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Atmospheric Input of Silica in Crimea and Factors Affecting it

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Abstract
Silica is one of the main nutrients (N, P, Si) and is a part of a large number of natural minerals, so it is constantly present in natural waters. It is mainly present as salts of silicic acid (silica). Atmospheric precipitation can be an important additional source of silica in the ecosystem. The purpose of this work is to estimate the silica content in the atmospheric precipitation based on long-term data, analyze the spatial and temporal variability of this content, and identify possible factors influencing the atmospheric silica input. The paper presents the results of continuous monitoring of silica input with the atmospheric precipitation in the Crimean coastal region in 2015–2021. Precipitation samples were collected in Sevastopol and Katsiveli in two types of samplers: a permanently open one to collect total (dry + wet) atmospheric precipitation and a wet-only one. It is shown that in the inter-annual dynamics of silica flux with the atmospheric precipitation in the both sampling points, the maximum input amount of this nutrient was determined in 2017–2018. The main factors influencing the amount of silica input with the atmospheric precipitation were determined. One of the main factors influencing the silica concentration in precipitation is the intensity of dust transport.

Keywords: silica, sampling, atmospheric precipitation, Crimea, dust atmospheric precipitation, long-term changes

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Атмосферное поступление силикатов в Крыму и факторы, влияющие на него

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Аннотация
Кремний относится к основным биогенным элементам (N, P, Si) и входит в состав большого числа природных минералов, вследствие чего постоянно присутствует в природных водах. В природе он в основном присутствует в виде солей кремниевой кислоты (силикатов). Атмосферные осадки могут быть важным дополнительным источником поступления силикатов в экосистему. Целью данной работы является оценка содержания силикатов в атмосферных выпадениях на основе многолетних данных, анализ пространственно-временно́й изменчивости этого содержания, а также выявление возможных факторов, влияющих на атмосферное поступление силикатов. Представлены результаты непрерывного мониторинга поступления силикатов с атмосферными осадками в районе крымского побережья в 2015–2021 гг. Пробы осадков отбирались в г. Севастополе и п. Кацивели в два типа осадкосборников – постоянно открытый для отбора суммарных (сухие + влажные) атмосферных выпадений и для сбора только влажных атмосферных осадков. Показано, что в межгодовой динамике потока силикатов с атмосферными осадками в обоих пунктах отбора проб максимальная величина поступления этого биогенного элемента была определена в 2017–2018 гг. Выявлены основные факторы, влияющие на величину поступления силикатов с атмосферными осадками. Одним из основных факторов, влияющих на величину концентрации силикатов в осадках, является интенсивность пылевого переноса.

Ключевые слова: силикаты, отбор проб, атмосферные осадки, Крым, пылевые атмосферные выпадения, многолетнее изменение

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Introduction

Silica (Si) is the second most abundant (after oxygen) chemical element in the Earth's crust, where its content is about 29 % [1]. In nature, it is mainly present in the form of silicic acid salts (silica). Silica is one of the main elements in biogeochemical cycles in the biosphere and plays an important role in the life of many living organisms.

There are natural and anthropogenic sources of Si entering the environment. During weathering, silica compounds enter the ecosystem in the form of dissolved orthosilicic acid (H_4SiO_4), which is facilitated by chemical, physical, and biological factors [2]. Dust transport can also be a natural source of atmospheric Si input [3]. For example, it was shown in [4] that the rise of a large amount of dust aerosol by strong updrafts promotes migration of microbiota and minerals, including high concentrations of silica, over tens of thousands of kilometers.

The anthropogenic sources of silica entering the atmosphere are local in nature. For example, when burning brown and black coal [5], some ash containing silica is produced, and its particles are found in large quantities in areas with developed industry. However, there are no global estimates of industrial silica emissions [6]. Another source of atmospheric silica input can be grain handling companies. When unloading and transporting grain, a significant amount of grain dust is released, containing fertilizer elements, which also include silica [1)]. For example, there is AVAL Stevedoring Company in Sevastopol, which handles grain, container, bulk, oversized and heavy cargo. The total volume of grain transshipment by this company in 2017 reached 583.7 thousand tons, which is 2.5 times more than in 2016 [2)].

Silica belongs to the main nutrients (N, P, Si) and is part of a large number of natural minerals, that is why it is constantly present in natural waters [3)]. Si is mainly involved in the formation of the exoskeleton of the simplest hydrobionts, such as diatoms and silicoflagellates, corals, sponges, and radiolarians. Silica can potentially limit production of phytoplankton and affect the production cycle of diatoms [7].

