Silica removal at sewage treatment plants causes new silica deficiency

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The dissolved silicate (DSi) concentration in coastal waters has decreased due to anthropogenic activities. Many studies have indicated that dam construction is a main reason for this reduction. However, recently, dam construction alone has not been sufficient to explain the DSi reduction in some coastal waters. In this study, we focused on silica removal at sewage treatment plants (STPs). DSi and particulate silica (PSi) concentrations were measured in STP influent and effluent waters from September 2020 to September 2021. Dissolution experiments on PSi were also conducted to estimate the fraction of soluble PSi in the STP influent. DSi and PSi were removed by 29.5% and 96.9%, respectively, at the STP. In addition, the soluble PSi in the STP influent accounted for 20.3% of the PSi removed. Therefore, in addition to the DSi removal in STPs, removal of soluble PSi can also cause potential DSi depletion in downstream and coastal waters. In addition to the effect of dams, the silica supply delivered to coastal waters may be further reduced in the future due to the progress of sewage treatment development in coastal areas.

Dissolved silicate (DSi) in rivers and coastal waters is essential for some aquatic plants and organisms. For example, diatoms, which play a significant role as primary producers in marine ecosystems, require DSi to produce silicate shells1. Primary production derived from diatoms accounts for approximately 45% of the total primary production in the ocean2,3. When the DSi concentration in the water decreases, the growth of diatoms is suppressed. Consequently, the development of non-diatom taxa, such as dinoflagellates, is promoted, resulting in the replacement of primary producers4. Dinoflagellates are responsible for harmful algal blooms and shellfish poisoning. Therefore, it is essential to understand the current status of DSi concentrations in the ocean to consider the ecosystems of coastal waters.

The most significant anthropogenic sink for DSi is artificial dams5. The damming of the upper Danube River increased the water residence time behind the dam and decreased the DSi load delivered downstream due to diatom blooms and particulate silica (PSi) sedimentation (silica deficiency hypothesis). In contrast, dissolved inorganic nitrogen and phosphate are also used for growth, but these are then quickly decomposed; therefore, most of these elements are supplied to regions downstream. Therefore, in the Black Sea, where the Danube River debouches, DSi has decreased relative to nitrogen, and phosphorus and non-silica algae have increased6. Since the report of Humborg et al.5, silica deficiency attributable to the construction of dams has been reported in coastal waters worldwide (e.g.,7,9). However, a decrease in the DSi concentration in Tokyo Bay has been reported in recent years, and dam construction cannot explain this decrease10.

The number of sewage treatment plants (STPs) has increased with the rapid urbanization of coastal areas11. However, although many studies have considered the removal of dissolved inorganic nitrogen and phosphate in STPs (e.g.,12,13), none have focused on DSi. Maguire and Fulweiler14 estimated DSi removal for the first time based on the change in the DSi concentrations between STP influent and effluent throughout the year at the Deer Island STP in the United States. They concluded that there was no significant DSi removal or supply at the STP. However, this is the only study in which silica removal by an STP has been estimated. In addition, Maguire and Fulweiler14 did not evaluate the reduction in PSi. Although phytoplankton cannot utilize PSi directly, it can be a potential source of DSi if PSi dissolves rapidly.

In this study, we collected influent and effluent from the Nakajima STP in the city of Shizuoka throughout the year to evaluate the influence of STPs on the silica cycle in the river and coastal waters quantitatively. We estimated the amounts of DSi and PSi removed by the STP. The dissolution characteristics of PSi were also evaluated by conducting dissolution experiments using the STP influent.
Methods
The observation was conducted at the Nakajima STP in Shizuoka (34°56’06.7” N 138°23’50.7” E), which includes sewerage of separate systems, and was conducted up to the secondary treatment stage. Samples were collected from the STP influent and effluent to estimate the amounts of DSi and PSi removed. Forty-six observations were carried out through the one year from September 2020 to September 2021. The collected water was filtered through a nucleopore filter (PC MB, pore size 0.6 µm, Whatman, UK), the filtrate was used for DSi analysis, and the filter was used as the sample for PSi analysis. Samples for the PSi dissolution experiments were collected from STP influent. For the dissolution experiments, the STP influent was filtered through a 2 mm mesh stainless steel sieve. Then, 1.0 L of filtered STP influent, 1.0 mL of HgCl₂, and a stirrer bar were placed in a polyethylene beaker and incubated with Parafilm to prevent evaporation to the greatest extent possible. The dissolution experiments were conducted in the incubator at 22°C for one week with a sample stirring in a stirrer to agitate the suspended material to prevent it from sinking. The experiment was carried out in quadruplicate. The dissolution amount was estimated from the change in the DSi and PSi concentrations from before to after incubation. The rate of change in DSi and PSi concentration from before to after the incubation experiment was shown in ΔDSi and ΔPSi, respectively. All DSi and PSi analyses were conducted according to Kubo and Yamahira using a spectrophotometer with a syringe shipper unit (UVmini1240, Shimadzu, Japan)¹⁵.

