica is of marine origin. In Fig. 9, while the carbonate values at stations 7, 8 and 9 are almost the same (5%, 5.33% and 4.7% respectively), BSi values vary significantly. *Scrippsiella trochoidea*, *Emilliania huxleyii, Chrysochromulina* in the inner bay of the Gulf of Izmir was reported by Koray, (2001). *S. trochoidea* accumulates $CaCO_3$ on the cyst, while *E. Huxleyii* and *Chrysochromulina* form $CaCO_3$ on the scales on the outer surface of their cells. These carbonate structures therefore constitute different marine carbonate sources.

Carbonate values independent of biogenic silica at stations 9, 13, 14, 15 and 16 during spring may indicate a different marine source. This was clarified by the relationship between Ca-Ti below (see Fig. 11). The negative relationship observed between the two parameters at other stations (1, 2, 3, 4, 5, 6, 7, 8, 10, 11 and 12) may indicate that the biogenic silica in the sediment dilutes the carbonate. *S. trochoidea* cysts also prevent $CO_3^{-2}$ accumulation due to the productivity of diatom, as it reduces $CO_3^{-2}$ content in sea water by precipitating it as $CaCO_3$ (Janofske 2000, Shin et al. 2013, Koray et al. 1992, Jantschke et al. 2019). These processes may be referred to as *biogenic carbonate precipitation*. Relationships between biogenic silica and carbonate are extremely weak in summer and autumn, seasons that may be considered to have different dominant species from winter and spring.

Strong linear regressions between BSi-chl-*a* are noted for all four seasons. BSi explains the changes in chl-*a* in between 98% and 99% per season (Fig. 10). Increased $CaCO_3$ precipitation with an increase in biogenic silica should occur with live diatom. Dead diatom cannot produce primary productivity. Since benthic diatoms make an important contribution to primary productivity, 99% of BSi should probably be living diatom. Increased pH may also prevent the decay of chl-*a* in the diatom following carbonate precipitation. The regressions are extremely close to each other for all four seasons. The intercepts explaining the chl-*a* of dinoflagellate are between 1.1 and 2.5 (Fig. 10). Dinoflagellat pigments add a bias to the diatom/chl-*a* relationships.

The fact that Ti-Ca relations are strong-negative in all four seasons explains that terrestrial Ti is diluted by the autigenic Ca (Fig. 11). The negative relationship observed in each graph shows that Ca and Ti sources are of different origins. The fact that Ca is of marine origin explains that $CaCO_3$ precipitates in the water column or overlying water.

In winter there is a strong correlation between $CO_3^{-2}$ and Mn except at station 1. Changes in carbonate may explain changes in Mn by 79.66% (Fig. 12, Table 3). Station 4 appears as the center of carbonate precipitation and also the source of Mn in winter and spring. The strong relationship observed may be explained by the participation of Mn in the $CaCO_3$ crystal lattice. The master variable is bio-mediated carbonate, since Mn levels are between 400 ppm and 700 ppm, while carbonate levels are between 2% and 11% (10000 ppm = 1%). Manganese is only an indicator