In [8], using Gelendzhik Bay as an example, the dependence of the development of the large diatom *Rhizosolenia calcaravis* on the concentration of silica was considered. It is shown that with a decrease in the content of silica in water, the intensity of its development and the amount of biomass decrease. As a result, the natural balance of Black Sea phytoplankton species can be restored (*Sceletonema costatum* and *Talassionema nitzschioides*) with a high content of mineral compounds of nitrogen and phosphorus [8].

According to the document [4)], the decrease in the abundance of silicoflagellates, which are sensitive to the content of silica, coincides with a decrease

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[1)] *Purification of Atmospheric Discharge (Pollutants) in Manufacturing of Products (Goods), as well as Performing Works and Providing Services at Large Enterprises*. Information and Technical Reference Book for Best Available Techniques: ITS 22-2016 (in Russian).

[2)] TASS, 2017. *Novorossiysk Port is the Leader of 2017 among Cargo Terminals in Russia.* [online] Available at: https://www.korabel.ru/news/comments/novorossiyskiy_port_-_lider_2017_goda_sredi_gruzovyh_terminalov_rossii.html [Accessed: 2 April 2023] (in Russian).

[3)] Arkhipova, I.V., Ktitorova, E.N., Lukyanov, Yu.S. and Alyukaeva, A.F., 2020. [*РД 52.10.744-2020. Mass Concentration of Silicium in Seawater. Methods of Measurement by Photometric Method as Blue Form of Silicomolybdic Acid*]. Moscow: Rosgidromet, 9 p. (in Russian).

[4)] Mikaelyan, A.S., 2018. [*Temporal Dynamics of Phytoplankton in the Deep Basin of the Black Sea. Extended Abstract of Doctoral Thesis*]. Moscow, 51 p. (in Russian).

in the Si concentration in the pycnocline and the cold intermediate layer (CIL). The author of this work suggests that, in contrast to diatoms, a long-term decrease in the content of silica in the pycnocline and CIL and, as a result, in the photic zone could well lead to a limitation in the growth of silicoflagellates in the deep-water basin.

There are additional sources of silica entering the ecosystem (see Regulatory Document [3]) and [9]):

– domestic sewage formed as a result of the use of synthetic detergents containing silica;

– wastewater from industrial enterprises producing silicate materials;

– underground waters and rivers, which wash the land and take away huge amounts of silica in the form of suspensions of clay particles, fragments of aluminosilicates and solutions;

– mainland runoff.

The contribution of large rivers to the balance of nutrients flowing into the Black Sea, according to scientists [10], is from 2 to 6 %, however, the work [10] does not take into account the contribution of medium and small rivers.

The work [5]) shows that in the near mouth area of the Danube, as a result of the rise of bottom waters to the surface (upwelling), a significant increase in the content of nutrients in surface waters was recorded. At the same time, in the bottom waters, the concentrations that exceeded the content of silica in the surface estuarine waters were noted under hypoxic conditions.

One of the sources of Si entering water bodies is also bottom sediments, which are formed as a result of the death and decomposition of the remains of terrestrial (coniferous, cereal, sedge) and aquatic (diatom) plants capable of concentrating silica [9]. Diatoms extract 70–80 % of silica from water. After death, they dissolve, silica is released and passes into a soluble form. Insoluble parts settle to the bottom, forming extensive deposits of diatomaceous ooze. This is how the biogeochemical cycle of silica is formed [6]).

Human activity in the 20th century has significantly changed the cycle of nutrients, including silica [11]. At the same time, the more conservative properties of silica, in contrast to, for example, phosphorus and nitrogen, contribute to a lower intensity of changes in the silica cycle. However, disproportionate changes in the cycling and abundance of phosphate and inorganic nitrogen in marine ecosystems can lead to a relative decline in silica content. In turn, this limitation can affect the development of diatoms and shift the balance in ecosystems.

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[5]) Eremchenko, O.Z., 2010. [*Theory of Bioshpere. Organized Nature of Biosphere and Biogeochemical Cycles. Tutorial*]. Perm: Izdatelstvo PGU, 104 p. (in Russian).

[6]) Zavaltseva, O.A., 2012. [*Biogeochemistry Basics: Tutorial for Bachelor Progamme Students in Disciplines “Soil Sciences”, “Ecology”, “Enbironmental Management”, “Chemistry”*]. Ulyanovsk: UlGU, 71 p. (in Russian).

