Enhanced silicon availability leads to increased methane production, nutrient and toxicant mobility in peatlands

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Peatlands perform important ecosystem functions, such as carbon storage and nutrient retention, which are affected, among other factors, by vegetation and peat decomposition. The availability of silicon (Si) in peatlands differs strongly, ranging from $<1$ to $>25$ mg L$^{-1}$. Since decomposition of organic material was recently shown to be accelerated by Si, the aim of this study was to examine how Si influences decomposition of carbon and nutrient and toxicant mobilization in peatlands. We selected a fen site in Northern Bavaria with naturally bioavailable Si pore water concentrations of 5 mg/L and conducted a Si addition experiment. At a fourfold higher Si availability, dissolved organic carbon, carbon dioxide, and methane concentrations increased significantly. Furthermore, dissolved nitrogen, phosphorus, iron, manganese, cobalt, zinc, and arsenic concentrations were significantly higher under high Si availability. This enhanced mobilization may result from Si competing for binding sites but also from stronger reducing conditions, caused by accelerated respiration. The stronger reducing conditions also increased reduction of arsenate to arsenite and thus the mobility of this toxicant. Hence, higher Si availability is suggested to decrease carbon storage and increase nutrient and toxicant mobility in peatland ecosystems.

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Effects of silicon availability on the biogeochemistry of peatlands. Silicon (Si) is known to be important for stability of litter in peat ecosystems, because increased Si concentrations can be expected to be low in comparison to other ecosystems like forests. Fen ecosystems connected to local groundwater percolating through mineral matter could be expected to plot in an intermediate range. Most available data for Si, however, is based on bulk concentrations derived from X-ray fluorescence analyses (XRF), which are unable to distinguish between bioavailable Si and refractory forms like quartz.

Recent research has focused on the role of Si in peatlands. Silicon was recently shown to be important for stability of litter, because increased Si contents increase decomposition. Peatlands and other terrestrial ecosystems represent large reservoirs and filters for Si, controlling the Si transfer to the oceans. Land use change during the last 250 years has decreased Si availability in soils by increasing export and decreasing Si storage due to higher erosion and a decrease in vegetation potentially accumulating Si, and has led to a twofold to threefold decrease of the base flow delivery of Si. Due to differences in peat parent material, land use, and peat layer thickness, the Si availability in peatlands is highly variable. Especially in ombrotrophic peatlands, in which mineral weathering and plant growth are mostly decoupled from the peat layer, Si concentrations can be expected to be low in comparison to other ecosystems like forests. Fen ecosystems connected to local groundwater percolating through mineral matter could be expected to plot in an intermediate range. Most available data for Si, however, is based on bulk concentrations derived from X-ray fluorescence analyses (XRF), which are unable to distinguish between bioavailable Si and refractory forms like quartz.

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Figure 1. Mean ± SD values of Si, DOC, CH₄, and CO₂ concentrations, conductivity, and the molar ratio CO₂:CH₄ in pore water under high (Si⁺) and low (control) Si availability, n = 4.

Figure 2. Mean ± SD values of N, P, Fe, Mn, Co, and Zn concentrations in pore water under high (Si⁺) and low (control) Si availability, n = 4. Note that N, P, and Fe concentrations are plotted in mg/L, whereas Mn, Co, and Zn are plotted in µg/L.
treatments were, differences were statistically insignificant (n.s., t-test) (Fig. 3B). At the beginning of the experiment, directly after the installation of the pore water samplers, arsenic concentrations were higher and organic As species were less abundant than in the following months. In both treatments, inorganic As species dominated (79–95%). Under high Si availability ~70% more arsenite and ~48% less arsenate occurred compared to low Si availability. Furthermore, one month after the Si addition less organic As species occurred in the Si+ treatments, which was reversed thereafter. Under low Si availability, MMA was the dominant organic As species, whereas under high Si availability, DMA was more abundant. Interestingly, in some cases under high Si availability minor amounts of mono-, di-, and trithioarsenate occurred (<0.8 μg/L). Details about the As species (Table S1), general soil characteristics (Table S2), weather data (Figure S1), pH, and temperature in pore water (Figure S2) can be found in the supporting information.