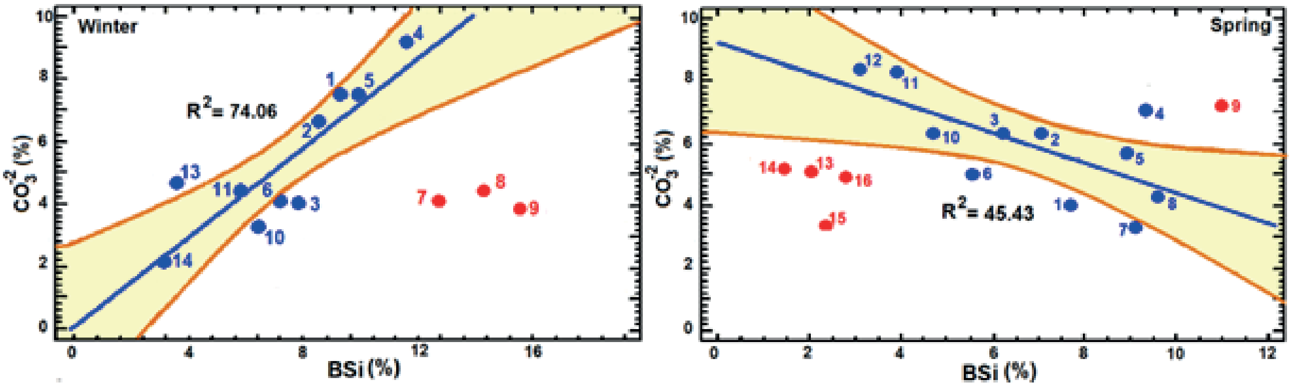


**Figure 9**

Relationships of biogenic silica and $CaCO_3^{-2}$ concentrations in sediment

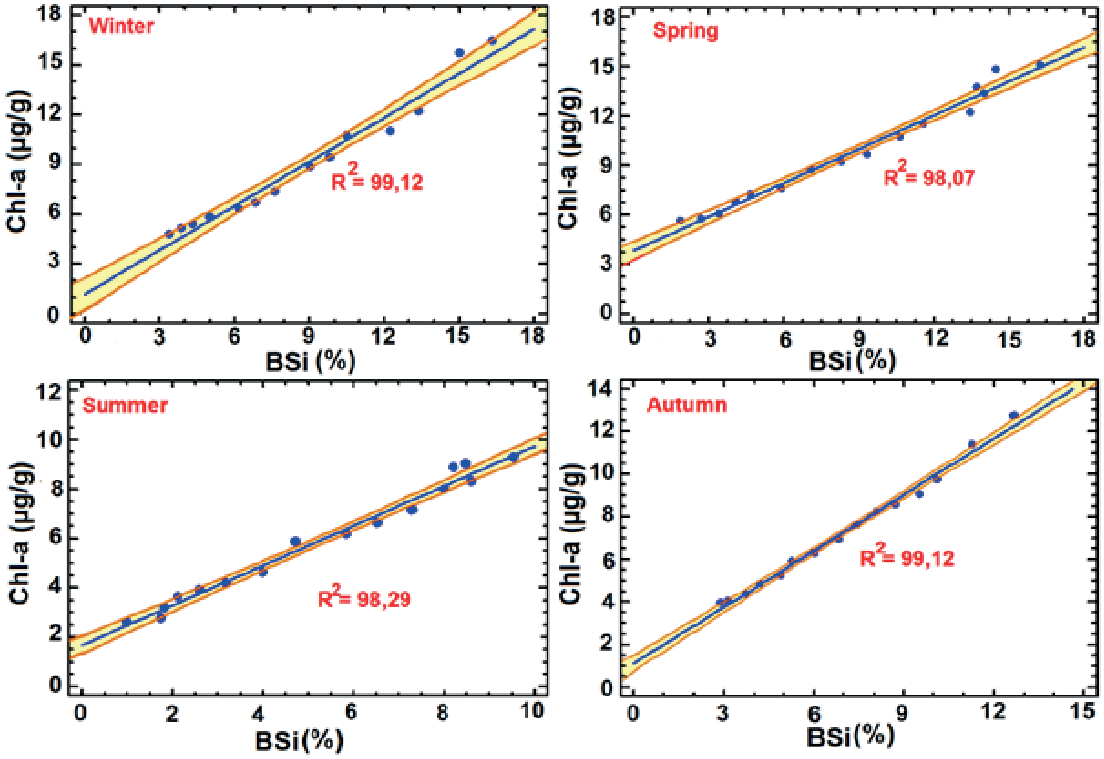


**Figure 10**

Relationships of biogenic silica against Chl-*a* concentrations in sediment

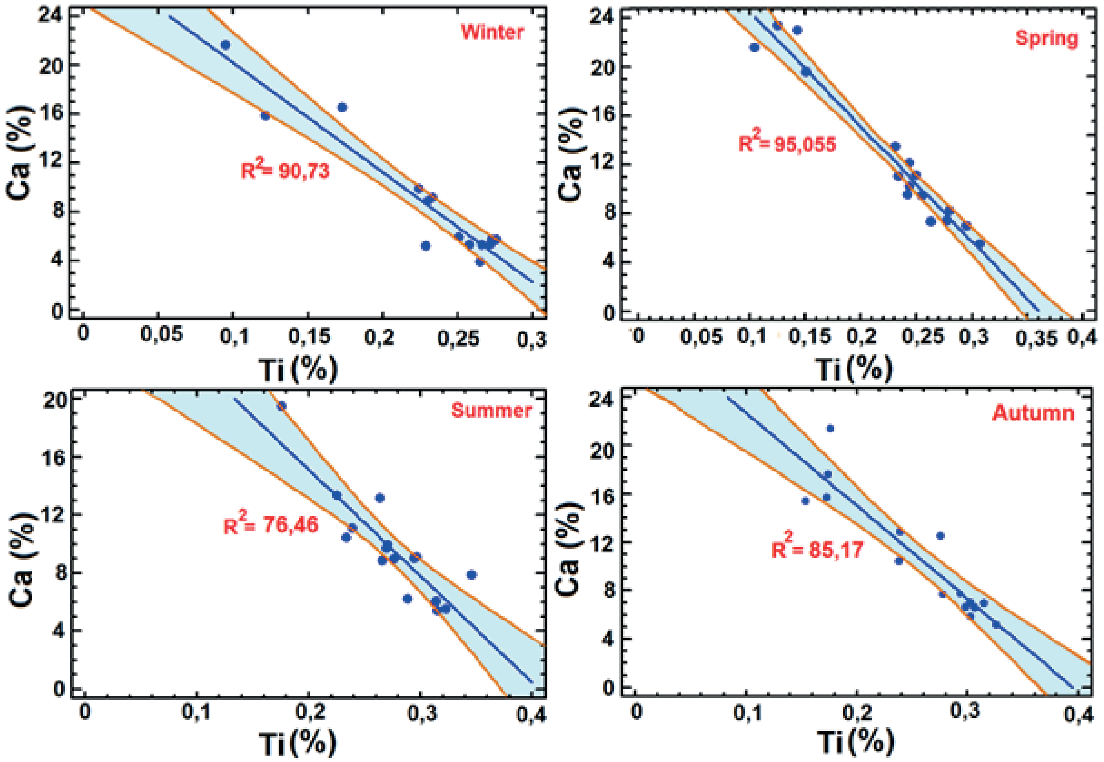


**Figure 11**

Relationships of Ca(%) and Ti(%) concentrations in sediment

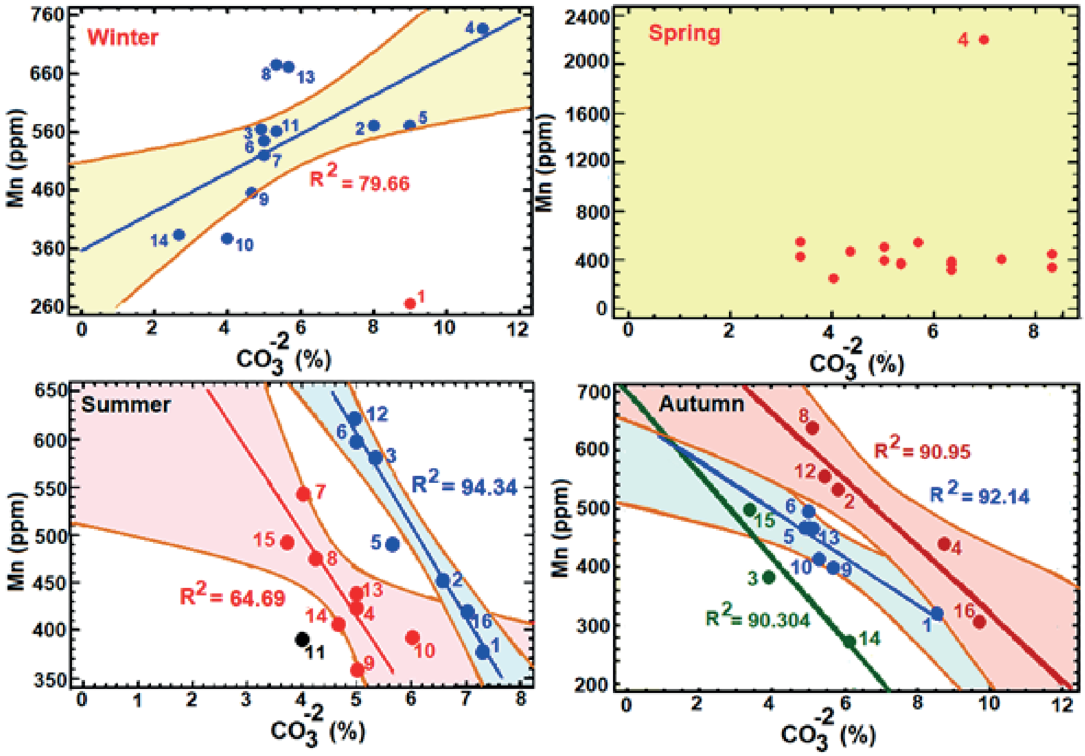


**Figure 12**

Relationships of Mn (ppm) and $CO_3^{-2}$ (%) concentrations in sediment

of carbonate precipitation. In other words, it may be thought that $CaCO_3$ and $MnCO_3$ co-precipitate in sediment.

The highest value of manganese in spring (2217 ppm) was seen at station 4 (Fig. 12). At other stations the Mn value was around 400 ppm and was almost constant. This situation may be attributed to the reduced state of the sediment with increasing productivity in the water column and the mobility of manganese towards the sediment surface. The Mn/$CO_3^{-2}$ relationship was not observed in this season. Negative relationships between Mn/$CO_3^{-2}$ in summer and autumn may be interpreted as Mn and $CO_3^{-2}$ and have different sources or are in separate solid phases (Mn: terrestrial/sediment origin, $CO_3^{-2}$: marine origin). In other words, $CO_3^{-2}$ dilutes Mn. $CO_3^{-2}$ may be said to be of biogenic origin.

