Arctic soil CO_2 release during freeze-thaw cycles modulated by silicon and calcium

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Abstract

Arctic soils are the largest pool of soil organic carbon worldwide. Temperatures in the Arctic have risen faster than the global average during the last decades, decreasing annual freezing days and increasing the number of freeze-thaw cycles (temperature oscillations passing through zero degrees) per year as the temperature is expected to fluctuate more around 0°C. At the same time, proceeding deepening of seasonal thaw may increase silicon (Si) and calcium (Ca) concentrations in the active layer of Arctic soils as the concentrations in the thawing permafrost layer might be higher depending on location. We analyzed the importance of freeze-thaw cycles for Arctic soil CO_2 fluxes. Furthermore, we tested how Si (mobilizing organic C) and Ca (immobilizing organic C) interfere with the soil CO_2 fluxes in the context of freeze-thaw cycles. Our results show that with each freeze-thaw cycle the CO_2 fluxes from the Arctic soils decreased. Our data revealed a considerable CO_2 emission below 0°C. We also show that pronounced differences emerge in Arctic soil CO_2 fluxes with Si increasing and Ca decreasing CO_2 fluxes. Furthermore, we show that both Si and Ca concentrations in Arctic soils are central controls on Arctic soil CO_2 release, with Si increasing Arctic soil CO_2 release especially when temperatures are just below 0°C. Our findings could provide an important constraint on soil CO_2 emissions upon soil thaw, as well as on the greenhouse gas budget of high latitudes. Thus we call for work improving understanding of freeze-thaw cycles as well as the effect of Ca and Si on carbon fluxes, as well as for increased consideration of those factors in wide-scale assessments of carbon fluxes in the high latitudes.

Keywords: amorphous silica; Arctic soil; calcium; climate change; greenhouse gas release; nutrient; soil respiration

1 Introduction

There is large evidence from a variety of biomes covering temperate to higher latitudes that freeze-thaw cycles can strongly influence soil respiration (Kurganova et al., 2007; Ouyang et al., 2015; Skogland et al., 1988). While respiration is usually very low during the freeze phase, a brief strong CO_2 pulse often occurs during thaw, followed by a rapid decline in CO_2 release afterwards (Kim et al., 2012; Sapronov, 2021; Zhang et al., 2021). Such strong CO_2 release after thawing is likely to be important for soils which store large amounts of organic carbon vulnerable for microbial respiration (Skogland et al., 1988). Suchs soil with large amounts of vulnerable organic carbon are the soils in the Arctic (Hugelius et al., 2014).

Arctic soils are the largest pool of soil organic carbon (C) worldwide (Strauss et al. 2017). Approximately, 1300 Tg of organic C are stored within the first 3 m (Hugelius et al. 2014). Temperatures in the high latitudes have risen faster as the global average in the last decades, decreasing annual freezing days (Henry, 2007; Stocker et al., 2014). Thawing of permafrost in Arctic soils due to climate warming exposes large amounts of organic C vulnerable to microbial degradation (Heslop et al., 2019; Mueller et al., 2015; Treat et al., 2021), thus potentially increasing C emissions of Arctic terrestrial systems, which potentially warms the climate through the greenhouse effect. Accordingly, CO_2 released from Arctic soils to the atmosphere as a result of soil organic matter degradation by microorganisms (heterotrophic respiration) could strongly impact future climate change, and should be considered for defining current climate goals (Anderson et al., 2016; Canadell et al., 2021; Schuur et al., 2015).

The few studies that have been conducted on Arctic soils in this regard mostly follow the picture of experiments from other biomes showing a strong CO_2 release after each thaw

event (Kim et al., 2012; Ludwig et al., 2006; Sapronov, 2021; Schimel and Clein, 1996; Wang et al., 2014).

In deeper Arctic soils, which were previously permanently frozen, increased temperatures will firstly expose permanently frozen parts of the soil to freeze thaw cycles and secondly increase the number of freeze-thaw cycles per year (oscillation around 0°C), as the temperature is fluctuating more around 0°C (Henry, 2008). Each thawing is accompanied by a strong increase in the concentration and quantities of both microbial degradable organic compounds and a number of other elements in the soil solution (Loiko et al., 2017; Payandi-Rolland et al., 2020). Such increase in element availability by thawing may be particularly important for silicon (Si) and calcium (Ca) altering the concentrations of both elements in the soil active layer (Alfredsson et al., 2016; Stimmler et al., in revision; Walker et al., 2001). Both elements may strongly interfere with soil organic C mineralization and soil CO_2 release (Schaller et al., 2019). Ca is known to bind organic C by cation bridging in Arctic soils (Whittinghill and Hobbie, 2012), while Si mobilizes organic C due to competition for binding at the surface of soil particles (Hömberg et al., 2020; Reithmaier et al., 2017; Schaller et al., 2019). These effects on organic C mobility have been reported to substantially affect the soil CO_2 release in incubation experiments of high-Arctic soils (Schaller et al., 2019; Stimmler et al., 2022). Consequently, we expect that Si increases and Ca decreases Arctic soil C fluxes. However, up to now, no study analyzed the importance of freeze-thaw cycles (potentially mobilizing organic C) while considering effects caused by Si (mobilizing organic C) or Ca (immobilizing organic C) for Arctic soil CO_2 release especially under freezing conditions and upon thaw. In this study, we hypothesize that (i) every freeze-thaw cycle will lead to a consistent pronounced CO_2 release after thaw and (ii) Si is positively and Ca negatively related to Arctic soil CO_2 emissions. To investigate this, we used controlled laboratory incubation experiments to test the combination of freeze-thaw cycles, as well as Si and Ca for