The input of silica into marine ecosystems also occurs as a result of dry and wet sedimentation processes [12], where they are in a soluble form and in the form of mineral particles suspended in water [3]. The chemical composition of atmospheric precipitation is characterized by temporal and spatial variability, and is also a sensitive indicator of atmospheric pollution and, to a certain extent, can reflect the general regional load on a given territory [13]. According to estimates in [5], from 600 million to 1.6 billion tons of aeolian dust enter the ocean from the continents. The atmospheric precipitation containing nutrients can change the classical Redfield ratio [14], which can affect the general state of the ecosystem and lead to eutrophication.

It was previously mentioned [15] that silica does not belong to polluting elements, however, the Si distribution analysis makes it possible to assess the influence of natural processes and anthropogenic factors on the formation of the hydrochemical structure of waters.

The purpose of this article is to estimate the content of silica in atmospheric precipitation based on long-term data obtained at the MHI, to analyze the spatial and temporal variability of this content, and to identify possible factors affecting the atmospheric silica input.

Methods and materials

Sampling area

Atmospheric precipitation samples were collected at two points on the Crimean coast – the city of Sevastopol and the settlement of Katsiveli (Fig. 1). For each case of precipitations, the meteorological conditions (wind speed and direction, air temperature and humidity, atmospheric pressure) at the start of precipitations, as well as the amount of precipitations, were recorded.

F i g . 1 . The location of the precipitation sampling point (the source of the inset map: https://gidcrima.ru/sevastopol/dostoprimechatel-nosti/buhty-sevastopolya/)

In Sevastopol, the samples were collected into two types of samplers – permanently open for sampling total (wet + dry) precipitations and wet-only. An automatic sampler was installed at a height of 1.5 m above the underlying surface at a weather station operating around the clock. Until the middle of 2016, the Tretyakov rain gauge was used as a sampler in Katsiveli, which made it possible to select only total (dry + wet) atmospheric precipitations. In the middle of 2016, we purchased and installed an automatic sampler in Katsiveli. As a result, it became possible to receive both total and wet-only precipitations, without the influence of dry precipitations. At both sampling points, samplers were installed in open areas away from buildings and trees.

Sampling method

Precipitation samples were taken for each rain or snow event. If the break in precipitations was more than 1 hour and the cloudiness changed, then the next precipitation was taken as a separate sample. All samples were poured into prewashed nalgen jars and frozen to exclude the possibility of chemical and microbiological transformation of the samples. Then, the samples were delivered to the Marine Biogeochemistry Department of Marine Hydrophysical Institute for chemical analysis.

Chemical method of analysis

Only the precipitation samples whose volume allowed chemical analysis were analyzed for the silica content. The spectrophotometric method for silica determination is based on the formation of a blue silicomolybdenum complex. The range of determined concentrations is 0.05–20 μmol/L. According to the work[7)], the error of the method is 20 % when determining concentrations up to 0.36 μmol/L, ±10 % when determining concentrations up to 0.71 μmol/L and ±3…5 % when determining higher concentrations.

Results

During the study period, more than 500 samples were analyzed for each sampler in Sevastopol, more than 200 samples were collected in an open sampler, and more than 350 samples were collected in a wet-only sampler in Katsiveli. The content of silica in the atmospheric precipitations of Sevastopol exceeded the content in the precipitations of Katsiveli. The maximum concentration in the open sampler in Sevastopol was determined in November, in the wet-only one – in September. At the same time, in Katsiveli, for both types of samplers, the maximum concentrations of silica were more typical for the warm period (June – July), which corresponds to previously published data [2].

Some statistical characteristics of silica concentrations are presented in the Table.

In the inter-annual dynamics of the silica flux with atmospheric precipitations, a similar quasi-periodic change is observed at both monitoring points (Fig. 2).