The weak relationships observed between BSi and Ti during all four seasons may be the result of nutrients and other physicochemical parameters acting on diatom growth (Table 1). BSi is therefore controlled by factors such as nutrient levels, carbon dioxide and light intensity in each station. For this reason, Ti and BSi are independent of each other in all four seasons, especially in winter and autumn.

The relationship Ti/$CO_3^{-2}$ is negative in all seasons except spring. In these three seasons the source of $CO_3^{-2}$ should therefore be different from the source of Titanium (terrestrial source). We may therefore say that most $CO_3^{-2}$ is in the form of $CaCO_3$ and is of marine origin. As a matter of fact, Table 2 shows us that $Ca^{+2}$ is of marine origin. In spring the relationship Ti/$CO_3^{-2}$ is not observed. It is likely that $CO_3^{-2}$ is secreted from dinoflagellate cysts or by haptophyte members.

Relationships between dark silicate flux and BSi, $CO_3^{-2}$, OrgC, Mn were examined according to seasons. The reason silicate flux experiments are not emphasized in the light is the simplification of the processes (photodegradation, photosynthesis, etc.) affecting the sediment.

The correlation between the RSi flux and both BSi and $CO_3^{-2}$ in a dark environment is negative at all stations (Figs 13a and 13b) with the exception of station 6 (Fig. 13b) in winter. It may be either a feedback mechanism or an indirect mechanism that biogenic silica controlled silica flux. The decrease in flux with BSi, which increases as a result of the proliferation of larger benthic diatom species, may be due to the decrease in the surface areas of diatom species per cell volume. As a feedback mechanism, with increasing alkalinity in overlying water via primary productivity, carbonate precipitation increases except at stations 7, 8 and 9 (see Fig. 9, winter). Stations 7, 8, 9 have carbonate levels much lower than expected from

**Table 1**

Parameters (a and b), correlation coefficients (r) and $R^2$ values obtained from linear regression analysis between titanium (%) and biogenic silica (%)

| BSi = a ± b * Ti | | | | r |
|---|---|---|---|---|
| Seasons | a | b | $R^2$ | |
| Winter | - | - | - | - |
| Spring | 10.888 | -219.094 | 18.583 | 0.433 |
| Summer | 13.759 | -310.132 | 20.385 | 0.451 |
| Autumn | - | - | - | - |

**Table 2**

Parameters (a and b), correlation coefficients (r) and $R^2$ values obtained from linear regression analysis between titanium (%) and carbonate (%)

| $CO_3^{-2}$ = a ± b * Ti | | | | r |
|---|---|---|---|---|
| Seasons | a | b | $R^2$ | |
| Winter | 11.288 | -24.432 | 30.058 | 0.554 |
| Spring | - | - | - | - |
| Summer | 10.058 | -17.552 | 48.329 | 0.693 |
| Autumn | 12.048 | -24.162 | 65.813 | 0.811 |

the linear model, as a result of low levels of benthic productivity. The low carbonate levels in stations are provided by control of the organic coating as a result of increased exuding of orgC due to a reduction in other nutrients with the exception of silica. In Fig. 13b the difference in silica flux between the value modeled and the observed at station 6 may be explained by BSi levels. In Fig. 13b, three separate negatively sloped and almost parallel lines may therefore represent three distinct diatom size groups. In general, diatom size groups add bias to $CO_3^{-2}$/JSi regressions changing the intercept of the line. Nature reduces laterally dissolved silica export (loss of silica) by vertical sinking of diatom skeletons from the bay due to the sufficiently dissolved silica from point or nonpoint sources throughout the region's rainy winter. As a matter of fact, it causes a slow dissolution of the silica skeletons from the fecal pellets left by the benthic gastropods, *Crepidula fornicata*, grazing on the benthic microalgae in Brest Bay. In the dry and silicate-poor summer the silicate in the water column therefore remains in the Brest Bay (Fouillaron et al. 2007). Similarly, the existing diatoms in the water column are transported to the sediment

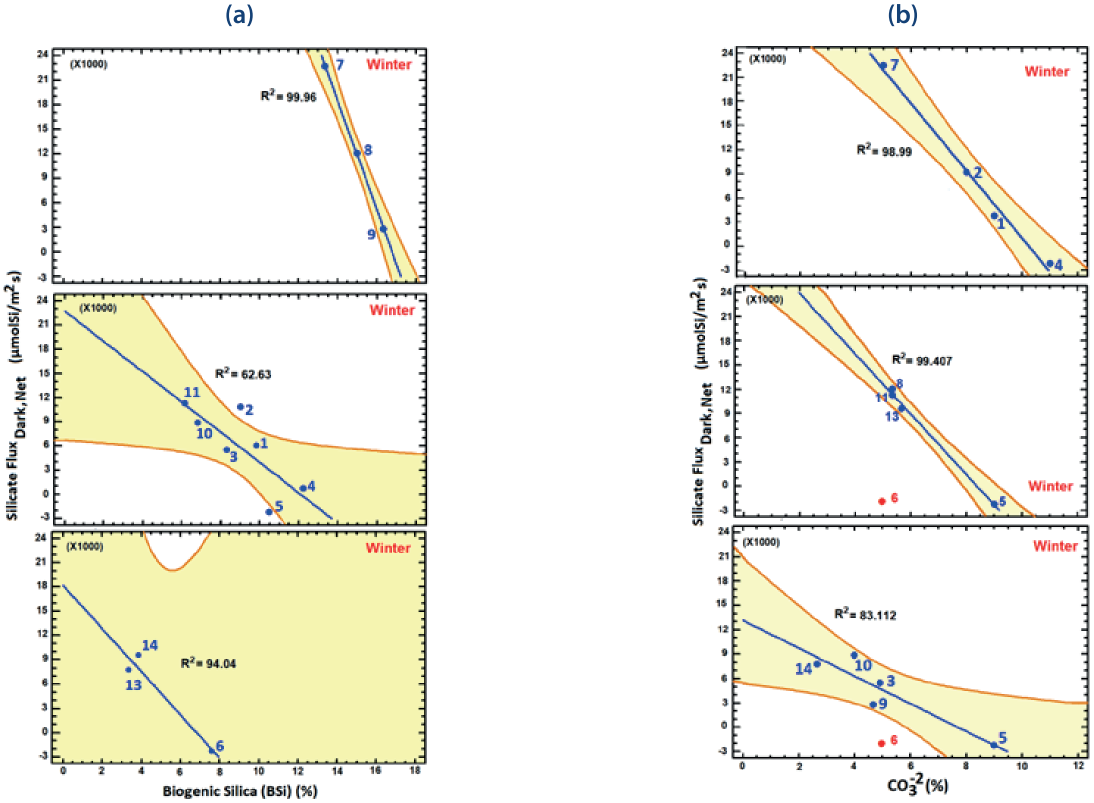


**Figure 13**

**a** - Relationships of silica flux dark net (μmol Si/m² day) and BSi (%) concentrations in sediment in winter; **b** - Relationships of silica flux dark net (μmol Si/m² day) and $CO_3^{-2}$ (%) concentrations in sediment in winter.

in the form of fecal pellets either by sinking or grazing in the inner bay. This mechanism in the water column also reduces the lateral export of the silicate.