Arctic soil CO_2 release. To make the freeze-thaw experiments comparable with natural conditions we adapted the freeze-thaw regime to the natural freeze-thaw cycle of the Arctic soils to make sure that freezing as well as thawing periods allowed the soil microbes to adapt.

2 Materials and Methods

2.1 Soil material used for experiments

The soil used for the present study was taken from a wet tussock tundra ecosystem near Chersky, Northeast Siberia, Russia (68,61586°N; -161,35228°E), underlain by continuous permafrost (Göckede et al., 2017; Göckede et al., 2019). The soil, which was sampled from the mineral active layer from 50 to 60 cm depth, was gently crushed in frozen state using a steel mortar in a first processing step. The frozen material was split and sieved under frozen conditions through a two mm sieve until all particles passed through the sieve. The soil had an amorphous Si content of 3mg g^{-1}, and Mehlich(III) extractable concentrations of 0.08mg g^{-1} for Si, and 0.6mg g^{-1} for Ca (Stimmler et al., in revision). The soil samples were completely saturated with water during the whole experiment.

2.2 Experimental design and analysis

To make the freeze-thaw experiments comparable with natural conditions, we adapted the laboratory freeze-thaw regime to the natural freeze-thaw cycle as observed within the Arctic soils at the sampling site near Chersky. For this, the soils were incubated at +5°C until the CO_2 efflux was at equilibrium (Fig. 1). Afterwards, the soil temperature was decreased to +1°C within two days. The temperature of +1°C was held for two days. and afterwards the temperature was decreased to -1°C and held for two days, again. Thereafter, the temperature

was decreased to -9°C (Fig. 1). This temperature profile allows microbes to adapt to the temperatures is analog to field conditions. Such adaptation is important as microbes are sensitive toward freezing at too fast rates (Lipson et al., 2000). The chosen moderate temperature gradients prevent lysis as shown for such conditions before (Grogan et al., 2004). Linear extrapolated CO_2 flux rates, initially measured during -1°C, were used in this study as a conservative estimate for CO_2 efflux during freeze periods.

2.3 Measurements and data analysis

We incubated four different sample treatments, namely a natural soil (control), and three further treatments with added silicon (+Si), added calcium (+Ca), and both added silicon and calcium (+Si+Ca). CO_2 and CH_4 fluxes from the samples were analyzed for three thaw periods (Table 1). For each treatment, four replicates of 20g each were incubated in parallel using the incubation system described in detail by Rillig et al. (2021. The used incubation system works in a flow-through, steady-state mode corresponding to Livingston and Hutchinson (1995. It contains 16 airtight, cylindrical incubation vessels (50 mL PE centrifuge vials), for the samples to be incubated, and a control channel through which ambient air passes the incubation vessels directly from the pressure vessel to the gas analyzer (Picarro G2508; PICARRO, INC., Santa Clara, USA). Ambient air flows was continuously through the headspace of all incubation vessels via channels connecting the pressure vessel and the gas analyzer directly, using a multiplexer and a special circular channel. Air was circulated between the incubation unit headspace and the CRDS analyzer at 250 mL min^{-1} using a low-leak diaphragm pump (A0702, Picarro, Santa Clara, CA, USA). To increase the sensitivity of the incubation system, flow rate and measurement time per channel were adjusted according to the expected CO_2 flux rate. The temperature was controlled in the incubation vessels by means of a climate chamber. During the thawing phases, the samples were weighed several

times to compensate for possible soil water losses. CO_2 fluxes were calculated from the measured CO_2 gas concentration in the respective channel, and the temporally corresponding concentration in the control channel according to Equation 1:

$$F = \frac{(M * \rho * V * (\Delta c))}{(C * R * t * T)}$$

where F is the flux rate (µg CO_2-C $core^{-1}$ h^{-1}), M is the molar mass of CO_2, ρ the atmospheric pressure (Pa), V is the air flow rate into the headspace and the channels (m^3 h^{-1}), Δc is the difference of CO_2 concentrations [mol] between outlet of a specific vessel and the corresponding, linear interpolated control channel CO_2 concentration, C is the soil sample area (m^2), R the gas constant (m^3 Pa K^{-1} mol^{-1}), t is the time over which the concentration change was observed, and T the incubation temperature (K).