The data for the wet-only sampler in Katsiveli is not enough to draw a trend line, but the same quasi-periodic change in the flux of silica is visible. The maximum silica flux with atmospheric precipitation was determined in 2017–2018 at both sampling points. At the same time, it can be seen that the silica input with precipitations in Katsiveli, according to the concentration data determined in the samples of the wet-only sampler, is much less than the input in Sevastopol. However, estimating the silica flux according to the data for the open sampler, we see that the flux is less only in 2017–2018, while in other years it even exceeds

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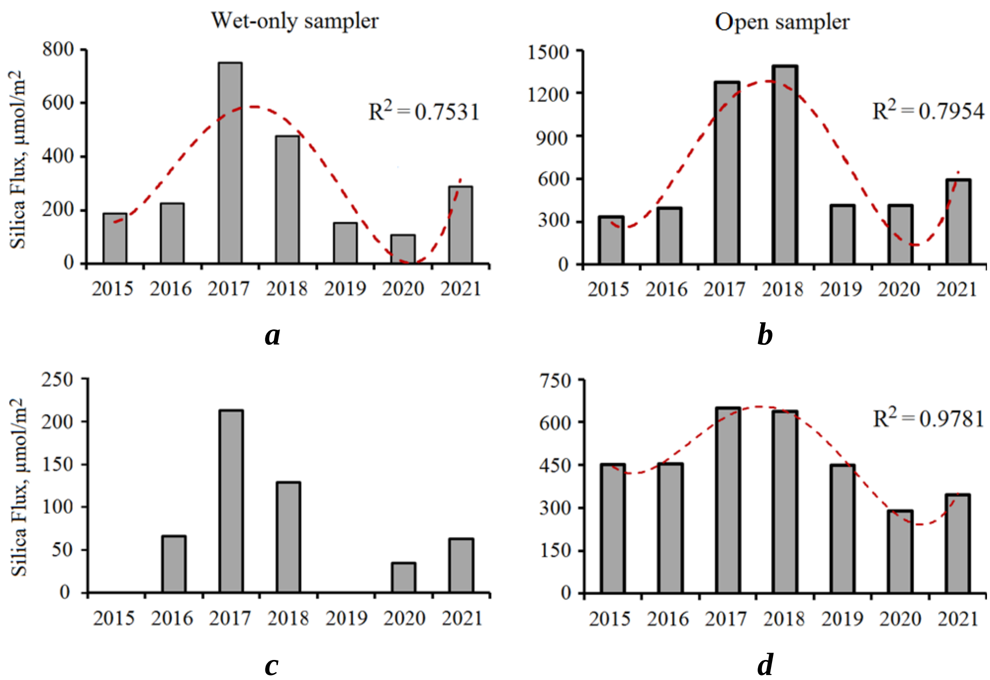
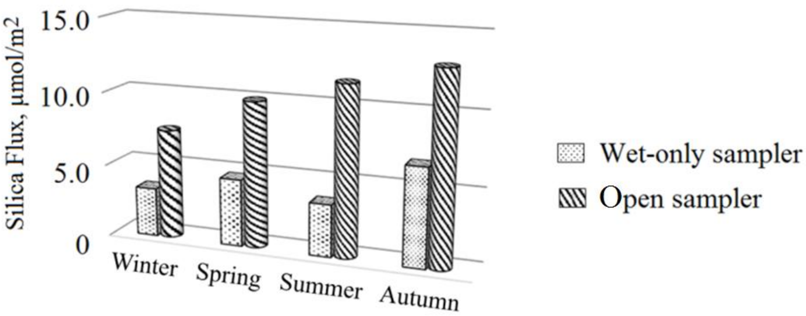
[7)] Bordovsky, O.K. and Ivanenkov, V.N., 1978. [*Ocean Hydrochemical Research Methods*]. Moscow: Nauka, 271 p. (in Russian).

Statistical characteristics of silica content in precipitation samples

Characteristic	Sevastopol		Katsiveli	
	Wet-only sampler	Open sampler	Wet-only sampler	Open sampler
Maximum concentration, μmol/L	34.46	36.79	4.96	13.58
Minimum concentration, μmol/L	0	0	0	0
Volume-weighted mean concentration, μmol/L	0.78	1.78	0.23	1.14
Standard deviation, μmol/L	2.69	4.56	0.63	1.69



F i g . 2 . Inter-annual variation in silica flux with the precipitation in Sevastopol (*a*, *b*) and Katsiveli (*c*, *d*)



F i g . 3 . Seasonal variation in silica flux with the atmospheric precipitation in Sevastopol

the flux in Sevastopol. A possible reason for this may be an active development of the territory of the southern coast of Crimea, including Katsiveli. And if in Sevastopol the main contribution to the silica input can be made by atmospheric dust transport, then in Katsiveli, due to the geographical location, the contribution of dust transport is approximately equal to the contribution of the anthropogenic component, for example, construction work and the associated emission of silica into the atmosphere.