The main mechanism that controls the RSi flux is $CO_3^{-2}$ precipitation. BSi controls the flux indirectly because it controls both diatom surface area (Fig. 13a) and carbonate (see Fig. 9) according to their biological activities.

Fig. 14a is similar to Fig. 13a. because BSi and OrgC represent biomass. Organic carbon controlling silica flux is similar to BSi and yields a negative linear relationship (Table 3). There are negative relationships between organic carbon and silica flux in winter. These negative relationships indicate that a significant part of the biogenic silica is living diatom (see Figs 10 and 14a). In Fig. 14a the organic matter may be thought to control the silica flux because the $CO_3^{-2}$ values are very close to each other at stations 7, 8, 9 and 10 (5%, 5.33%, 4.70% and 4.1% respectively). Organic carbon cannot clearly explain the silica flux at stations 1, 2, 3, 11, 13 and 14. It may be said that carbonate and BSi rather than organic carbon better explains the silica flux at these stations. The unit of Mn is ppm and the unit of $CaCO_3$ is %. There is homogeneous dispersion of $MnCO_3$ in the $CaCO_3$ crystal lattice in bio-mediated carbonate precipitation. For these reasons Mn is not a control mechanism of silica flux, but just a flux control indicator (Fig. 14b) in winter.

Fig. 15a shows three different situations between dark silica flux and BSi, two negative and one positive relationship (Table 3). A separate pattern with a positive linear relationship was distinguished with the pattern defined by two different equations with BSi and dark silica fluxes that are negatively related in spring (Fig. 15a). As may be understood from the two negative equations, as the BSi increases, so the dark silicate flux decreases as in winter. This decrease of the dark silica flux shows both the increase of the diatom size and the decrease of diatom surface area. There is a positive relationship between dark silicate flux and BSi at stations 2, 8, 9, 10, 13, 14 and 16 in the lower graph of Fig. 15a showing a decrease in diatom size with increase in BSi or biomass. Increase in total diatom surface area related to diatom size decrease means increasing silica flux. Another explanation of this positive correlation suggests the dilution of biogenic silica by biogenic carbonate of marine origin as a cause. Biogenic carbonate is unrelated to dark silica flux. Carbonate added to sediment reduces the biogenic silica content. In these stations it may

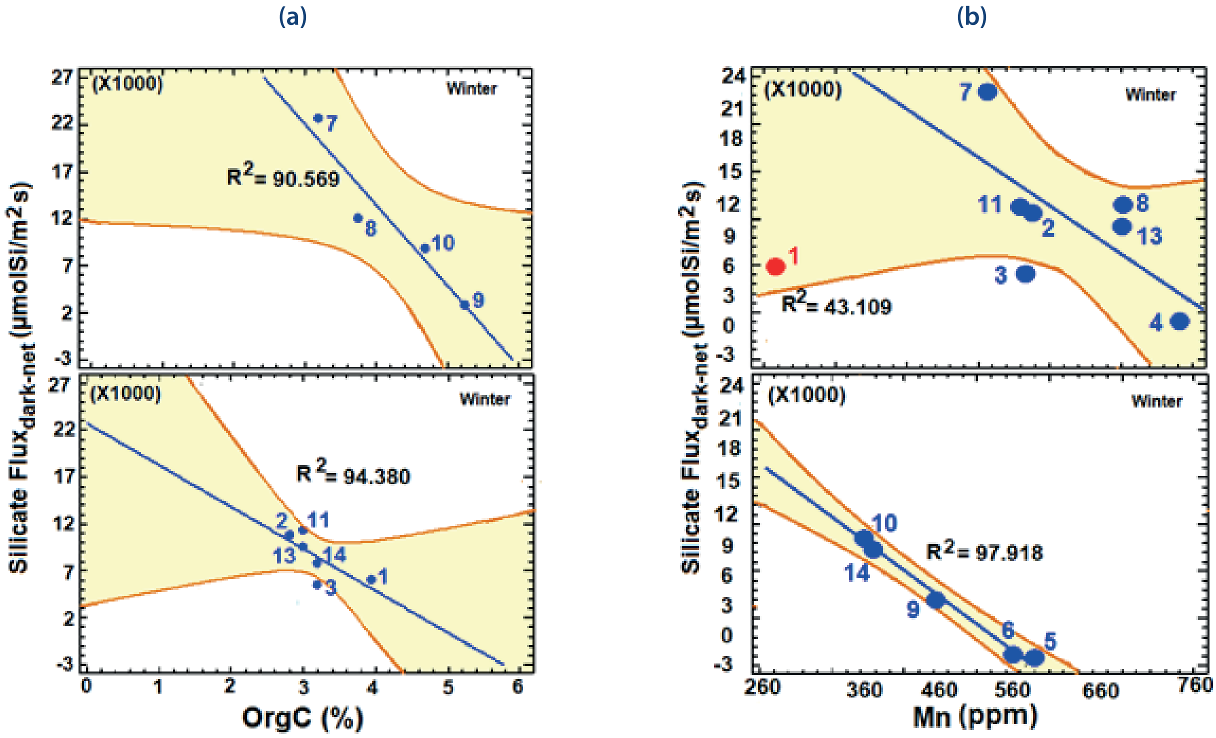
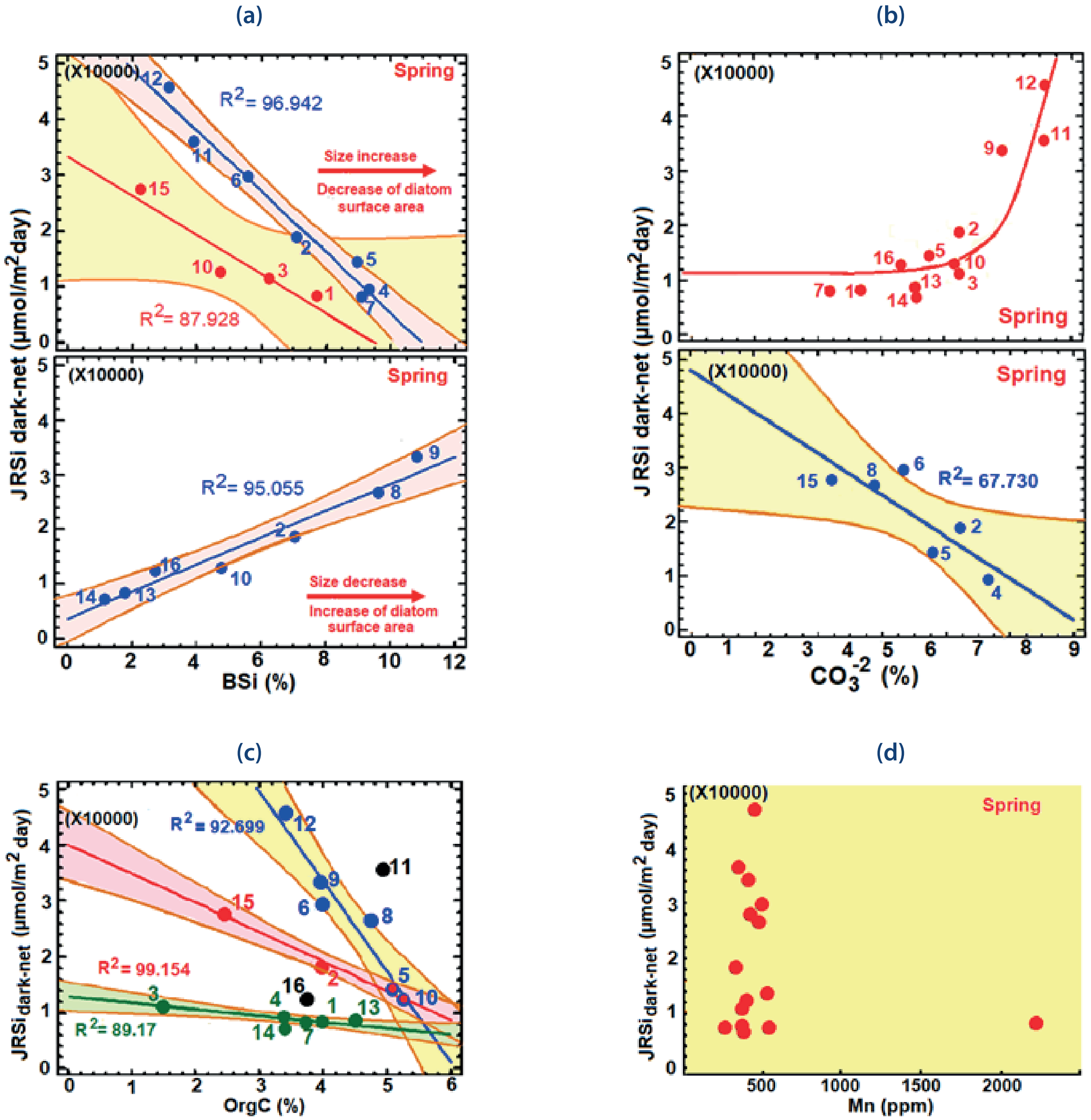