Fluxes were calculated using an R script. Influence of diurnal cycles in measured ambient air within the control channel on calculated CO_2 fluxes was minimized by linear interpolation of CO_2 concentrations measured for the control channel, rather than using adjacent control channel CO_2 concentration measurements only. To avoid bias caused by measurements on the previous channel, only values determined in the last minute of each channel measurement were used to calculate CO_2 fluxes. For calculation of CO_2 emissions, biased, negative CO_2 fluxes were rejected (<6%).

3 Results

3.1 CO_2 release decreased with progressing number of thaw-freeze periods

CO_2 fluxes during the whole incubation period generally decreased within all treatments as the number of thaw (Fig. 2) and freeze periods (Fig. 3) proceeds. Treatments of +Si and +CaSi however, decreased with -57% and -52% much more rapidly from the first to the last observed thaw period (period with temperature >1°C) compared to the control and +Ca treatment with -24% and -40%, respectively. The same was observed for the change from the first to the last observed freeze period (period with temperature <-1°C), were +Si and +CaSi decreased by -82% and -70%, while CO_2 fluxes of the control and +Ca treatment decreased by -40% and -60%. As a result, differences between treatments during freeze periods with +Si being significantly higher diminished during the second freeze period (p =0.015, compare the second and the third period) and only significant difference (p <0.01) during thaw periods between treatments persist.

However, despite completely water saturated soil samples, no CH_4 emissions for any of the treatments were found.

3.2 Silicon increased and calcium decreased CO_2 fluxes and emissions

CO_2 fluxes generally showed very high variability over time. Therefore, especially the effects of changing temperatures were not immediately recognizable at a glance (Fig. S1). However, average CO_2 fluxes during the whole incubation period in the +Si treatment with a median of 0.055 µmol m^{-2} s^{-1} were 22% higher and significantly different (p=0.01, Wilcoxon test) compared to the control (0.045 µmol m^{-2} s^{-1}). In comparison to the +Ca and the +Ca+Si treatments, which produced CO_2 flux medians of 0.021 µmol m^{-2} s^{-1} and 0.023 µmol m^{-2} s^{-1}, respectively, the +Si treatment yielded also significantly higher CO_2 fluxes (p<0.01, Wilcoxon test) (Fig. 4a). The same holds true for the CO_2 fluxes from the control treatment, which were

also significantly higher (p<0.01, Wilcoxon test) compared to the +Ca and the +Ca+Si treatments. No significant differences in CO_2 fluxes were found between the +Ca and the +Ca+Si treatment (p=0.015; Wilcoxon test). Daily differences in CO_2 fluxes of the different treatments compared to control were shown in Figure S1.

CO_2 fluxes above +1°C of both the control treatment with a median of 0.043 µmol m^{-2} s^{-1} and the +Si treatment with a median of 0.049 µmol m^{-2} s^{-1} were significantly higher (p<0.01, Wilcoxon test) compared to those of the +Ca with a median of 0.022 µmol m^{-2} s^{-1} and the +Ca+Si treatment with a median of 0.025 µmol m^{-2} s^{-1} (Fig. 4b). Focusing on the CO_2 fluxes below -1°C we found a strong and significant increase in CO_2 fluxes by 100% in the +Si treatment with a median of 0.030 µmol m^{-2} s^{-1} compared to the control treatment with a median of 0.015 µmol m^{-2} s^{-1}. No significant difference were found between the control treatment and both the +Ca treatment with a median of 0.014 µmol m^{-2} s^{-1} and the +Ca+Si treatment with a median of 0.016 µmol m^{-2} s^{-1} (Fig. 4c). For the CO_2 fluxes above +1°C the pattern was different compared with those fluxes below -1°C.

Cumulative CO_2 emissions per treatment during the whole incubation period are shown in Fig. 5. Similar to average fluxes, the +Si treatment yielded 28% higher cumulative CO_2 emission (2.44 mg CO_2-C per sample) when compared to the control treatment (1.90 mg CO_2-C $sample^{-1}$). The +Ca and +Ca+Si treatments showed lower cumulative CO_2 emissions (1.13 and 1.47 mg CO_2-C $sample^{-1}$) compared to the control, with +Ca evidencing the lowest cumulative CO_2 emissions. Neither of both +Ca and +Ca+Si treatments showed a clear difference when compared to a proxy for the absence of frost-thaw, represented by the cumulative CO_2 emission, estimated based on the linear extrapolated, initially measured, average CO_2 flux of the control treatment at -1°C incubation temperature. Only the +Si treatment yielded in substantially higher cumulative CO_2 emissions.

4 Discussion

The main finding of our study is that with each freeze-thaw cycle the CO_2 fluxes from the Arctic soils decreased, refuting hypothesis (i). We also found pronounced differences between the tested treatments with Si increasing and Ca decreasing Arctic soil CO_2 fluxes, confirming hypothesis (ii).