Discussion

Silicon controls on carbon turnover. The increased concentrations of CO₂, CH₄, and DOC in pore water under high Si availability clearly confirm the relevance of Si for the carbon cycle and support hypothesis (i) that increased Si availability increases concentrations of CO₂ and CH₄ in the peat and leads to a release of DOC into porewater (Fig. 1). Assuming otherwise similar conditions of diffusivity and transport as in the control, higher concentrations of CO₂ and CH₄ would indicate higher emissions of these gases and thus higher rates of decomposition. Moreover, a higher release of DOC into the porewater constitutes another potentially mobile fraction of carbon and thus increased losses of carbon from the system due to increased Si availability. We are aware that increased concentrations would not necessarily be a proof for increased production rates. However, assuming that diffusivity, peat properties, and water saturation of treatment and control remained similar during our experiment and assuming a steady state of production and diffusive emission, increased concentration levels can be interpreted as a result of higher production of CO₂ and CH₄ in the peat. Since those three components (CO₂, CH₄ and DOC) represent products of organic matter decomposition Si seems to accelerate decomposition and therefore presumably influences the carbon turnover of such ecosystems. This is in line with the findings of Schaller and Struyf⁵⁴, who showed a positive correlation of plant litter Si concentration and microbial decomposition rate in a laboratory experiment. The same positive effect of Si on litter decomposition was also proven in a field experiment. Since in our study plants were not present in the mesocosms, direct plant effects on CO₂ formation via assimilation, advection, bubble formation, and direct transfer by vascular plants are the possible transport mechanisms of CO₂ and CH₄ production at first. Thereafter, upon depletion of thermodynamically favorable electron acceptors, like nitrate and ferric iron, methanogenesis increased under high Si availability. Simultaneously, decomposition led to a reductive dissolution of redox labile phases, and mobilized DOC and associated elements. This release increased the ionic strength in Si+ treatments as shown before. In summary, high Si availability increased CO₂ as well as CH₄ production and DOC release in fens and favored the rapid onset of reducing conditions.

Enhanced decomposition can not only increase CO₂ and CH₄ concentrations in pore water, but can also increase outgassing of these GHGs. The extent of the outgassing depends on production, consumption, and transport of the GHGs in pore water, which were, however, not studied in further detail here. In general, outflow, diffusion, advection, bubble formation, and direct transfer by vascular plants are the possible transport mechanisms of CO₂ and CH₄. Even though in the present study some of the CH₄ was probably reoxidized to CO₂ and the fate of CH₄ was not studied in detail, three months after Si addition, the CH₄ concentrations were high enough to form bubbles (>390 μM equivalent to CH₄ partial pressures around 0.2 atm) followed by outgassing. Hence, an increased GHG production is supposed to increase GHG emissions under elevated Si availability.
Silicon controls on nutrient mobilization. High Si availability considerably increased concentrations of N and P in pore water (Fig. 2), confirming hypothesis (ii) that Si mobilizes nutrients. This higher release of N and P into the pore water may be due to dissolved Si competing with other elements for binding sites at organic matter and mineral surfaces. This process was already suggested by Seyfferth and Fendorf for As, who determined that Si effectively competes with P for binding sites of Fe and Al(hydr)oxides in rice paddy fields and Neu et al. showing a higher P uptake by plants under high Si availability suggesting elevated P mobility. The fact that Si highly correlated with P in our experiment strongly supports that P is displaced by Si at the binding sites. From previous studies it is known that at this particular fen site, but likely also in other fens, iron oxides are present in notable quantities. Additional to the competition at binding sites, Si also apparently accelerated the mineralization of organic matter, as obvious from increases in CO₂ and CH₄, causing additional N and P release from decomposition into the pore water. The fact that N and P concentrations decreased towards initial concentrations within a few months after the Si application may have partly resulted from increased microbial assimilation of nutrients. However, leaching might also have been effective due to high runoff rates after intensive precipitation events at the study site (Figure S1). Most probably some of the Si also leached out, but the dissolution of Si from the Si-nanoparticle addition (amorphous Si), which remained in suspension, may have buffered the Si leaching.