(a)
(b)

**Figure 14**

**a** - Relationships of silica flux dark net (μmol Si/m² day) and OrgC (%) concentrations in sediment in winter; **b** - Relationships of silica flux dark net (μmol Si/m² day) and Mn (ppm) concentrations in sediment in winter.



## Figure 15

**a** - Relationships of silica flux dark net (µmol Si/$m^2$ day) and BSi (%) concentrations in sediment in spring; **b** - Relationships of silica flux dark net (µmol Si/$m^2$ day) and $CO_3^{-2}$ (%) concentrations in sediment in spring; **c** - Relationships of silica flux dark net (µmol Si/$m^2$ day) and OrgC (%) concentrations in sediment in spring; **d** - Relatinships of silica flux dark net (µmol Si/$m^2$ day) and Mn (ppm) concentrations in sediment in spring.

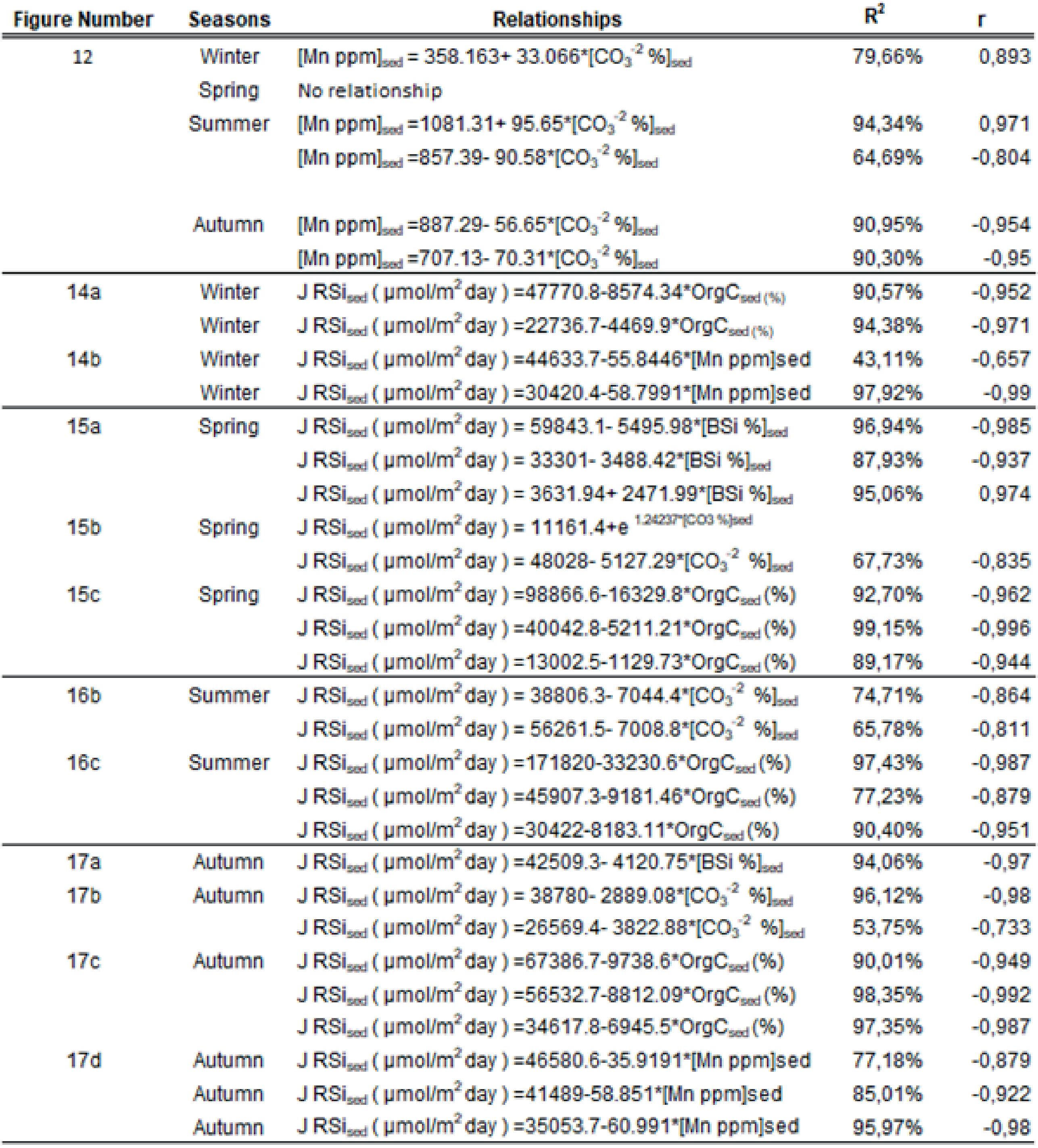
also be that *Scripsiella trchoidea* cysts, which are a dinoflagellate, are dominant or the inclusion of scales formed by haptophyte members in the sediment may provide this dilution (Koray 2001). In this case the $CaCO_3$ formed by both cysts and haptophyte scales may block the carbonate precipitation of diatom productivity by lowering the concentration of dissolved carbonate in the bottom water to under saturation.