Frozen conditions prevent organic matter (OM) from microbial degradation (Mann et al., 2022) and low temperatures around the freezing point greatly reduce CH_4 emissions (Yvon-Durocher et al., 2014). This is also a possible explanation for the absence of CH_4 emissions in our investigations, despite soil samples being completely saturated with water during the entire experiment. Our data revealed a considerable CO_2 emission below 0°C, especially for the Si fertilized treatments. This is in line with earlier findings also showing CO_2 emission from Arctic soil until minus 5°C (Ludwig et al., 2006; Sapronov, 2021; Schimel and Clein, 1996; Wang et al., 2014). Consistent with our data, other studies of Arctic soils also experienced a decrease in CO_2 release with increasing number of freeze-thaw cycles (Ludwig et al., 2006; Schimel and Clein, 1996; Wang et al., 2014). This means that the labile organic carbon in Arctic soils is likely degraded rapidly, once the soil is thawed, needing only few freeze-thaw cycles to be mineralized and released to the atmosphere.

Consequently, higher Arctic temperatures with subsequent increased number of freeze-thaw cycles per year (oscillation around 0°C) (Henry, 2008) may contribute only to a minor extent to an increased soil CO_2 release in future, as long as no labile C input by e.g. plants occurs, since labile C may potentially increases the microbial organic C degradation and subsequent C release from Arctic soils (Oztas and Fayetorbay, 2003).

It is debated in literature how stabile Arctic C is upon soil thaw and the timescale of organic C degradation in high latitude systems is still unknown (Schuur et al., 2015). Our results

indicate that a strong response in CO_2 could take place rapidly after only few thawing cycles, thus soil thaw could have a direct impact on climate change in the near-future.

The effects of Si enhancing CO_2 fluxes from Arctic soils is in line with previous studies on Greenlandic soils (Schaller et al., 2019) or peatlands (Hömberg et al., 2021; Reithmaier et al., 2017). This enhanced CO_2 fluxes from Arctic soils by Si may be explained by an increase of available water (Schaller et al., 2020) without increasing salinity. Another potential mechanism underlying the enhancing CO_2 fluxes from Arctic soils by Si may be arising from the mobilization of silicic acid from the ASi (Schaller et al., 2021). Since silicic acid competes with phosphate for binding at the surfaces of soil particles, previously unavailable phosphate is potentially mobilized reducing the phosphate limitation for the decomposing microbes (Hömberg et al., 2020; Schaller et al., 2019). As the strongest effect of +Si treatment enhancing CO_2 fluxes from Arctic soils was shown for temperatures below 0°C, the Si effect may have something to do with water availability below 0°C with increased "supercooled" water content under higher Si concentrations, which has been previously found for increased silt fractions enhancing the fractions of "supercooled" water at freezing conditions (Schaefer and Jafarov, 2016). Si in solution was found long time ago to reduce the water freezing point (Kahlenberg and Lincoln, 1898), which was confirmed recently (Kumar et al., 2019). This may lead to an increased water availability below 0°C by Si being a potential the reason for the higher CO_2 fluxes from the Arctic soil below 0°C in the +Si treatment (Fig. 4c) as microbes need available water.

The decrease of the soil CO_2 production rate by Ca is in line with earlier finding (Schaller et al., 2019; Whittinghill and Hobbie, 2012). This effect of Ca decreasing the soil CO_2 production rate may be explained by either cation bridging of soil organic matter by Ca ions (making the organic matter unavailable for microbial decomposition) (Schaller et al., 2019; Whittinghill and Hobbie, 2012) or by increasing salinity due to Ca addition potentially

decreasing activity of microbial decomposer community (Mavi et al., 2012). It was recently shown that Si may be able to increase and Ca decrease the activity of microbial decomposers and change the microbial decomposer community structure (Stimmler et al., 2022).

We show that both Si and Ca concentrations in Arctic soils are a main controls on Arctic soil CO_2 release, with Si increasing soil CO_2 release especially when temperatures are below 0°C. High-Arctic permafrost soils store vast amounts of Si and Ca (Alfredsson et al., 2016; Stimmler et al., in revision; Walker et al., 2001), which could be released upon thaw. These feedbacks which affect soil organic matter stabilization in Arctic soil (potentially by Ca) are poorly understood and such effects of stabilization of organic matter by Ca potentially decreasing soil respiration and/ or a mobilization of nutrient like phosphate by Si potentially increasing soil respiration are not taken into account in present global-scale assessments of the Arctic carbon budget (Canadell et al., 2021). If our findings regarding soil respiration effects of Si and Ca on Arctic soil organic matter turn out to be true on larger scales, they could provide an important constraint on soil CO_2 emissions upon soil thaw, as well as on the greenhouse gas budget of high latitudes. We thus call for work improving understanding on Ca and Si feedbacks on carbon fluxes, as well as for increased consideration of factors that affect the stability of Arctic soil carbon in wide-scale assessments.