Besides the macronutrients N and P, also the concentrations of micronutrients and potentially toxic elements such as Fe, Mn, Co, Zn, and As increased in pore water after Si addition (Fig. 3), confirming hypothesis (iii) that increased Si availability can deteriorate water quality by mobilizing potentially toxic trace elements. Similar to N and P, these elements may have been replaced by Si at the binding sites, and as a result the re-adsorption may be controlled by the competition between these elements. Additionally, Fe, Mn, Co, and As are redox-sensitive, as already mentioned above. Therefore, their release might be driven by the more rapid and stronger decrease in redox conditions towards methanogenesis under high Si availability. Consequently, elements bound to ferric iron phases and DOC co-precipitated with iron were released into solution. In comparison to the other studied elements, the decrease of Fe was delayed hinting to ongoing reductive dissolution of a large pool of iron phases under continuously reduced conditions. Moreover, the dissolution of Fe and Mn (hydro)oxides may have released bound As and P into solution. Due to the high activity of sulfate reduction and subsequent formation of sulﬁdes at the site the potential of As and P re-adsorption is low and the elements remain in solution. The shift towards reducing conditions was also reﬂected in the increase of the reduced As species arsenite under high Si availability (Fig. 3). Furthermore, the continuous methylation from MMA to DMA under high Si availability conditions occurred simultaneously to the increased activity of methanogens, which are able to methylate As. Lafferty and Loeppert showed a decrease of As adsorption at Fe (hydr)oxide surfaces by increased methyl substitution of As. This may explain the increased As release under high Si availability. Nevertheless, high Si availability did not only increase total As concentrations but also released higher concentrations of the more toxic and mobile arsenite into the pore water. These observations also demonstrate that the analysis of As speciation provided additional insight into the particular biogeochemical conditions, i.e., with Si favoring strongly reducing conditions with concomitant sulfate reduction and methanogenesis.

In conclusion, Si availability among different peatlands is highly different and thus may indeed exert an important control on biogeochemical processes as observed in our study. Our results revealed that high Si availability leads to N and P mobilization (Fig. 4). However, high Si availability in fens is potentially accelerating organic matter decomposition by increasing CO₂ and especially CH₄ production (Fig. 4). Competing with other elements, such as N, P, and As, for binding sites and promoting reducing conditions, high Si availability causes an enhanced nutrient and toxicant mobilization into solution (Fig. 4). In summary, Si exerts an important and so far little considered control on carbon and nutrient turnover in peatlands.
Methods

Sampling site. The Si addition experiment was conducted at the “Schlöppnerbrunnen fen site”, which is located in the Lehestenbach catchment (4.2 km²) in northeastern Bavaria (50°07′56.8″ N, 11°52′55.5″ E, 697 m asl). The study area is characterized by a continental temperate climate with a mean annual precipitation of 1038 mm (1994–2015) and mean annual temperature of 6.5 °C (1994–2015). The minerotrophic peatland has a central open area, which is surrounded by a spruce forest (Picea abies). The open area is covered by grasses and bryophytes. The thickness of the peat varies from 30 to 120 cm and the organic material is highly decomposed below 5–10 cm depth. The site has been intensively studied previously with regard to carbon turnover and redox processes (e.g., refs 34, 47), carbon export, CO₂ exchange, and microbiology (e.g., ref. 49). During the experiment, the peat was waterlogged and the water tables were constantly 2 cm above the soil surface.