In this study, direct microscopic cell observations were not made. The groups that produced $CaCO_3$ are not only *S. trochoidea* but also *E. huxleyii* (Koray 2001), and some flagellates (ex. genus *Chrysochromulina*) have been reported to form $CaCO_3$ scales (Raymond 1980).

There are two different there are two differences between silicate flux and carbonate in the spring (upper graph of Fig. 15b). The first are low dark silica

**Table 3**

The equations, coefficients of variation ($R^2$) and correlation coefficients (r) of the relations given in the figures 12, 14, 15, 16 and 17 (95% confidence intervals are shown on all the figures)



| Figure Number | Seasons | Relationships | $R^2$ | r |
|---|---|---|---|---|
| 12 | Winter | $[\mathrm{Mn\ ppm}]_{sed} = 358.163+ 33.066*[CO_3^{-2}\ \%]_{sed}$ | 79,66% | 0,893 |
| | Spring | No relationship | | |
| | Summer | $[\mathrm{Mn\ ppm}]_{sed} =1081.31+ 95.65*[CO_3^{-2}\ \%]_{sed}$ | 94,34% | 0,971 |
| | | $[\mathrm{Mn\ ppm}]_{sed} =857.39- 90.58*[CO_3^{-2}\ \%]_{sed}$ | 64,69% | -0,804 |
| | Autumn | $[\mathrm{Mn\ ppm}]_{sed} =887.29- 56.65*[CO_3^{-2}\ \%]_{sed}$ | 90,95% | -0,954 |
| | | $[\mathrm{Mn\ ppm}]_{sed} =707.13- 70.31*[CO_3^{-2}\ \%]_{sed}$ | 90,30% | -0,95 |
| 14a | Winter | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =47770.8-8574.34*$OrgC_{sed\ (\%)}$ | 90,57% | -0,952 |
| | Winter | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =22736.7-4469.9*$OrgC_{sed\ (\%)}$ | 94,38% | -0,971 |
| 14b | Winter | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =44633.7-55.8446*[Mn ppm]sed | 43,11% | -0,657 |
| | Winter | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =30420.4-58.7991*[Mn ppm]sed | 97,92% | -0,99 |
| 15a | Spring | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) = 59843.1- 5495.98*$[\mathrm{BSi}\ \%]_{sed}$ | 96,94% | -0,985 |
| | | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) = 33301- 3488.42*$[\mathrm{BSi}\ \%]_{sed}$ | 87,93% | -0,937 |
| | | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) = 3631.94+ 2471.99*$[\mathrm{BSi}\ \%]_{sed}$ | 95,06% | 0,974 |
| 15b | Spring | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) = 11161.4+$e^{1.24237*[CO3\ \%]sed}$ | | |
| | | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) = 48028- 5127.29*$[CO_3^{-2}\ \%]_{sed}$ | 67,73% | -0,835 |
| 15c | Spring | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =98866.6-16329.8*$OrgC_{sed}$ (%) | 92,70% | -0,962 |
| | | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =40042.8-5211.21*$OrgC_{sed}$ (%) | 99,15% | -0,996 |
| | | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =13002.5-1129.73*$OrgC_{sed}$ (%) | 89,17% | -0,944 |
| 16b | Summer | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) = 38806.3- 7044.4*$[CO_3^{-2}\ \%]_{sed}$ | 74,71% | -0,864 |
| | | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) = 56261.5- 7008.8*$[CO_3^{-2}\ \%]_{sed}$ | 65,78% | -0,811 |
| 16c | Summer | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =171820-33230.6*$OrgC_{sed}$ (%) | 97,43% | -0,987 |
| | | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =45907.3-9181.46*$OrgC_{sed}$ (%) | 77,23% | -0,879 |
| | | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =30422-8183.11*$OrgC_{sed}$ (%) | 90,40% | -0,951 |
| 17a | Autumn | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =42509.3- 4120.75*$[\mathrm{BSi}\ \%]_{sed}$ | 94,06% | -0,97 |
| 17b | Autumn | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) = 38780- 2889.08*$[CO_3^{-2}\ \%]_{sed}$ | 96,12% | -0,98 |
| | | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =26569.4- 3822.88*$[CO_3^{-2}\ \%]_{sed}$ | 53,75% | -0,733 |
| 17c | Autumn | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =67386.7-9738.6*$OrgC_{sed}$ (%) | 90,01% | -0,949 |
| | | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =56532.7-8812.09*$OrgC_{sed}$ (%) | 98,35% | -0,992 |
| | | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =34617.8-6945.5*$OrgC_{sed}$ (%) | 97,35% | -0,987 |
| 17d | Autumn | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =46580.6-35.9191*[Mn ppm]sed | 77,18% | -0,879 |
| | Autumn | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =41489-58.851*[Mn ppm]sed | 85,01% | -0,922 |
| | Autumn | $J\ RSi_{sed}$ ( µmol/$m^2$ day ) =35053.7-60.991*[Mn ppm]sed | 95,97% | -0,98 |

flux values, where the carbonate value is less than 7% and the high dark silica flux values, where the carbonate value is greater than 7%. The second is the control line showing that dark silica flux reduces carbonate values between 3% and 7% (lower graph of Fig. 15b). A single group of diatom sizes may therefore be mentioned in which silica flux is controlled by bio-mediated carbonate in spring (Fig. 15b).

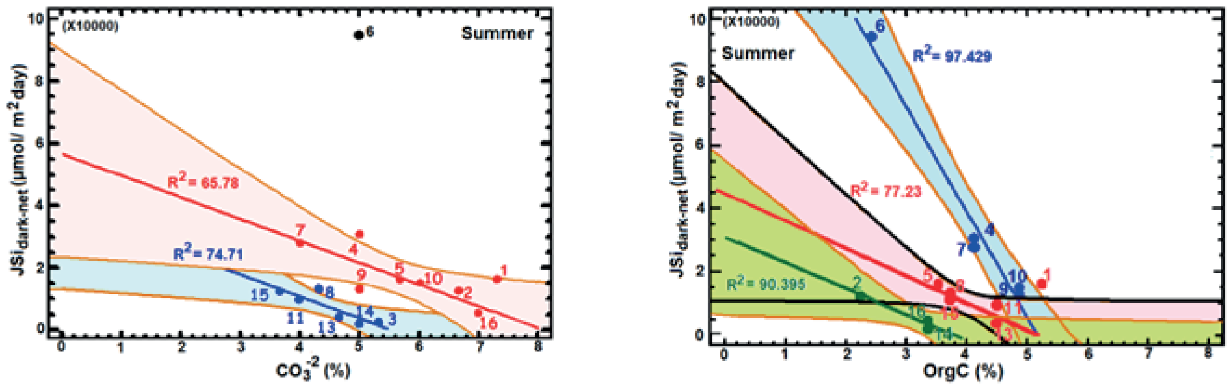
It is worthy of note that three separate lines with a negative slope are statistically strong between OrgC and silicate flux (Fig. 15c). Organic carbon, BSi and Chl-*a* values are a measure of diatom biomass in surface sediment. OrgC also has a controlling mechanism on silica flux.