A first step towards this is the development of an experimental design for the studies, which accurately captures the real conditions on thawed Arctic soils. An important impetus for this is the small post-thaw CO_2 pulse in our studies, which further decreased with proceeding freeze-thaw cycles. While a strong CO_2 pulse occurred in three of the studies that looked at the effect of freeze-thaw cycles on Arctic soils (Sapronov, 2021; Schimel and Clein, 1996; Wang et al., 2014), it was also absent in Ludwig et al. (2006. Apparently, this was because, in agreement with Ludwig et al. (2006, we had only slowly changed the temperature during the transition between freeze-thaw or vice versa, as actually occurring under natural conditions in

Arctic soils. In other words, the CO_2 pulse observed by most other studies may be a result of an abrupt transition between temperature phases does not reflect the real situation on thawing Arctic soils. However, it is possible that the very high-frequency measurement of CO_2 fluxes used by our study and the study of Ludwig et al. (2006 simply made visible that CO_2 fluxes in Arctic soils fluctuate much more than previously perceived. The same holds true for the generalizability of the conclusions obtained in incubation experiments with small amounts of soil to the reduction of CO_2 release with increasing number of freeze-thaw cycles. At least, it cannot be excluded that factors such as the presence of temperature and matter gradients in the soil profile, soil movements due to cryoturbation, and the diverse activities of plants alter the effects of freeze-thaw cycles on CO_2 release in the field (Mauritz et al., 2021; Olid et al., 2020; Treat et al., 2021). Therefore, the focus of future investigations should be to clarify exactly this.

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Author contributions: JS, PS and MH designed the study. MG provided the soil. MH did the measurements. All authors discussed the results and contributed substantially to the manuscript.

Competing interests: The authors declare no comparing interests.

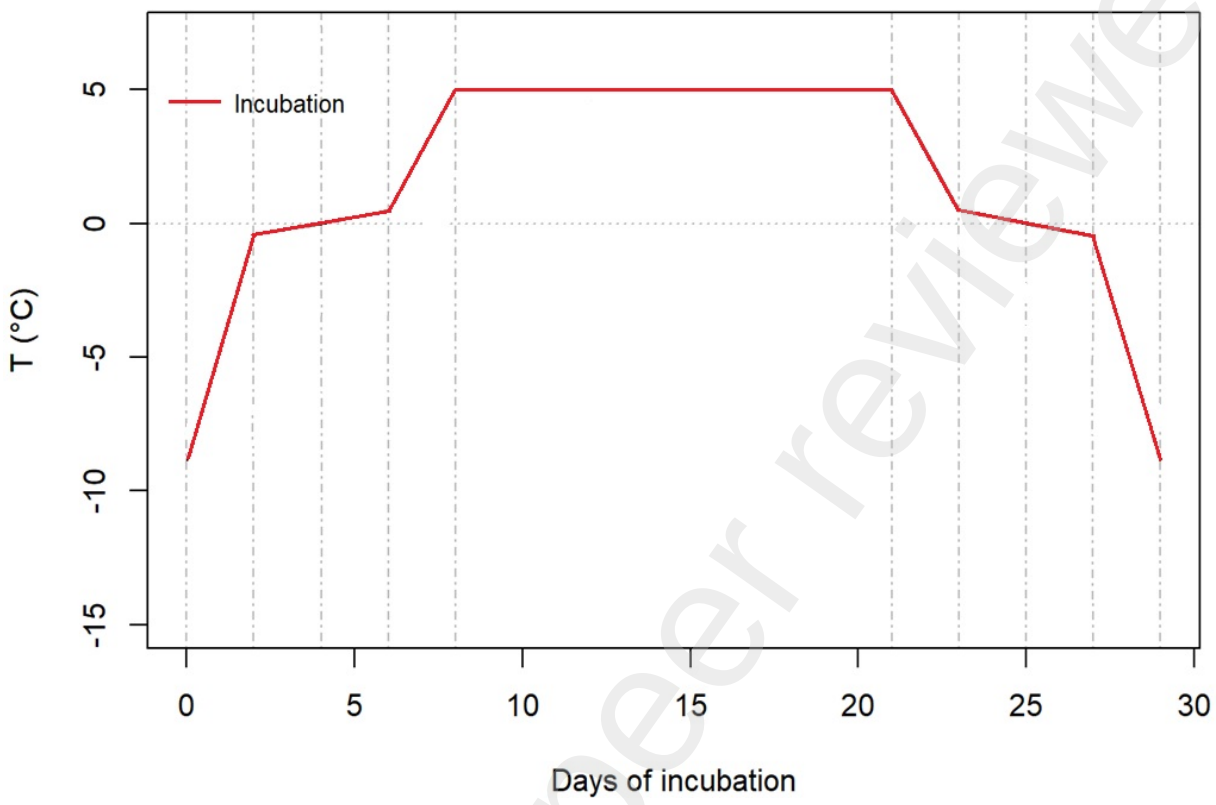
Tables

Tab. 1: average measured CO_2, CH_4 and N_2O fluxes for the different treatments during the repetitive freeze-thaw-cycle