Experimental setup. The experiment was set up in July 2015. Eight mesocosms (PVC tubes, length: 40 cm, diameter: 15 cm) were installed in pairs (each containing one control and one treatment with Si addition about 10 cm apart from each other) randomly selected within homogeneous but sparse vegetation of Carex rostrata. However, those plants died due to installation of the tubes before the start of the experiment. Soil samples from the top peat layer were taken close to the pairs of mesocosms. Each pair consisted of a mesocosm to which 50 g of low acidic (pH ~ 4.7), synthetic amorphous silica (Aerosil 300; Evonik Industries AG) was added, which is equal to 25 g of elemental Si, suspended in 1 L deionized water (Si+ treatment) and a control watered with 1 L deionized water. The synthetic amorphous silica is highly soluble even at lower pH and is an analogue to nano particulate volcanic ash. The Si was added only once at the beginning of the experiment.

Field sampling. Pore water and gas samples were obtained from each mesocosm on a monthly basis between July and November, with the first sampling starting directly before Si addition to the Si treatment. To this end, gas samplers (polysiloxane tubes allowing diffusive equilibration) were installed in the top peat layer just below the surface. The polysiloxane tubes were connected to impermeable polyurethane tubes and closed by three-way stopcocks for sampling following a sampling procedure described previously. The gas samples were taken with plastic syringes (3 ml, Omnifix, Braun). Pore water was sampled by polystyrenechloride tubes (length: 50 cm, diameter: 1 cm), which were installed in the top peat layer of each mesocosm. The lowest 15 cm of the tubes, which were placed in the top peat layer just below the surface, were perforated at 5 mm intervals. To eliminate coarse particles, the tubes were covered by nylon prefilters. The pore water samples were taken by syringes to measure pH, temperature (HQ40d Multi, PHC101 electrode, Hach), and conductivity (Winlab, Winadas). For the analysis of total element and species concentrations, all water samples were filtered after extraction (0.2 µm, cellulose-acetate filter, Chromafil). To prevent precipitation of sulfide or iron minerals, samples for total element analysis 150 µL of H₂O₂ (analytical grade, 30%, Fisher Scientific) and 250 µL HNO₃ (analytical grade, 70%, Fisher Scientific) were added per 10 mL sample. Samples used for total N and DOC measurement were frozen after the sampling. Samples for species analysis of As were preserved by immediate flash-freezing in dry ice on site.

Laboratory analysis. Concentrations of CO₂ and CH₄ in the gas samples, which were obtained from the diffusive equilibration samplers, were measured within three hours after the sampling by a gas chromatograph (SRI 8610 C equipped with methanizer and flame ionization detector, SRI Instruments). Concentrations of the dissolved gas in the pore water were recalculated applying the Henry's law and a temperature correction for in-situ temperatures. The soil samples were freeze-dried and then ground to fine powder with a zirconium ball in-situ (SRI 8610 C equipped with methanizer and flame ionization detector, SRI Instruments). Concentrations of the lowest 15 cm of the tubes, which were placed in the top peat layer just below the surface, were perforated at 5 mm intervals. To eliminate coarse particles, the tubes were covered by nylon prefilters. The pore water samples were taken by syringes to measure pH, temperature (HQ40d Multi, PHC101 electrode, Hach), and conductivity (Winlab, Winadas). For the analysis of total element and species concentrations, all water samples were filtered after extraction (0.2 µm, cellulose-acetate filter, Chromafil). To prevent precipitation of sulfide or iron minerals, samples for total element analysis 150 µL of H₂O₂ (analytical grade, 30%, Fisher Scientific) and 250 µL HNO₃ (analytical grade, 70%, Fisher Scientific) were added per 10 mL sample. Samples used for total N and DOC measurement were frozen after the sampling. Samples for species analysis of As were preserved by immediate flash-freezing in dry ice on site.

Statistical analysis. A t-test and a multifactorial analysis of variance (ANOVA) of the factors treatment (high and low Si availability) and time (month) were applied using SPSS version 16.01.

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**Author Contributions**

J.S. designed the experiment with help from K.H.K.; S.A. contributed to discussion on ecological implications and field work. G.M.S.R. conducted the experiments, analyzed samples and data with help from J.S. and K.H.K.; G.M.S.R. wrote the manuscript with major contributions from J.S., K.H.K. and B.P.F. All authors revised and approved the final manuscript.

**Additional Information**

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