When considering the intra-annual change in the flux of silica with precipitation in Sevastopol, it was found that the maximum flux was observed in the period from September to November for both wet-only and open samplers (Fig. 3).

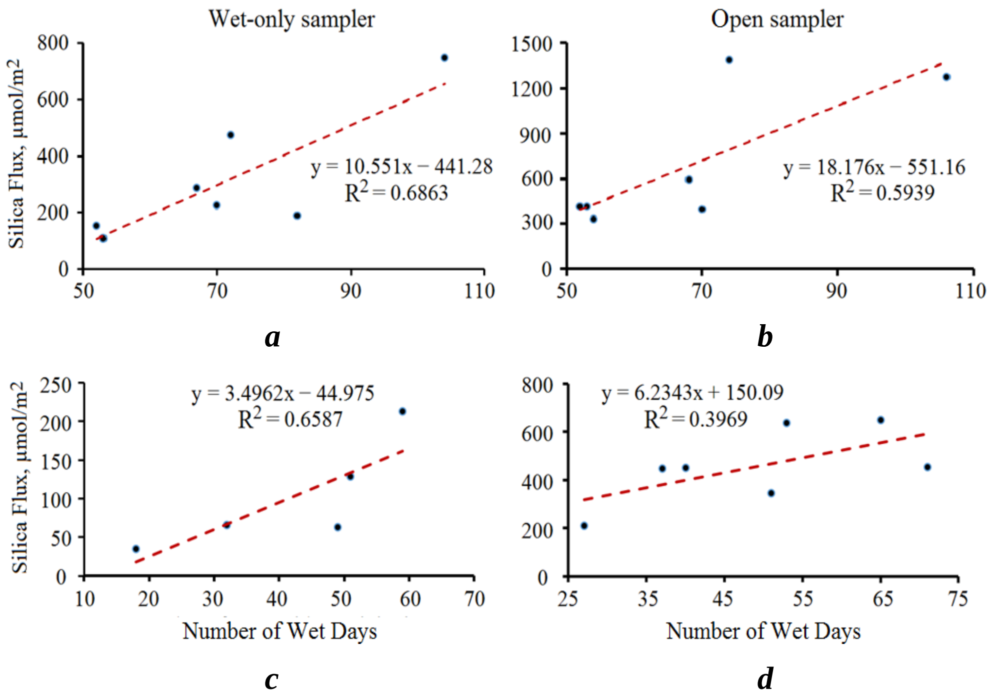
The open sampler was characterized by a gradual flux increase from winter to autumn. For samples from a wet-only sampler, a periodic change in the silica flux was observed with a gradual increase in spring and autumn, and a decrease in winter and summer.

Discussion of the results

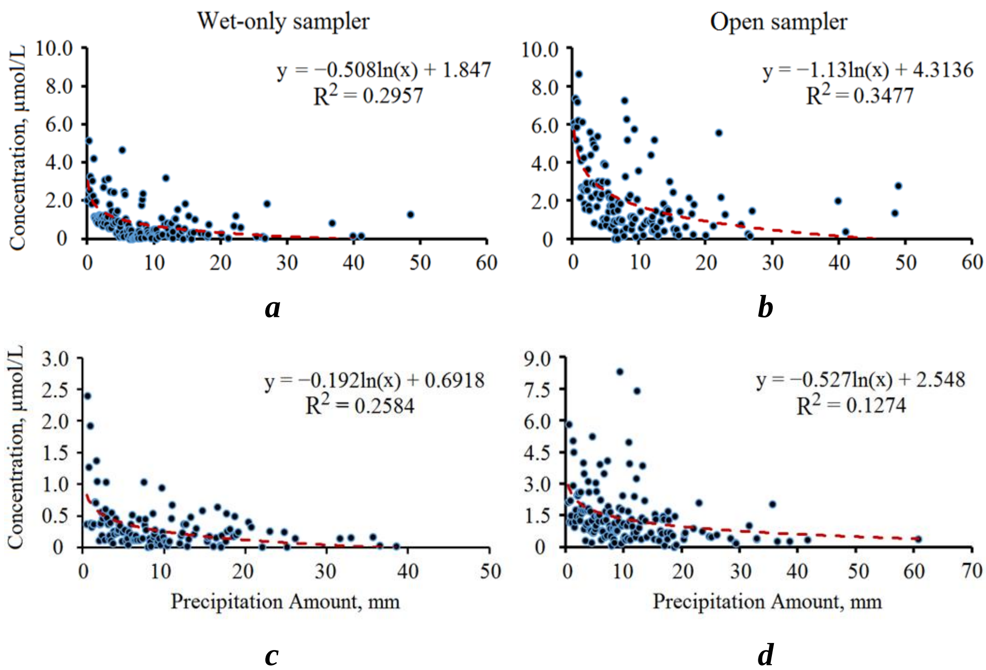
Factors affecting the flux of silica with atmospheric precipitations