Period	Treatment	Temp.	CO_2	CH_4	N_2O
		°C		nmol m^{-2} s^{-1}	
1st thaw	control	4.0	52	-0.01	0.01
	+Ca	4.0	25	-0.02	<0.00
	+Si	4.0	76	0.02	<0.00
	+Ca+Si	4.0	35	0.01	<0.00
1st freeze	control	-3.2	21	<0.00	0.01
	+Ca	-3.5	34	-0.02	0.01
	+Si	-3.4	61	0.02	0.03
	+Ca+Si	-3.2	51	0.02	0.01
2nd thaw	control	3.5	57	-0.01	<0.00
	+Ca	3.4	31	0.01	<0.00
	+Si	3.5	49	<0.00	<0.00
	+Ca+Si	3.5	33	<0.00	<0.00
2nd freeze	control	-3.6	9	<0.00	0.01
	+Ca	-3.8	13	<0.00	-0.01
	+Si	-3.8	16	<0.00	<0.00
	+Ca+Si	-3.5	6	<0.00	0.01
3rd thaw	control	3.4	36	<0.00	<0.00
	+Ca	3.5	17	0.01	<0.00
	+Si	3.6	26	0.01	-0.01
	+Ca+Si	3.5	8	-0.01	-0.01

471 **Figures**

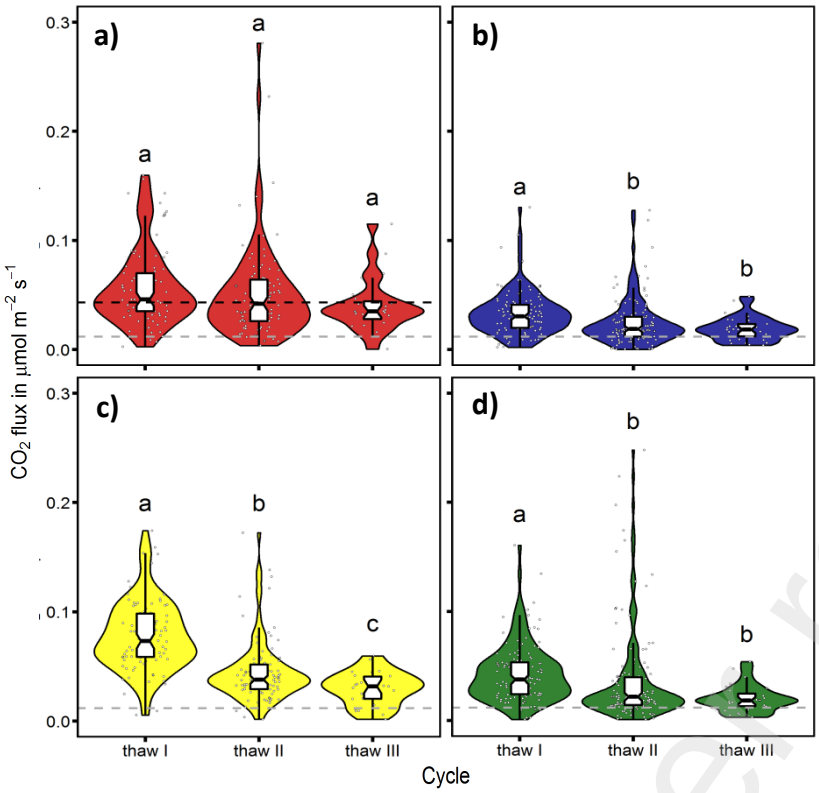
472



473

474 Fig. 1: Schematic representation of the time schedule and temperature regime of one freeze-

475 thaw-cycle simulated during the incubation experiment



476

477 Fig. 2: Measured CO_2 fluxes of the a) control, b) +Ca, c) +Si and d) +Si+Ca treatment during
478 the first, second and third thaw period (defined as incubation temperature >+1°C following
479 freeze) within the incubation period. The dashed black horizontal line indicated the median
480 CO_2 flux of the control treatment (a), the dashed gray horizontal line the initially measured,
481 average CO_2 flux of the control treatment at -1°C. Different letters indicate significant
482 (p<0.05) difference between CO_2 fluxes of the different thawing periods.