Only in bio-mediated carbonate precipitation, manganese precipitates together with $CaCO_3$ and joins the $CaCO_3$ lattice (Sturm et al. 1982). No relation was therefore observed between manganese and silicate flux, since dinoflagellate cysts or Haptophyt members secreting calcium carbonate include no manganese in the lattice (Fig. 15d).

During summer there is no correlation between BSi and silica flux at all stations and low silica fluxes were observed except at station 6. The highest silica flux was observed as 94353 μmol/m$^2$day at station 6. Two separate negatively inclined linear lines were obtained between carbonate and silica fluxes at all stations except station 6 (Fig. 16a and Table 3). In the graph between silicate flux and $CO_3^{-2}$ the fact that there is almost no change in silicate flux versus a 1% change in carbonate values at stations 4 to 7 and 9 and 10 may indicate that part of $CaCO_3$ is of biogenic origin (Fig. 16a). The slopes of the two lines shown in Fig. 16a have -7006.8 and -7044.4 μmol/m$^2$ day $CO_3^{-2}$% values and are very close to each other. This may indicate that each line describes the dominant diatom size groups. The statistically strong presence of three separate negative sloped lines between the OrgC and silicate flux shows that OrgC is one of the mechanisms that control the silicate flux (Fig. 16b). Both Org C values and silica flux values at stations 4 to 7 and 9 and 10 are very close to each other. The factor controlling the silicate flux here is organic carbon rather than carbonate (Fig. 16b). The introduction of biogenic carbonate into the environment in summer means that there was no relationship between manganese and silica flux due to.

There is a negative relationship between the silicate flux and BSi in autumn at stations 2, 3, 5, 6, 10, 12, 15 and 16 (Fig. 17a, Table 3). Diatom skeletons may be said to dominate in autumn as in other seasons. Statistical analysis does not apply for stations 1 to 4 and 9 to 16, due to lack of data. Two lines with negative slopes may be distinguished between the silicate flux and $CO_3^{-2}$ (Fig. 17b). Two dominant size groups are observed. Three separate negative lines were obtained between OrgC and silicate flux (Fig. 17c). On the other hand, when looking at the relationship between OrgC and BSi, a strong positive linear relationship was observed at stations 4, 5, 6 and 16 ($R^2 = 0.963$) and stations 1, 2, 3, 8, 9 and 10 ($R^2 = 0.997$). Similarly, strong positive linear relationships ($R^2 = 0.947$ for stations 4,5,6 and 16; $R^2 = 0.992$ for stations 1, 2, 3, 8, 9 and 10) were obtained between OrgC and Chla for the same station groups. OrgC is therefore understood to explain living diatom content such as protoplasm, chla and organic template on the silica skeleton. There are two strong negative linear relationships between Mn and Silicate flux (Fig. 17d). Carbonate ($CaCO_3$ and $MnCO_3$) may be said to precipitate on diatom valves together with Mn, as in winter. Here the major variable is $CaCO_3$.

When the relations between silicate flux and BSi are examined, statistically linear negative relationships are consequently observed in winter and autumn, while one positive and two negative strong linear relationships are observed in spring. There was no relationship between these two parameters in the summer season. The growth rate of small phytoplankton is known to be higher than that of



(a)

(b)

**Figure 16**

**a** - Relationships of silica flux dark net (μmol Si/ m$^2$ day) and $CO_3^{-2}$ (%) concentrations in sediment in summer; **b** - Relationships of silica flux dark net (μmol Si/ m$^2$ day) and OrgC (%) concentrations in sediment in summer.