The annual loadings of DSi and PSi at the STP were estimated using Beal’s unbiased ratio estimator, which is ideally suited to situations in which flow rate information is abundant but there is relatively little information on concentration¹⁴,¹⁶.

Results and discussion
The annual mean DSi concentrations of the influent and effluent at the STP were 235.4 ± 42.8 µmol L⁻¹ (annual mean concentration ± standard deviation) and 193.9 ± 47.6 µmol L⁻¹, respectively (Fig. 1). The DSi concentration of the effluent was significantly lower than the concentration of the influent in 40 of the 46 observations (t-test, p < 0.0001). The annual mean DSi influent and effluent loads at the observation date were 16,959 ± 3596 mol day⁻¹ and 12,093 ± 3542 mol day⁻¹, respectively, and the effluent had a significantly lower load than the influent (t-test, p < 0.0001). The annual DSi loadings were 6.28 × 10⁶ mol year⁻¹ for influent and 4.43 × 10⁵ mol year⁻¹ for effluent (Fig. 2). In contrast, the annual mean PSi concentrations of the influent and effluent at the STP were
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Figure 2. Si cycling model in an STP. Each line shows the Si amount of STP influent, effluent, and removal, respectively. The reduction of DSI and soluble PSi by the STP creates a new silica deficiency hypothesis (the illustration was created by the image library, free material provided by the Integration and Application Network, University of Maryland Center for Environmental Science [ian.umces.edu/imagelibrary/]).
In this study, the DSI and PSI loadings decreased due to the progress of sewage maintenance in the watershed. Thus, the future construction of STPs in coastal watersheds causes a “new silica deficiency hypothesis” for coastal waters around the world (Fig. 2). However, at present, time-series observations of DSI in many coastal waters are less available than those of nitrogen and phosphorus. Therefore, data on DSI, as an essential parameter for environmental change, should be accumulated continuously from the present time before any changes occur.

**Conclusions**
In this study, both DSI and PSI were significantly removed by the STP (26.5% and 96.9%, respectively). The removal of DSI can be attributed to coprecipitation with metal ions contained in the sewage effluent and/or to uptake by bacteria universally present in the activated sludge. In addition, the soluble PSI in the STP influent accounted for about 20.3% of the PSI removed. The removal of DSI and soluble PSI attributable to the progress of sewage maintenance worldwide could cause new silica deficiency problem in coastal waters.

**Data availability**
The datasets of DSI and PSI during the current study are available from the corresponding author on reasonable request.

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Table 1. Results of the PSI dissolution experiment. The results at time 0 and the time of 7 days indicate the concentrations of STP influent before and after the incubation experiment, respectively. ΔDSi and ΔPSi show the rate of change in DSI and PSI concentration from before to after the incubation experiment.

| Time   | DSI (µmol L⁻¹) | PSI (µmol L⁻¹) | TSI (µmol L⁻¹) | ΔDSi% | ΔPSi% |
|--------|----------------|----------------|----------------|-------|-------|
| Time 0 | 214.5          | 257.1 ± 10.0   | 149.9          | 109.4 ± 16.4 | 364.4 | 366.5 ± 15.7 | +19.9 | −27.0 |
| Incubation 1 (6/2/2021) | 219.2 | 229.3 ± 2.9 | 72.1 | 66.7 ± 3.8 | 291.2 | 296 ± 1.7 | +4.6 | −7.5 |
| Incubation 2 (6/8/2021) | 212.5 | 220.5 ± 1.9 | 66.3 | 51.0 ± 5.5 | 278.9 | 271.5 ± 3.7 | +3.8 | −23.2 |
| Incubation 3 (6/8/2021) | 222.2 | 231.4 ± 3.1 | 59.2 | 45.4 ± 1.2 | 281.5 | 276.8 ± 2.5 | +4.1 | −23.4 |
| Average | 217.1 ± 3.8 | 234.6 ± 13.6 | 86.9 ± 36.7 | 62.6 ± 31.1 | 304.0 ± 35.2 | 297.2 ± 42.6 | 8.1 ± 6.8 | −20.3 ± 7.5 |
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Author contributions
A.K. conceived the study. A.K. and K.K. measured DSi and PSi concentrations. A.K, K.K., and H.H. conducted field observations. A.K. wrote the manuscript and developed the figures. All authors contributed to discussion and input to the manuscript.

Competing interests
The authors declare no competing interests.

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