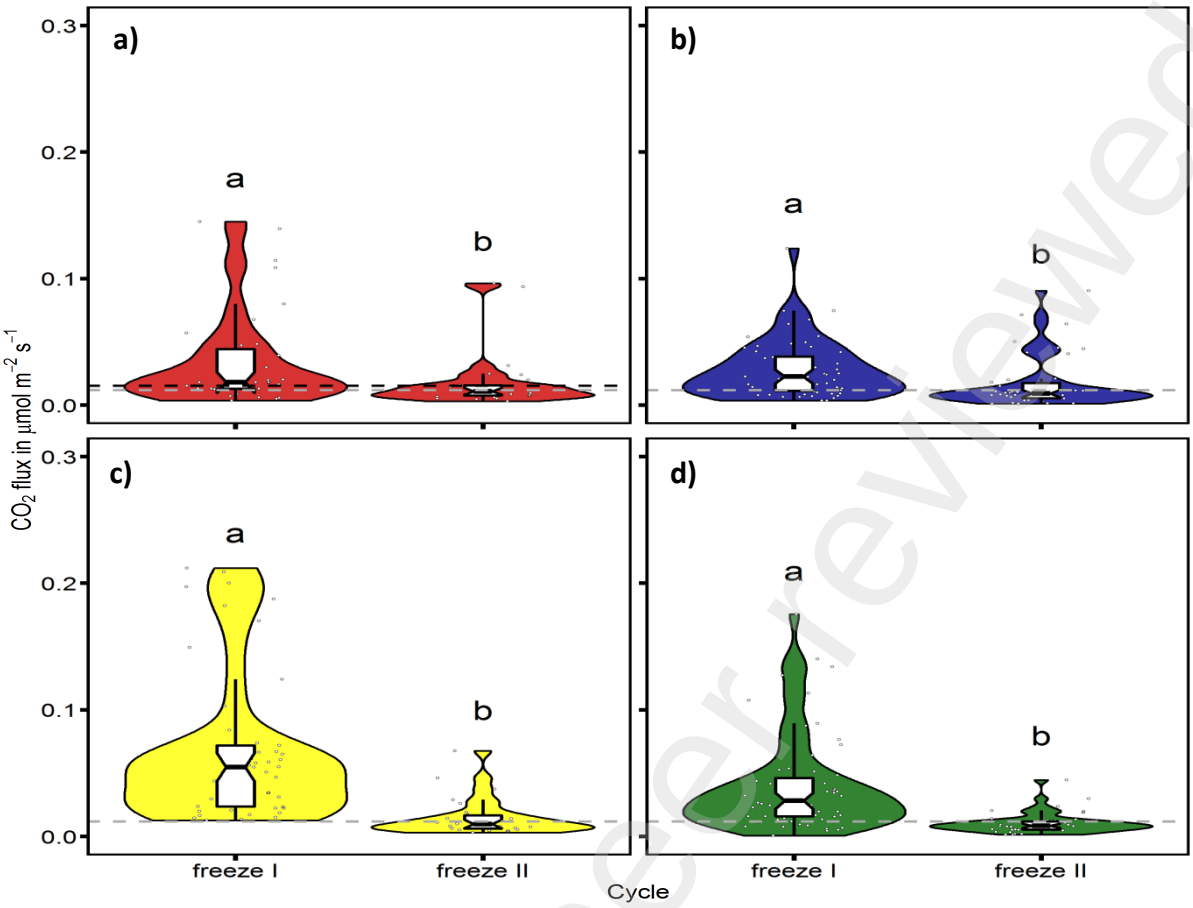
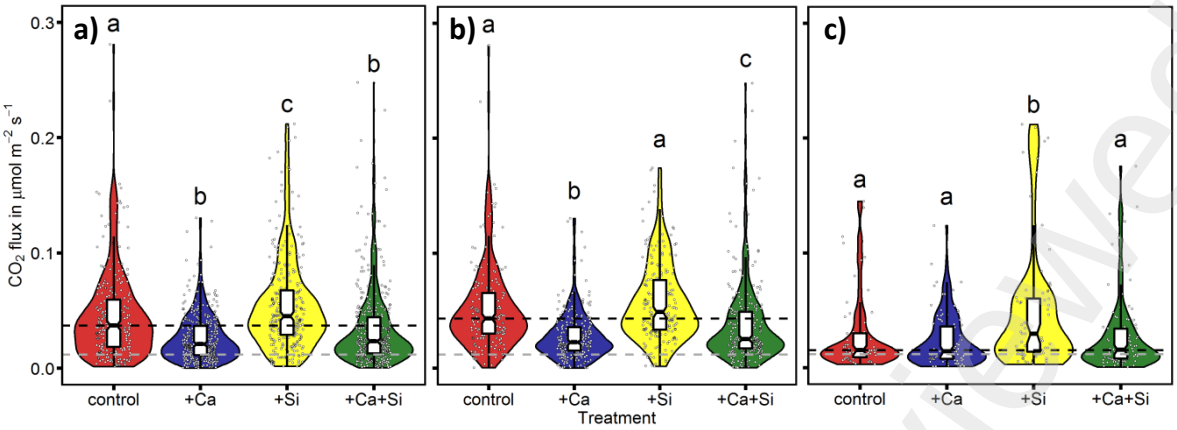


Fig. 3: Measured CO_2 fluxes of the of the a) control, b) +Ca, c) +Si and d) +Si+Ca treatment during the first and second freeze period (defined as incubation temperature <-1°C following thaw) within the incubation period. The dashed black horizontal line indicates the median CO_2 flux of the control treatment (a). The dashed gray horizontal line indicates the initially measured, average CO_2 flux of the control treatment at -1°C. Different letters indicate significant ($p<0.05$) difference between CO_2 fluxes of the different freeze cycles.