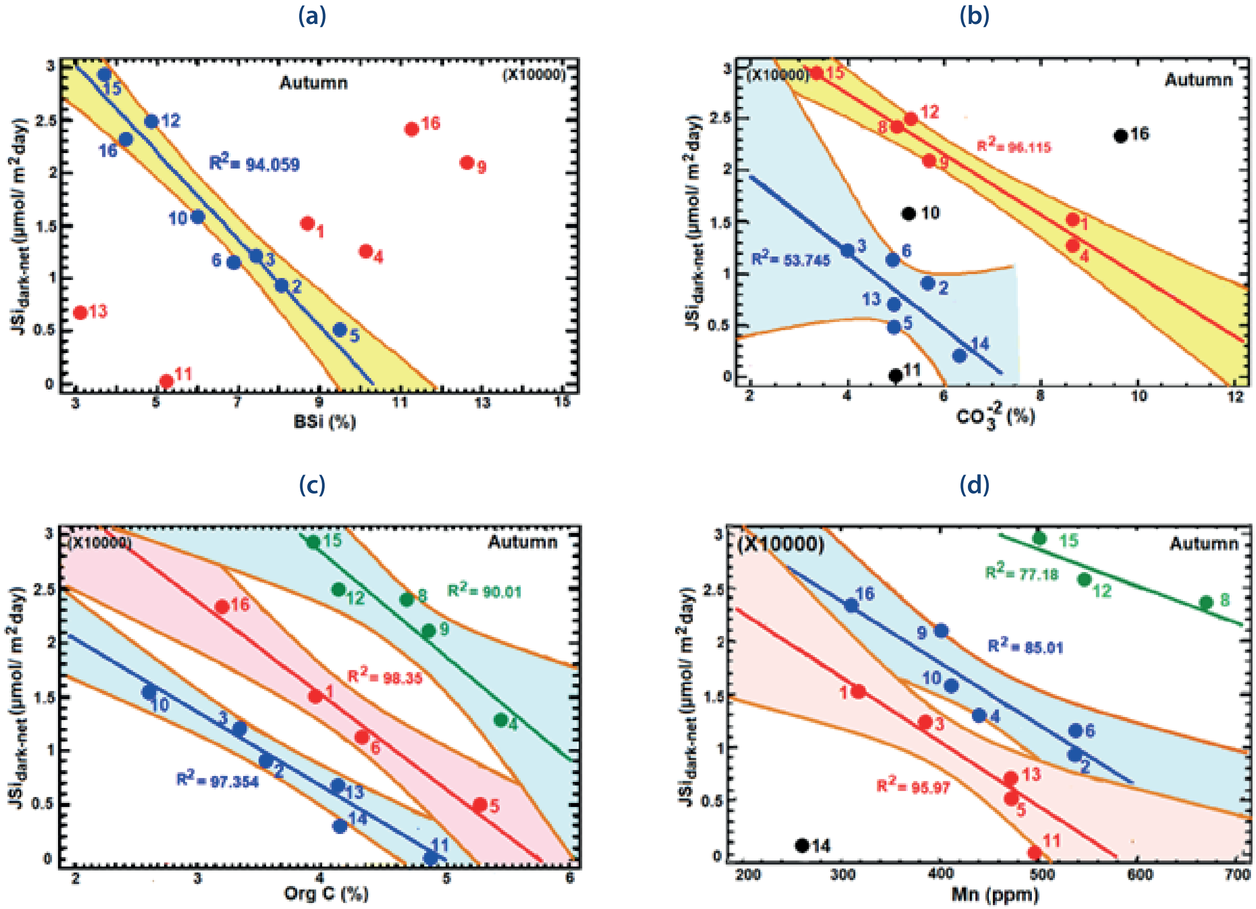


**Figure 17**

**a** - Relationships of silica flux dark net (μmol Si/$m^2$ day) and BSi (%) concentrations in sediment in autumn; **b** - Relationships of silica flux dark net (μmol Si/$m^2$ day) and $CO_3^{-2}$ (%) concentrations in sediment in autumn; **c** - Relationships of silica flux dark net (μmol Si/$m^2$ day) and OrgC (%) concentrations in sediment in autumn; **d** - Relatinships of silica flux dark net (μmol Si/$m^2$ day) and Mn (ppm) concentrations in sediment in autumn.

large phytoplankton (Stenuite et al. 2007). The smaller size individuals may be said to be more abundant as biomass, with the reduction in diatom size group (which increases the surface area of diatom per unit volume) at stations 2, 8, 9, 10, 13, 14 and 16, where a positive linear relationship is observed in spring. At stations where each negative linear relationship is observed between BSi and silicate flux in spring, there is a diatom size spectrum.

There is at least one and at most three negative linear relationships between the silicate flux and $CO_3^{-2}$ in all seasons. The stations on each line that form negative relationships may therefore be said to contain diatoms belonging to a single size group. The $CaCO_3$ secreted from both *Scripsiella trochoidea* cysts and haptophytes scales clearly emphasizes that there is no relationship between the Mn and silicate flux at stations 1, 3, 5, 7, 9, 10, 11, 12, 13 and 14, where there is no relationship between silicate flux and carbonate, especially in spring. $CaCO_3$ forms a separate phase independent of diatom and does not control silicate flux. Scripsiella trochoidea may be said to reproduce vegetatively in the water column in other seasons (Ishikawa&Taniguchi 1996, Nuzzo&Montresor 1999).

While two negative linear relationships were observed between silicate flux and OrgC in winter, three negative linear relationships were found in other seasons. The strong relationship of orgC with both BSi and chla also explains that almost the majority of benthic diatoms are alive.

No relationship was observed between the Mn/Silicate flux in spring and summer. In summer Mn is therefore of terrestrial origin due to its very strong positive relationships with Ti ($R^2$=0.992; $R^2$=0.883). In winter and autumn at least two, at most three statistically significant negative linear relationships between the Mn and Silicate flux were observed. Negative linear relationships in both seasons, while orgC forms a significant benthic microalgae protoplasm, mean it is possible to include Mn in the protoplasm with benthic microalgae uptake. Mn therefore seems to play the role of indicator in this control mechanism, while OrgC controls the silicate flux, especially at stations with very close carbonate values.

## 4. Conclusion

The results obtained from this study are given below:

- The silica flux is controlled by the $CaCO_3$ coating on the diatom skeletons due to the fact that diatom skeletons act as crystallization nuclei in the calcite precipitation that is biologically affected. On the other hand, $CaCO_3$ either comes through rivers as an allocthonous or joins the sediment as autochthonous. $CaCO_3$, which precipitates autochthonously, contains two components: the first is $CaCO_3$ secreted by haptophyte members and some dinoflagellate cysts, the second is the inorganic $CaCO_3$ formed in sea water by the productivity of benthic diatoms, cyanobacteria, marine phanerogams such as Posidonia. It is therefore possible to distinguish both biogenic and bio-mediated precipitation.

- Silica fluxes from the sediment that provide dissolved silicate to the water column may stimulate diatom growth during the dry season, causing diatoms to dominate. Diatom dominance may create a healthier marine environment. Nor may the temperature effect be ignored in this process.

- The main mechanism controlling the reactive silica flux is carbonate precipitation. The relationship between carbonate and dark silica fluxes allows the separation of diatom/diatom skeletons size groups. Each of the $CO_3^{-2}$/JSi straight lines explains the size plasticity of a particular taxon. Different taxons in terms of size only change the intercept of the lines.

- BSi controls the flux indirectly because it controls both diatom surface area and carbonate according to their biological activities. Negative relationships between BSi and dark silica flux in sampling stations also show the diatom size spectrum in sediments. In these negative relationships, the silica flux decreases due to the decreased diatom surface area in turn due to the increasing biomass and the predominance of large diatoms. Such a situation may only be possible if larger taxa are replaced by smaller taxa at other stations. The positive relationships between BSi and dark silica flux may involve two components: the first reveals the dilution of biogenic silica by biogenic carbonate in sediment. The second reveals that the diatom community in biogenic carbonate precipitation is dominated by small-sized taxons in the diatom size spectrum with the increase of biogenic silica spatially. Due to the larger surface area of smaller diatoms, more silica flux occurs. So small-sized diatoms set up a strategy to compete with other algal classes. The stations with predominantly biogenic carbonate precipitation may be distinguished from stations containing bio-mediated carbonate precipitation.

- Negative relationships between terrestrial Ti and Ca reveal that Ca is of marine origin. Due to the low values of manganese in ppm levels, it has been revealed that manganese has negative relationships with silica fluxes in autumn and winter. It is understood that manganese precipitates with calcium carbonate and is homogeneously distributed in the $CaCO_3$ lattice as ppm level. This indicates that the bio-mediated carbonate controls the silica flux. Bio-mediated carbonate is in brief a master variable.

- It gives strong and negatively sloped relationships with orgC and dark silica fluxes. The observation of different silica flux values at stations with the same carbonate values may be explained by OrgC. At the same time, the observation of the same silica flux values in stations with different carbonate values may also be explained by orgC. It may therefore be said that organic carbon also controls silica fluxes. In general, organic carbon clarifies the variation observed in the relationships between BSi/JSi and $CO_3^{-2}$/JSi.

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## Declarations

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Not applicable

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### Authors' contributions

**E. Yesim Özkan:** Conceptualization, Methodology, Investigation, administration, Supervision, Writing - Review & Editing.

**H. Baha Büyükışık:** Conceptualization, Funding acquisition, , Writing, Original Draft, Formal analysis.

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