One of the factors determining the content of various pollutants in atmospheric precipitations is the content of these substances in the atmosphere [8)]. At the same time, under certain conditions, such as: temperature inversions, calm weather, a break between precipitations, accumulation of pollutants in the air can occur. Therefore, we estimated the change in silica concentration in precipitation samples at each monitoring point depending on the number of "dry" days between precipitation events (Fig. 4).

[8)] Morozov, A.E. and Starodubtseva, N.I., 2020. [*Meteorological Conditions and Atmospheric Pollution: Tutorial*]. Yekaterinburg: UGLTU, 128 p. (in Russian).



F i g . 4 . Silica concentration in precipitation in Sevastopol (*a*, *b*) and Katsiveli (*c*, *d*) depending on the number of “dry” days between precipitation events



F i g . 5 . Silica concentration in precipitation in Sevastopol (*a*, *b*) and Katsiveli (*c*, *d*) depending on changes in precipitation amount

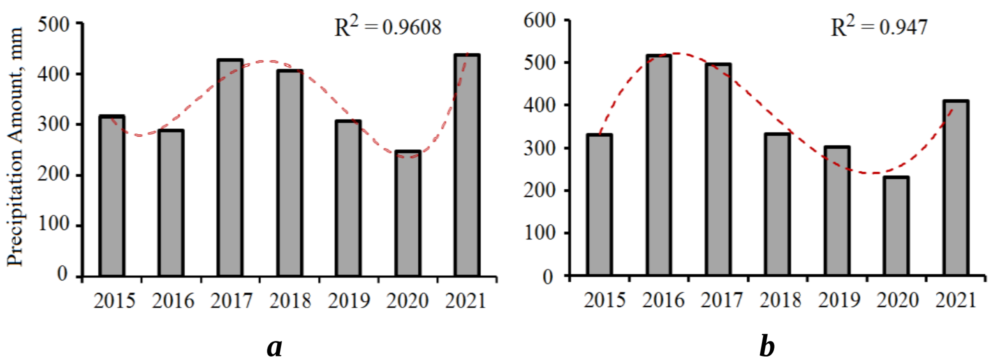
With an increase in the duration of the interval between precipitations, an increase in the silica concentration in the precipitation samples is observed. This is a consequence of the silica accumulation in the atmosphere.

Atmospheric precipitations wash away the impurities contained in the atmosphere. Fig. 5 shows the change in the silica concentration in the samples for open and wet-only samplers at each observation point depending on the amount of precipitations.

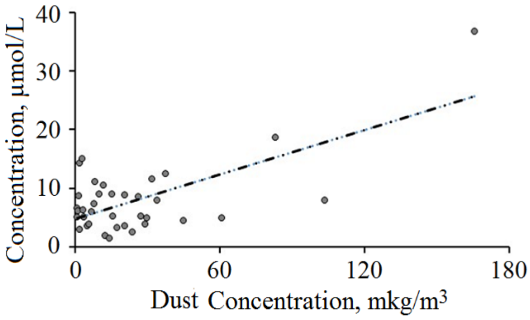
As can be seen from the graphs in Fig. 5, the silica concentration decreases with increasing the amount of precipitations, since some dilution occurs. These data are consistent with the previously published results [16, 17] for other substances contained in atmospheric precipitation.

Previously [18], it was shown for inorganic nitrogen that changes in the flux of this nutrient element in atmospheric precipitation are determined primarily by changes in the amount of precipitations: the more precipitation falls, the greater the flux of inorganic nitrogen that comes with it. Therefore, we analyzed the change in precipitation amount for each year of the study period. Fig. 6 shows histograms of changes in the total amount of precipitations for each year of observation (for analyzed samples).