497

498 Fig. 4: Measured CO_2 fluxes of the a) different treatments for the entire incubation period; b)
499 shows measured CO_2 fluxes for the different treatments when incubation temperature was
500 above +1°C and c) shows measured CO_2 fluxes for the different treatments when incubation
501 temperature was below -1°C. The dashed black horizontal line indicated the median CO_2 flux
502 of the control treatment, the dashed gray horizontal line the initially measured, average CO_2
503 flux of the control treatment at -1°C incubation temperature. Different letters indicate
504 significant (p<0.05) differences between CO_2 fluxes of the different treatments.

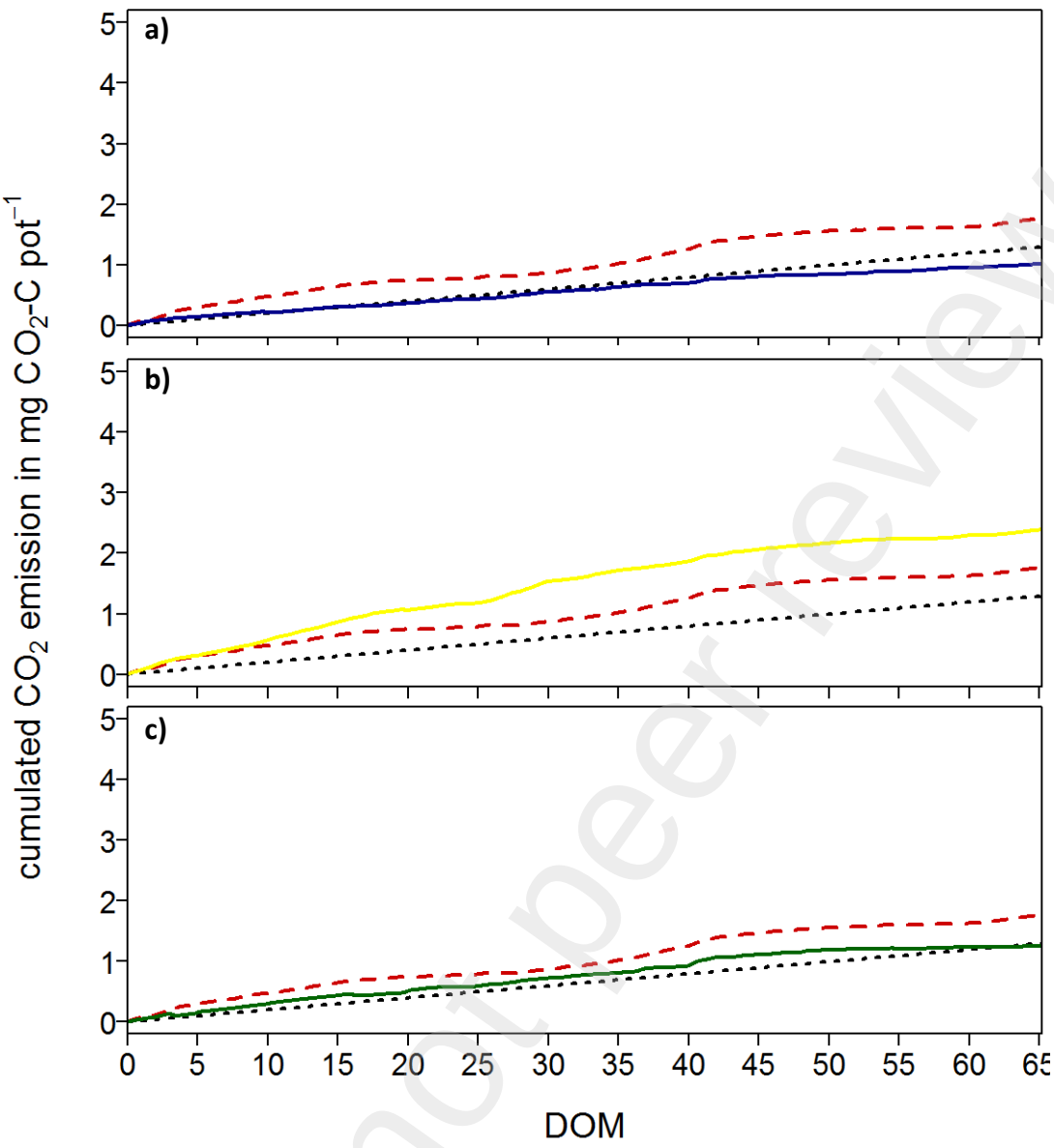


Fig. 5: Cumulative CO_2 emissions over the whole incubation period for the a) +Ca, b) +Si and c) +Ca+Si treatment. The dashed, red line represents the cumulative CO_2 emission of the control treatment. The dotted black line indicated the cumulative CO_2 flux based on the initially measured, average CO_2 flux of the control treatment at -1°C.