As can be seen from the graphs, there is a similar periodicity in the change in both the amount of precipitations (Fig. 6) and the silica flow (Fig. 2) in Sevastopol. The maximum annual precipitation amount was in 2017–2018 and 2021. At the same time, for Katsiveli, there is some difference in the frequency of change in the silica flux (Fig. 2) and the total annual amount of precipitations (Fig. 6): in 2016, the amount of precipitations during the year was at its maximum, while the silica flux remained at the level of 2015. At the same time, in Sevastopol, the change in the amount of precipitations (Fig. 6) occurs more smoothly compared to the change in the silica flux during the same years (Fig. 2). Taking into account that silica is a terrigenous nutrient element and does not have such solubility as, for example, inorganic nitrogen, both wind erosion of the soil cover near the sampling area and the dust transboundary transport can influence the change in its content to a greater extent.



F i g . 6 . Inter-annual variation in precipitation amount in Sevastopol (*a*) and Katsiveli (*b*)



F i g . 7 . Silica flux with the atmospheric precipitation in Sevastopol depending on the dust transport intensity

An analysis was made of the data on silica concentration in atmospheric precipitations and mass concentration of dust in the atmospheric air of Sevastopol, which were obtained from satellite monitoring data [9)] in September – November for the entire study period. As a result, it was found that the more intense the dust transport was, the higher the silica concentration was in the samples of atmospheric precipitations (Fig. 7). Based on the obtained intra-annual distribution of the silica flux with atmospheric precipitations (see Fig. 3), we assumed that dust transport can have the maximum effect on the silica content in the atmospheric air of the study area during this period.

After analyzing the correlation of two data sets using the Data Analysis package in Excel, we found that the correlation coefficient was 0.61. The correlation coefficient evaluation using Student's t-test showed the statistical significance of the obtained dependence.

Potential impact of atmospheric silica precipitations on marine ecosystems

The possible effect of atmospheric silica precipitations on the value of primary production can be calculated based on the C:N:P:Si ratio, which is 106:16:1:15 [19]. Marine primary production depends on many external (atmospheric, riverine and industrial nutrient input) and internal (upwelling nutrient input) factors.

During the study period, the average silica flux with atmospheric precipitations in Sevastopol was 0.75 $\mu mol \cdot m^{-2} \cdot yr^{-1}$. At the C:Si = 106:15 ratio, the additional amount of produced organic carbon will be 5.30 $\mu mol \cdot m^{-2} \cdot yr^{-1}$. According to [20], the average annual primary production in coastal areas is 140 $gC \cdot m^{-2} \cdot yr^{-1}$ (11,667 $\mu mol \cdot m^{-2} \cdot yr^{-1}$). Based on the data obtained, the average annual silica input with atmospheric precipitations in Sevastopol can lead to an insignificant change in the content of organic carbon in the seawater – less than 0.1 %. At the same time, according to the analysis of the main nutrients input with atmospheric precipitations, the N:P:Si ratio in the atmospheric precipitations of Sevastopol is 79:1:1.9, which is very different from the classical Redfield ratio. This may

[9)] Available at: https://giovanni.gsfc.nasa.gov/giovanni/ [Accessed: 05 April 2023].

contribute to the fact that, under conditions of high input of inorganic nitrogen with atmospheric precipitations, silica can become a limiting nutrient element in the coastal waters of the Black Sea.

Conclusion

The paper considers the silica input with atmospheric precipitation at two points on the Crimean coast – the city of Sevastopol and the Katsiveli settlement. It is shown that in the inter-annual dynamics of the silica flux with precipitations at both monitoring points, a similar quasi-periodic change is observed – the maximum flux of this nutrient element was determined in 2017–2018. The main factors influencing the amount of the silica input with atmospheric precipitations are revealed. With an increase in the duration of the interval between precipitations, an increase in the silica concentration in the precipitation samples was observed, which is a consequence of the silica accumulation in the atmosphere. As a result of the analysis of the data on silica concentration in precipitations and mass concentration of dust in the atmospheric air of Sevastopol, it was found that the more intense the dust transport was, the higher the silica concentration was in the atmospheric precipitations samples. When assessing the possible impact of silica influx with atmospheric precipitations on the value of primary production of coastal areas of the Crimea, it was found that the direct contribution of the silica flux can be insignificant. However, under conditions of varying input of inorganic nitrogen and phosphates with atmospheric precipitations, further studies are needed to assess silica contribution to the state of marine coastal ecosystems.

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Diana V. Tarasevich – review of the related literature, qualitative and quantitative analysis of the results and their interpretation

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